Direct core functionalization of naphthalenediimides by iridium catalysed C-H borylation

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General Experimental Procedures

Reactions which required the use of anhydrous, inert atmosphere techniques were carried out under an atmosphere of nitrogen or argon. The reagents for the C-H borylation reactions were measured out into round bottom flasks or microwave vials in an argon-filled mBraun labmaster glovebox (2005). Reaction solvents were dried and degassed by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system, except for hexafluorobenzene, which was purchased from Fluorochem Ltd. (Item #001356) and used as supplied. The iridium catalyst precursor was purchased from Strem Chemicals Inc.

Petrol refers to petroleum ether, bp 40-60 °C. TLCs were performed using aluminium-backed plates precoated with Alugram®SIL G/UV and visualized by UV light (254 nm) and KMnO₄ followed by gentle warming. Flash column chromatography was carried out using Davisil LC 60Å silica gel (35-70 micron) purchased from Fisher Scientific.

IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrometer with absorbances quoted as ν in cm⁻¹. Mass spectra were recorded with a microTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik). UV/Vis spectra were recorded on a Chirascan CS/LD instrument. Reactions performed under conditions of microwave acceleration used a Biotage Initiator 2.0 instrument.

NMR spectra were run in CDCl₃ (unless otherwise specified) on Bruker Avance 250, 300, 400 or 500 MHz instruments at 298 K. ¹H and ¹³C NMR spectra were calibrated to internal solvent signals (CDCl₃ using ¹H 7.26 and ¹³C 77.0 ppm; DMSO-d₆ using ¹H 2.50 and ¹³C 39.5 ppm); ¹⁹F NMR spectra were calibrated to external CFCl₃ (0.00 ppm); ¹¹B NMR spectra were calibrated to external BF₃Et₂O (0.00 ppm).
To a stirring suspension of 1,4,5,8-naphthalenetetracarboxylic dianhydride (1.0 eq., 1.00 g, 3.73 mmol) in DMF (40 mL) was added 2-ethylbutyl-1-amine (2.2 eq., 830 mg, 8.20 mmol). The resulting mixture was heated to 120 °C for 4 h. After cooling to rt, the reaction mixture was poured over 1.0 M aqueous HCl (100 mL). The organic product was extracted with CHCl₃ (3 × 50 mL) and organic layers were washed with saturated aqueous LiCl solution and dried over MgSO₄. Concentration under reduced pressure afforded 5 as a pale orange solid in 92% yield (1.49 g).

**Naphthalenediimide 5:** δH (300 MHz, CDCl₃) 8.75 (4H, s, Ar-H), 4.15 (4H, d, J = 7.5 Hz, N-CH₂), 1.95-1.82 (2H, m, methine protons), 1.47-1.32 (8H, m, CH₃-CH₂), 0.95 (12H, t, J = 7.5 Hz, CH₃); δC (75 MHz, CDCl₃) 163.2 (C=O), 131.0 (Ar), 126.7 (Ar), 44.3 (N-CH₂), 39.3 (N-CH₂-CH₂), 23.4 (-CH₂-CH₂), 10.6 (CH₃); νmax 2962, 2933, 2857, 1699, 1653, 1581, 1454, 1333, 1242, 1080, 770 cm⁻¹; TOF-MS (ESI⁺) m/z calcd for (C₂₀H₃₀N₂O₄)⁺ 435.2278; found 435.2314.

To a stirring suspension of 1,4,5,8-naphthalenetetracarboxylic dianhydride (1.0 eq., 178 mg, 0.66 mmol) in DMF (20 mL) was added (R)-2-aminononane (2.1 eq., 200 mg, 1.40 mmol). The resulting mixture was heated to 120 °C for 4 h. After cooling to rt, the reaction mixture was poured over 1.0 M aqueous HCl (50 mL). The organic product was extracted with EtOAc (3 × 30 mL) and organic layers were washed with saturated aqueous LiCl solution and dried over MgSO₄. Concentration under reduced pressure afforded 9 as a pale orange solid in 93% yield (329 mg).

**Naphthalenediimide 9:** δH (250 MHz, CDCl₃) 8.72 (4H, s, Naphthyl-H), 5.26 (2H, tq, J = 7.5 Hz, 6.5 Hz, N-CH), 2.23-2.10 (2H, m), 1.93-1.85 (2H, m), 1.58 (6H, d, J = 7.5 Hz, CH-CH₃), 1.33-1.16 (20H, m, (CH₃)₃), 0.83 (6H, t, J = 6.5 Hz, CH₂-CH₃); δC (75 MHz, CDCl₃) 163.2 (C=O), 130.8 (Ar CH), 126.7 (Ar), 126.6 (Ar), 50.3 (N-CH), 33.3 (CH₂), 31.7 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 27.0 (CH₂), 22.5 (CH₂), 18.2 (CHCH₃), 14.0 (CH₂-CH₂); [α]D²⁵ = -17.8 (c 0.6, CHCl₃); νmax 2952, 2922, 2854, 1709, 1648, 1582, 1454, 1333, 1246, 1184, 766 cm⁻¹; TOF-MS (ESI⁺) m/z calcd for (C₃₂H₄₂N₂O₄)⁺ 519.3217; found 519.3258.
To a stirring suspension of 1,4,5,8-naphthalenetetracarboxylic dianhydride (1.0 eq., 500 mg, 1.87 mmol) in DMF (20 mL) was added benzyamine (2.2 eq., 439 mg, 4.10 mmol). The resulting mixture was heated to 120 °C for 4 h. After cooling to rt, the reaction mixture was poured over 1.0 M aqueous HCl (100 mL). The organic product was extracted with EtOAc (3 × 50 mL) and organic layers were washed with saturated aqueous LiCl solution and dried over MgSO₄. Concentration under reduced pressure afforded 13 as a pale yellow solid in 96% yield (801 mg).

**Naphthalenediamide 13**: δH (300 MHz, CDCl₃) 8.77 (4H, s, Naphthyl-H), 7.57-7.54 (4H, m, Ph-H), 7.35-7.28 (6H, m, Ph-H), 5.39 (4H, s, CH₂); δC (75 MHz, CDCl₃) 162.8, 136.5, 131.1, 129.1, 128.5, 127.8, 126.7, 126.6, 44.0. ¹H NMR values correspond to literature values, except for the aliphatic methylene resonance which was previously reported at 3.7 ppm.²¹

To a stirring suspension of 1,4,5,8-naphthalenetetracarboxylic dianhydride (1.0 eq., 500 mg, 1.87 mmol) in H₂O (90 mL) was added aqueous KOH solution (1.0 M, 9 mL) and heated to 50 °C until 1,4,5,8-naphthalenetetracarboxylic dianhydride dissolved. Aqueous H₃PO₄ solution (1.0 M) was used to acidify the reaction mixture to pH 6.4, then butylamine (1.0 eq, 136 mg, 1.87 mmol) was added. Further H₃PO₄ solution was used to readjust the solution to pH 6.4, then heated to 110 °C for 16 h. After cooling to rt, glacial acetic acid (≈3 mL) was added and a precipitate formed. Precipitate filtered and washed with H₂O, then dried under vacuum giving 27 as an off-white solid, in 62% yield (396 mg).

**Naphthalenemonoimide 27**: δH (250 MHz, DMSO-d₆) 8.54 (2H, d, J = 7.5 Hz, Naphthyl-H), 8.17 (2H, d, J = 7.5 Hz, Naphthyl-H), 4.04 (2H, t, J = 7.5 Hz, N-CH₂), 1.63 (2H, quintet, J = 7.5 Hz, CH₂-CH₂-CH₂), 1.36 (2H, sextet, J = 7.5 Hz, CH₂-CH₂), 0.93 (3H, t, J = 7.5 Hz, CH₃) ppm; δC (75 MHz, DMSO-d₆) 168.6, 162.9, 130.1, 129.1, 128.6, 125.5, 124.4, 39.6, 29.6, 19.8, 13.8 ppm. ¹H NMR values correspond with literature values.²²
To a stirring suspension of 27 (1.0 eq., 300 mg, 0.92 mmol) in DMF (20 mL) was added benzhydrylamine (1.0 eq., 164 mg, 0.92 mmol). The resulting mixture was heated to 140 °C for 16 h. After cooling to rt, the reaction mixture was poured over 1.0 M aqueous HCl (50 mL). The organic product was extracted with CHCl₃ (3 × 50 mL) and organic layers were washed with saturated aqueous LiCl solution and dried over MgSO₄. Concentration under reduced pressure afforded the pale orange solid, 17, in 93% yield (408 mg).

**Naphthalenediimide 17**: δ₉ (300 MHz, CDCl₃) 8.74 (4H, s, Naphthyl-H), 7.63 (1H, s, Ph-CH-PH), 7.48-7.45 (4H, m, Ph-H), 7.38-7.30 (6H, m, Ph-H), 4.20 (2H, t, J = 7.5 Hz, N-CH₂-), 1.76-1.68 (2H, m, CH₂-CH₂-CH₃), 1.46 (2H, sextet, J = 7.0 Hz, -CH₂-CH₃), 0.99 (3H, t, J = 7.0 Hz, -CH₃) ppm; δc (75 MHz, CDCl₃) 162.9 (C=O), 162.8 (C=O), 138.0 (Ar C), 131.4 (2C, Naphthyl CH), 130.9 (2C, Naphthyl CH), 130.1 (Ar C), 128.8 (4C, Ar CH), 128.3 (4C, Ar CH), 127.6 (2C, Ar CH), 126.8 (Ar C), 126.7 (Ar C), 126.7 (Ar C), 59.5 (Ph-CH-Ph), 40.8 (N-CH₃), 30.1 (N-CH₂-CH₂), 20.3 (CH₂-CH₃), 13.8 (CH₃) ppm; νmax 3063, 2955, 1702, 1656, 1578, 1451, 1336, 1244, 770, 696 cm⁻¹; TOF-MS (ESI+) m/z calcd for (C₃₁H₂₄N₂O₄+Na)⁺ 511.1634; found 511.1650.
General Conditions for Initial C-H Borylation Reactions

Bis(pinacolato)diboron and naphthalene diimide 5 (1.0 eq.) were weighed out into a round-bottomed flask with stirrer bar and condenser and transferred into an argon filled glovebox. [Ir(cod)OMe]_2 (0.03 eq.) and ligand (0.12 eq.) were added, then the sealed vessel was removed from the glovebox. The solvent was added via syringe through the suba-seal. The reaction mixture was subjected to thermal heating at 110 °C for 48 h under Ar. After cooling to rt, solvent was removed under reduced pressure and where stated, products were purified via column chromatography (CH₂Cl₂, graduated to 5% EtOAc in CH₂Cl₂).

C-H Borylation using previously reported PDI borylation conditions

The general procedure for C-H borylation was followed, using B₃pin₂ (8.0 eq., 884 mg, 3.48 mmol), 5 (189 mg, 0.435 mmol), [Ir(cod)OMe]₂ (8.8 mg, 0.0131 mmol) and perfluorotriphenylphosphine (28 mg, 0.0506 mmol) in dioxane (7.0 mL) for 48 h. 17% conversion to monoborylated product 6 and 76% conversion to diborylated products 7 and 8 (1:1 ratio) were calculated by °H NMR. The presence of large quantities of residual B₃pin₂ caused problems of co-elution upon chromatography; 2% isolated yield of monoborylated 6 (4 mg, Rf = 0.45 in 90:10 CH₂Cl₂/EtOAc) and 12% isolated yield of diborylated 7 and 8 (36 mg, Rf = 0.21 in 90:10 CH₂Cl₂/EtOAc) were obtained.

Monoborylated 6: δ_H (400 MHz, CDCl₃) 8.71 (3H, s, Naphthyl-H), 4.14 (2H, d, J = 7.2 Hz, N-CH₂), 4.11 (2H, d, J = 7.2 Hz, N-CH₂), 1.91-1.81 (2H, m, methine H), 1.51 (12H, s, C-CH₃), 1.43-1.34 (8H, m, CH₂-CH₃), 0.95 (12H, t, J = 7.4 Hz, CH₂-CH₃); δ_C (100 MHz, CDCl₃) 164.8, 163.5, 163.3, 163.3, 133.9, 130.9,
130.9, 129.9, 126.7, 126.5, 126.3, 126.0, 125.1, 84.9, 44.2, 44.1, 39.4, 39.4, 24.9, 23.5, 23.4, 10.6, 10.5; δH(11) (96 MHz, CDCl3) 36.9; νmax 2964, 2931, 2877, 1704, 1660, 1579, 1447, 1318, 1236, 1139, 849, 786, 730 cm⁻¹; TOF-MS (ESI⁺) m/z calcd for (C33H32BN2O6+Na)⁺ 583.2950; found 583.2876.

**Diborylated 7 and 8:** δH (500 MHz, CDCl3) 8.69 (2H, s, Naphthyl-H), 8.69 (2H, s, Naphthyl-H), 4.14 (2H, d, J = 7.3 Hz, N-CH2), 4.11 (4H, d, J = 7.1 Hz, N-CH2), 4.08 (2H, d, J = 7.1 Hz, N-CH2), 1.88-1.82 (4H, m, methine H), 1.51 (24H, B-O-C-CH3), 1.50 (24H, B-O-C-CH3), 1.40-1.34 (16H, m, CH2-CH3), 0.94 (12H, t, J = 7.3 Hz, CH2-CH3), 0.94 (12H, t, J = 7.3 Hz, CH2-CH3); δC (125 MHz, CDCl3) 164.9, 164.9, 163.5, 163.5, 139.9, 133.8, 129.8, 129.6, 126.8, 126.3, 126.0, 125.3, 125.0, 125.0, 124.9, 84.9, 44.1, 44.0, 43.8, 39.5, 39.4, 39.4, 24.9, 24.9, 23.6, 23.5, 23.4, 10.7, 10.5, 10.4; δH(11) (160 MHz, CDCl3) 30.6; νmax 2974, 2932, 1703, 1661, 1584, 1453, 1371, 1319, 1233, 1140, 851 cm⁻¹; TOF-MS (ESI⁺) m/z calcd for (C33H32BN2O6+Na)⁺ 709.3807; found 709.3816.

**C-H Borylation with 24 h Reaction Time**

The general procedure for C-H borylation was followed, using B2pin2 (8.0 eq., 884 mg, 3.48 mmol), 5 (189 mg, 0.435 mmol), [Ir(cod)OMe]2 (8.8 mg, 0.0131 mmol) and perfluorotriphenylphosphine (28 mg, 0.0506 mmol) in dioxane (7.0 mL) for 24 h. 28% conversion to monoborylated product 6 and 64% conversion to diborylated products 7 and 8 (1:1 ratio) were calculated by ²H NMR.
C-H Borylation with 4.0 equivalents of B$_2$pin$_2$

The general procedure for C-H borylation was followed, using B$_2$pin$_2$ (4.0 eq., 442 mg, 1.74 mmol), 5 (189 mg, 0.435 mmol), [Ir(cod)OMe]$\text{I}_2$ (8.8 mg, 0.0131 mmol) and perfluorotriphenylphosphine (28 mg, 0.0506 mmol) in dioxane (7.0 mL) for 48 h. 50% conversion to monoborylated product 6 and 25% conversion to diborylated products 7 and 8 (1:1 ratio) were calculated by $^1$H NMR.

C-H Borylation with Hexafluorobenzene

The general procedure for C-H borylation was followed, using B$_2$pin$_2$ (8.0 eq., 294 mg, 1.160 mmol), 5 (63 mg, 0.145 mmol), [Ir(cod)OMe]$\text{I}_2$ (2.9 mg, 0.0044 mmol) and perfluorotriphenylphosphine (9.3 mg, 0.0174 mmol) in hexafluorobenzene (3.0 mL) for 48 h. 18% conversion to monoborylated product 6 and 76% conversion to diborylated products 7 and 8 (1:1 ratio) were calculated by $^1$H NMR.
General Conditions for Reaction Optimisation of Microwave-Assisted C-H Borylation

Bis(pinacolato)diboron and naphthalene diimide 5 (1.0 eq.) were weighed out into a microwave vial with stirrer bar and transferred into a glovebox. [Ir(cod)OMe]₂ (0.03 eq.), ligand (0.12 eq.) and hexafluorobenzene were added and the crimp cap was sealed. The reaction mixture was subjected to microwave heating at 140 °C for 2 h. After cooling to rt, solvent was removed under reduced pressure and where stated, products were purified via silica gel column chromatography (eluent CH₂Cl₂, graduated to 5% EtOAc in CH₂Cl₂, unless otherwise stated).

C-H Borylation Ligand Screening

The general procedure for microwave-assisted C-H borylation was followed, using B₂pin₂ (4.0 eq., 147 mg, 0.580 mmol), 5 (63 mg, 0.145 mmol), [Ir(cod)OMe]₂ (2.9 mg, 0.0044 mmol) and ligand (0.0174 mmol) in hexafluorobenzene (3.0 mL). Conversion to monoborylated product 6 and to diborylated products 7 and 8 (1:1 ratio in every instance) were calculated by ¹H NMR.
### C-H Borylation using various quantities of B$_2$pin$_2$

The general procedure for microwave-assisted C-H borylation was followed, using B$_2$pin$_2$, 5 (63 mg, 0.145 mmol), [Ir(cod)OMe]$_2$ (2.9 mg, 0.0044 mmol) and perfluorotriphenylphosphine (9.3 mg, 0.0174 mmol) in hexafluorobenzene (3.0 mL). Conversion to monoborylated product 6 and to diborylated products 7 and 8 (1:1 ratio in every case) were calculated by $^1$H NMR.

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<tr>
<th>B$_2$pin$_2$</th>
<th>Conversion to 6</th>
<th>Conversion to 7 and 8</th>
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<tbody>
<tr>
<td>1.0 eq., 0.145 mmol</td>
<td>36%</td>
<td>9%</td>
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<tr>
<td>2.0 eq., 0.290 mmol</td>
<td>48%</td>
<td>42%</td>
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<td>3.0 eq., 0.435 mmol</td>
<td>22%</td>
<td>75%</td>
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<tr>
<td>8.0 eq., 1.160 mmol</td>
<td>7%</td>
<td>84%</td>
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C-H Borylation of Homochiral NDI

![C-H Borylation of Homochiral NDI](image)

The general procedure for microwave-assisted C-H borylation was followed, using B$_2$pin$_2$ (4.0 eq., 147 mg, 0.580 mmol), 9 (75 mg, 0.145 mmol), [Ir(cod)OMe]$_2$ (2.9 mg, 0.0044 mmol) and perfluorotriphenylphosphine (9.3 mg, 0.0174 mmol) in hexafluorobenzene (3.0 mL). 16% conversion to monoborylated product 10 and 81% conversion to diborylated products 11 and 12 (1:1 ratio) were calculated by $^1$H NMR. Monoborylated 10 was isolated in 9% yield (8 mg, $R_f$ = 0.40 in 95:5 hexane/EtOAc) and diborylated 11 and 12 were isolated as an inseparable 1:1 mixture in 61% yield (68 mg, $R_f$ = 0.23 in 95:5 hexane/EtOAc).

**Monoborylated 10:** $\delta_{n}$ (300 MHz, CDCl$_3$) 8.68 (3H, s, Ar-H), 5.30-5.16 (2H, m, 2 × N-CH$_2$), 2.24-2.07 (2H, m), 1.96-1.82 (2H, m), 1.57 (3H, d, $J$ = 7.0 Hz, CH-CH$_3$), 1.56 (3H, d, $J$ = 7.0 Hz, CH-CH$_3$), 1.51 (12H, s, B-O-C-CH$_3$), 1.31-1.18 (20H, m, CH$_2$), 0.84 (3H, t, $J$ = 7.0 Hz, CH$_2$-CH$_3$), 0.82 (3H, t, $J$ = 7.0 Hz, CH$_2$-CH$_3$); $\delta_C$ (75 MHz, CDCl$_3$) 164.9, 163.6, 163.4, 163.3, 133.8, 130.8, 130.7, 130.2, 126.6, 126.5, 125.9, 125.3, 84.8, 50.5, 50.3, 33.4, 31.8, 31.7, 29.3, 29.2, 27.0, 24.9, 24.9, 22.6, 22.6, 18.3, 18.2, 14.1, 14.0; $\delta_B$[11] (96 MHz, CDCl$_3$) 33.9; $\nu_{\text{max}}$ 2961, 2925, 2856, 1704, 1653, 1582, 1270, 909, 741 cm$^{-1}$; [\(\alpha\)]$_D^{24}$ = -15.0 (c 0.1, CHCl$_3$), TOF-MS (ESI+) m/z calcd for (C$_{36}$H$_{43}$BN$_2$O$_4$+Na)$^+$ 667.3894; found 667.3938.

**Diborylated 11 and 12:** $\delta_{n}$ (300 MHz, CDCl$_3$) 8.64 (2H, s, Naphthyl-H), 8.64 (2H, s, Naphthyl-H), 5.28-5.09 (4H, m, N-CH$_2$), 2.22-2.01 (4H, m), 1.95-1.81 (4H, m), 1.57 (3H, d, $J$ = 6.5 Hz, CH-CH$_3$ 11), 1.57 (6H, d, $J$ = 7.0 Hz, CH-CH$_3$ 12), 1.53 (3H, d, $J$ = 7.0 Hz, CH-CH$_3$ 13), 1.50 (24H, s, B-O-C-CH$_3$), 1.30-1.18 (40H, m, CH$_2$); 0.87-0.79 (12H, m, CH$_2$-CH$_3$); $\delta_C$ (75 MHz, CDCl$_3$) 164.9, 164.9, 163.6, 163.5, 138.3 (br), 133.8, 133.6, 130.0, 129.9, 126.7, 125.9, 125.1, 125.0, 84.8, 50.6, 50.4, 50.3, 33.4, 33.4, 31.8, 31.8, 31.7, 29.3, 29.1, 29.1, 27.0, 25.0, 24.9, 24.9, 24.8, 22.6, 18.3, 18.2, 18.1, 14.0; $\delta_B$[11] (96 MHz, CDCl$_3$) 33.2; $\nu_{\text{max}}$ 2977, 2926, 2857, 1701, 1656, 1585, 1448, 1304, 1136, 731 cm$^{-1}$; TOF-MS (ESI+) m/z calcd for (C$_{46}$H$_{64}$ B$_2$N$_2$O$_4$+Na)$^+$ 793.4746; found 793.4678.
C-H Borylation of Dibenzyl NDI

The general procedure for microwave-assisted C-H borylation was followed, using B_{3}pin_{2} (4.0 eq., 147 mg, 0.580 mmol), 13 (65 mg, 0.145 mmol), [Ir(cod)OMe]_{2} (2.9 mg, 0.0044 mmol) and perfluorotriphenylphosphine (9.3 mg, 0.0174 mmol) in hexafluorobenzene (3.0 mL). 42% conversion to monoborylated product 14 and 48% conversion to diborylated products 15 and 16 (1:1 ratio) were calculated by 1H NMR. Monoborylated 14 was isolated in 30% yield (25 mg, R_{f} = 0.18 in 85:15 petrol/EtOAc) and diborylated 15 and 16 were isolated as an inseparable 1:1 mixture in 34% yield (34 mg, R_{f} = 0.08 in 85:15 petrol/EtOAc).

**Monoborylated 14**: δ_{H} (300 MHz, CDCl_{3}) 8.74-8.72 (3H, m, Naphthyl-H), 7.55-7.52 (4H, m, Ph-H), 7.34-7.23 (6H, m, Ph-H), 5.38 (2H, s, N-CH_{2}), 5.35 (2H, s, N-CH_{2}), 1.52 (12H, s, CH_{2}); δ_{C} (75 MHz, CDCl_{3}) 164.5, 163.1, 162.8, 162.8, 136.5, 136.3, 134.2, 131.1, 131.0, 129.9, 129.4, 129.1, 128.6, 128.5, 127.8, 126.7, 126.6, 126.3, 126.0, 125.1, 85.0, 44.1, 44.0, 24.9; δ_{B(11)} (96 MHz, CDCl_{3}) 33.0; ν_{max} 2977, 2931, 1704, 1661, 1447, 1320, 1237, 1132, 851, 699 cm^{-1}; TOF-MS (ESI+) m/z calcd for (C_{34}H_{29}B\_\_N_{3}O_{6}^{+}Na)^{+} 595.2016; found 595.2065.

**Diborylated 15 and 16**: δ_{H} (300 MHz, CDCl_{3}) 8.70 (2H, s, Naphthyl-H), 8.69 (2H, s, Naphthyl-H), 7.54-7.51 (8H, m, Ar-H), 7.34-7.24 (12H, m, Ar-H), 5.38 (2H, s, N-CH_{2} 15), 5.35 (4H, s, N-CH_{2} 16), 5.31 (2H, s, N-CH_{2} 15), 1.52 (24H, s, B-O-C-CH_{3}), 1.51 (24H, s, B-O-C-CH_{3}); δ_{C} (75 MHz, CDCl_{3}) 164.5, 164.4, 163.1, 163.0, 136.6, 136.4, 134.1, 134.0, 129.8, 129.7, 129.6, 129.3, 129.1, 128.5, 128.5, 128.4, 127.8, 126.0, 125.1, 124.9, 85.0, 44.2, 44.0, 43.9, 24.9; δ_{B(11)} (96 MHz, CDCl_{3}) 33.4; ν_{max} 2977, 2931, 1703, 1660, 1584, 1448, 1313, 1232, 1133, 964, 852, 713 cm^{-1}; TOF-MS (ESI+) m/z calcd for (C_{40}H_{36}B_{2}N_{2}O_{6}^{+}Na)^{+} 721.2868; found 721.2896.
C-H Borylation of differentially N-substituted NDI

The general procedure for microwave-assisted C-H borylation was followed, using B$_2$pin$_2$ (4.0 eq., 147 mg, 0.580 mmol), 17 (71 mg, 0.145 mmol), [Ir(cod)OMe$_2$]$_2$ (2.9 mg, 0.0044 mmol) and perfluorotriphenylphosphine (9.3 g, 0.0174 mmol) in hexafluorobenzene (3.0 mL). Due to overlapping signals, conversion could not be determined by $^3$H NMR. Diborylated products were isolated via silica gel column chromatography (eluent CH$_2$Cl$_2$) graduated to 1.0% EtOAc in CH$_2$Cl$_2$ with $R_f$ = 0.10) in approximately a 1:2:1 ratio; 18 (17 mg, 16%), 20 (37 mg, 34%) and 19 (18 mg, 17%). Each isomer contained ≈15% of other isomers by $^3$H NMR, which could not be further separated.

**Diborylated 18**: $\delta$H (500 MHz, CDCl$_3$) 8.67 (2H, s, Naphthyl-H), 7.62 (1H, s, Ph-CH-Ph), 7.46-7.44 (4H, m, Ph-H), 7.34-7.29 (6H, m, Ph-H), 4.14 (2H, t, $J$ = 7.5 Hz, N-CH$_2$), 1.73-1.70 (2H, m, CH$_2$-CH$_2$-CH$_3$), 1.49 (24H, s, C-CH$_3$), 1.27-1.22 (2H, m, CH$_2$-CH$_3$), 0.97 (3H, t, $J$ = 7.0 Hz, CH$_2$-CH$_3$); $\delta$C (125 MHz, CDCl$_3$) 164.1, 163.2, 138.1, 134.4, 134.3, 128.7, 128.3, 128.2, 128.1, 127.5, 126.1, 125.1, 85.0, 59.6, 40.8, 29.9, 24.8, 20.2, 13.8; $\nu$$_{max}$ 2976, 2933, 1703, 1665, 1584, 1448, 1309, 1231, 908, 851, 697 cm$^{-1}$; TOF-MS (ESI$^+$) m/z calcd for (C$_{43}$H$_{46}$B$_2$N$_2$O$_8$+Na)$^+$ 763.3338; found 763.3296.

**Diborylated 19**: $\delta$H (400 MHz, CDCl$_3$) 8.67 (2H, s, Naphthyl-H), 7.50 (1H, s, Ph-CH-Ph), 7.43-7.38 (4H, m, Ph-H), 7.32-7.27 (6H, m, Ph-H), 4.19 (2H, t, $J$ = 7.5 Hz, N-CH$_2$), 1.74-1.66 (2H, m, CH$_2$-CH$_2$-CH$_3$), 1.41 (24H, s, B-O-C-CH$_3$), 1.26-1.24 (2H, m, CH$_2$-CH$_3$), 0.97 (3H, t, $J$ = 7.5 Hz, CH$_2$-CH$_3$); $\delta$C (100 MHz, CDCl$_3$) 164.4, 163.1, 137.9, 133.8, 129.1, 128.9, 128.3, 128.2, 127.4, 127.3, 127.2, 126.7, 125.1, 84.9, 60.0, 40.6, 30.1, 24.8, 20.3, 13.7; $\delta$$_{B(11)}$ (96 MHz, CDCl$_3$) 33.5; $\nu$$_{max}$ 2976, 2932, 1704, 1659, 1584, 1448, 1317, 1231, 1135, 851, 729 cm$^{-1}$; TOF-MS (ESI$^+$) m/z calcd for (C$_{43}$H$_{46}$B$_2$N$_2$O$_8$+Na)$^+$ 763.3338; found 763.3314.

**Diborylated 20**: $\delta$H (500 MHz, CDCl$_3$) 8.69 (1H, s, Naphthyl-H), 8.64 (1H, s, Naphthyl-H), 7.57 (1H, s, Ph-CH-Ph), 7.44-7.42 (4H, m, Ph-H), 7.33-7.31 (6H, m, Ph-H), 4.16 (2H, t, $J$ = 7.0 Hz, N-CH$_2$), 1.77-1.67 (2H, m, CH$_2$-CH$_2$-CH$_3$), 1.48 (12H, s, B-O-C-CH$_3$), 1.46 (12H, s, B-O-C-CH$_3$), 1.26-1.24 (2H, m, CH$_2$-CH$_3$), 0.98 (3H, t, $J$ = 7.0 Hz, CH$_2$-CH$_3$); $\delta$C (125 MHz, CDCl$_3$) 164.7, 164.4, 163.1, 162.9, 138.0, 134.2, 133.8, 129.9, 129.8, 128.9, 128.7, 128.3, 128.2, 127.4, 126.2, 125.9, 125.1, 124.9, 84.9, 59.7, 40.7, 30.0, 24.9, 20.2, 13.7; $\delta$$_{B(11)}$ (96 MHz, CDCl$_3$) 35.4; $\nu$$_{max}$ 2976, 2936, 1706, 1663, 1584, 1448, 1307, 1232, 936, 851 cm$^{-1}$; TOF-MS (ESI$^+$) m/z calcd for (C$_{43}$H$_{46}$B$_2$N$_2$O$_8$+Na)$^+$ 763.3338; found 763.3359.
General Procedure for Suzuki Reactions

To a stirring solution of borylated NDI (1.0 eq.) and R²-Br (1.3 eq. per boronic ester) in toluene (10 mL) and EtOH (0.1 mL) under Ar was added K₂CO₃ (5.6 eq. per boronic ester) in H₂O (1 mL) and Pd(PPh₃)₄ (0.15 eq.). The reaction mixture was heated to 80 °C under Ar and stirred for 16 h, before cooling to rt. The solvent was removed under reduced pressure and subjected to silica gel column chromatography with an eluent of petrol/EtOAc (graduated from 2% EtOAc to 15% EtOAc, unless otherwise stated).

Suzuki Reaction of 14 and bromobenzene

The general procedure for the Suzuki reaction was followed, using 14 (24 mg, 0.042 mmol), bromobenzene (9.0 mg, 0.055 mmol), K₂CO₃ (32 mg, 0.235 mmol) and Pd(PPh₃)₄ (7.0 mg, 0.006 mmol). 21 was isolated in 81% yield (18 mg, R₂ = 0.30 in 90:10 petrol/EtOAc).

Naphthalenediimide 21: δₛ (400 MHz, CDCl₃) 8.82 (1H, d, J = 7.7 Hz, Naphthyl-H), 8.76 (1H, d, J = 7.7 Hz, Naphthyl-H), 8.61 (1H, s, Naphthyl-H), 7.55-7.23 (15H, m, Ar-H), 5.39 (2H, s, N-CH₂), 5.28 (2H, s, N-CH₂); δₗ (100 MHz, CDCl₃) 162.9, 162.7, 162.6, 162.2, 148.5, 140.3, 136.6, 136.5, 135.8, 131.5, 130.7, 129.1, 129.0, 128.6, 128.4, 128.4, 128.0, 127.8, 127.8, 127.6, 127.0, 126.6, 126.1, 125.3, 123.0, 44.0, 43.8; IR ν max 3031, 2963, 2962, 1705, 1665, 1572, 1446, 1325, 1197, 753, 698 cm⁻¹; UV-Vis ν max 359 (ε 6710 L mol⁻¹ cm⁻¹), 379 (ε 8000 L mol⁻¹ cm⁻¹) nm; TOF-MS (ESI⁺) m/z calcld for (C₃₄H₂₂N₂O₄+Na)⁺ 545.1472; found 545.1507.
The general procedure for the Suzuki reaction was followed, using 14 (15 mg, 0.026 mmol), p-tolylbromide (6.0 mg, 0.034 mmol), K₂CO₃ (20 mg, 0.147 mmol) and Pd(PPh₃)₄ (5.0 mg, 0.004 mmol). 22 was isolated in 56% yield (8 mg, Rₛ = 0.34 in 90:10 petrol/EtOAc).

Naphthalenediimide 22: δ₁ (500 MHz, CDCl₃) 8.80 (1H, d, J = 7.6 Hz, Naphthyl-H), 8.75 (1H, d, J = 7.6 Hz, Naphthyl-H), 8.61 (1H, s, Naphthyl-H), 7.55-7.53 (2H, m, Ar-H), 7.46-7.43 (2H, m, Ar-H), 7.33-7.23 (10H, m, Ar-H), 5.39 (2H, s, N-CH₂), 5.29 (2H, s, N-CH₂), 2.47 (3H, s, CH₃); δ₁c (125 MHz, CDCl₃) 162.9, 162.7, 162.3, 148.7, 138.4, 137.3, 136.7, 136.5, 136.1, 131.4, 130.5, 129.2, 129.1, 129.0, 128.6, 128.4, 128.1, 127.8, 127.6, 126.9, 126.6, 125.2, 44.0, 43.8, 21.5; IR νmax 3032, 2965, 2926, 2854, 1705, 1665, 1434, 1324, 1222, 751, 698 cm⁻¹; UV-Vis νmax 359 (ε 6570 L mol⁻¹ cm⁻¹), 379 (ε 8040 L mol⁻¹ cm⁻¹) nm; TOF-MS (ESI+) m/z calcd for (C₂₃H₂₄N₂O₄⁺Na⁺) 559.1628; found 559.1664.

The general procedure for the Suzuki reaction was followed, using 14 (23 mg, 0.040 mmol), p-methoxyphenylbromide (10 mg, 0.052 mmol), K₂CO₃ (31 mg, 0.224 mmol) and Pd(PPh₃)₄ (7.0 mg, 0.006 mmol). 23 was isolated in 68% yield (15 mg, Rₛ = 0.19 in 85:15 petrol/EtOAc).

Naphthalenediimide 23: δ₁ (400 MHz, CDCl₃) 8.80 (1H, d, J = 7.5 Hz, Naphthyl-H), 8.74 (1H, d, J = 7.5 Hz, Naphthyl-H), 8.62 (1H, s, Naphthyl-H), 7.54 (2H, dt, J = 7.0, 1.5, o-Ph-H), 7.46 (2H, dt, J = 7.0, 1.5, o-Ph-H), 7.47-7.44 (2H, m, Ar-H), 7.33 (2H, d, J = 8.8 Hz, MeO-Ar-H), 7.33-7.23 (6H, m, Ph-H), 7.03 (2H, d, J = 8.8 Hz, MeO-Ar-H), 5.39 (2H, s, N-CH₂), 5.30 (2H, s, N-CH₂), 3.91 (3H, s, O-CH₃); δ₁c (100 MHz, CDCl₃) 162.9, 162.8, 162.7, 162.4, 159.9, 148.4, 136.7, 136.5, 136.3, 132.3, 131.4, 130.4, 129.9, 129.1, 129.0, 128.6, 128.4, 128.0, 127.8, 127.6, 126.9, 126.6, 125.9, 125.2, 122.7, 113.9, 55.3, 44.0, 43.8; IR νmax 3014, 2963, 2927, 2839, 1704, 1663, 1605, 1436, 1249, 1178, 750, 700 cm⁻¹; UV-Vis νmax 277 (ε 12500 L mol⁻¹ cm⁻¹), 360 (ε 17090 L mol⁻¹ cm⁻¹), 380 (ε 20180 L mol⁻¹ cm⁻¹), 459 (ε 3610 L mol⁻¹ cm⁻¹) nm; TOF-MS (ESI+) m/z calcd for (C₂₃H₂₄N₂O₄⁺Na⁺) 575.1577; found 575.1559.
The general procedure for the Suzuki reaction was followed, using 14 (27 mg, 0.047 mmol), p-nitrophenylbromide (12 mg, 0.061 mmol), K$_2$CO$_3$ (37 mg, 0.264 mmol) and Pd(PPh$_3$)$_4$ (8.0 mg, 0.007 mmol). 24 was isolated in 73% yield (19 mg, R$_f$ = 0.16 in 80:20 petrol/EtOAc).

**Naphthalenediimide 24**: δ$_\text{H}$ (400 MHz, CDCl$_3$) 8.87 (1H, d, J = 7.5 Hz, Naphthyl-H), 8.82 (1H, d, J = 7.5 Hz, Naphthyl-H), 8.53 (1H, s, Naphthyl-H), 8.37 (2H, d, J = 8.7 Hz, NO$_2$-Ar-H), 7.54 (2H, d, J = 7.2 Hz, Ph-H), 7.51 (2H, d, J = 8.7 Hz, NO$_2$-Ar-H), 7.43 (2H, d, J = 7.2 Hz, Ph-H), 7.34-7.23 (6H, m, Ar-H), 5.40 (2H, s, N-CH$_3$), 5.26 (2H, s, N-CH$_3$); δ$_\text{C}$ (100 MHz, CDCl$_3$) 162.6, 162.4, 162.4, 161.1, 147.7, 147.1, 145.5, 136.3, 136.3, 134.3, 132.0, 131.4, 129.2, 129.1, 129.0, 128.6, 128.5, 128.0, 127.9, 127.6, 127.0, 126.7, 126.5, 125.8, 123.7, 123.3, 44.1, 44.0; IR ν$_\text{max}$ 3030, 2926, 2854, 1705, 1665, 1518, 1439, 1346, 1310, 750, 699 cm$^{-1}$; UV-Vis ν$_\text{max}$ 280 (ε 13320 L mol$^{-1}$ cm$^{-1}$), 361 (ε 13540 L mol$^{-1}$ cm$^{-1}$), 380 (ε 14820 L mol$^{-1}$ cm$^{-1}$) nm; TOF-MS (ESI+) m/z calcld for (C$_{34}$H$_{27}$N$_2$O$_5$+Na)$^+$ 590.1323; found 590.1361.

The general procedure for the Suzuki reaction was followed, using 14 (22 mg, 0.038 mmol), p-trifluoromethylphenylbromide (11 mg, 0.050 mmol), K$_2$CO$_3$ (30 mg, 0.215 mmol) and Pd(PPh$_3$)$_4$ (7 mg, 0.006 mmol). 25 was isolated in 69% yield (16 mg, R$_f$ = 0.31 in 90:10 petrol/EtOAc).

**Naphthalenediimide 25**: δ$_\text{H}$ (400 MHz, CDCl$_3$) 8.85 (1H, d, J = 7.7 Hz, Naphthyl-H), 8.79 (1H, d, J = 7.7 Hz, Naphthyl-H), 8.54 (1H, s, Naphthyl-H), 7.77 (2H, d, J = 8.1 Hz, F$_3$C-Ar-H), 7.54 (2H, d, J = 7.0 Hz, Ph-H), 7.47 (2H, d, J = 8.1 Hz, F$_3$C-Ar-H), 7.44 (2H, d, J = 7.0 Hz, Ph-H), 7.34-7.23 (6H, m, Ph-H), 5.39 (2H, s, N-CH$_3$), 5.27 (2H, s, N-CH$_3$); δ$_\text{C}$ (100 MHz, CDCl$_3$) 162.7, 162.5, 162.5, 162.1, 146.6, 144.0, 136.4, 136.4, 135.1, 131.5 (q, J = 59 Hz, C-CF$_3$), 129.1, 129.0, 128.6, 128.5, 128.4, 128.1, 127.9, 127.8, 127.7, 127.0, 126.7, 126.3, 125.4 (2C, q, J = 4 Hz, C-CF$_3$), 124.4 (q, J = 238 Hz, CF$_3$), 44.0, 43.9; δ$_\text{C}$ (376 MHz, CDCl$_3$) -62.43; IR ν$_\text{max}$ 3018, 2966, 2926, 2852, 1705, 1665, 1438, 1324, 1066, 750, 698 cm$^{-1}$; UV-Vis ν$_\text{max}$ 360 (ε 5250 L mol$^{-1}$ cm$^{-1}$), 379 (ε 6030 L mol$^{-1}$ cm$^{-1}$) nm; TOF-MS (ESI+) m/z calcld for (C$_{35}$H$_{21}$F$_3$N$_2$O$_5$+Na)$^+$ 613.1346; found 613.1427.
Suzuki Reaction of 20 and bromobenzene

The general procedure for the Suzuki reaction was followed, using 20 (22 mg, 0.030 mmol), bromobenzene (12 mg, 0.077 mmol), K$_2$CO$_3$ (45 mg, 0.327 mmol) and Pd(PPh$_3$)$_4$ (10 mg, 0.009 mmol). 26 was isolated in 71% yield (13 mg, R$_f$ = 0.23 in 50:50 CH$_2$Cl$_2$/EtOAc), using silica gel column chromatography (eluent graduated from 20% CH$_2$Cl$_2$ in hexane to 55% CH$_2$Cl$_2$ in hexane). Purity of isolated 26 was determined to be 87% by $^1$H-NMR, with 13% isomeric impurities deriving from cross-coupling of 18 and 19 (present as impurities in the starting material).

Naphthalenediimide 26: $\delta_{H}$ (300 MHz, CDCl$_3$) 8.68 (1H, s, Naphthyl-H), 8.61 (1H, s, Naphthyl-H), 7.51-7.27 (21H, m, Ph-H and Ph-CH-Ph), 4.08 (2H, t, $J$ = 7.5 Hz, N-CH$_2$), 1.66-1.59 (2H, m, CH$_2$-CH$_2$-CH$_2$), 1.42-1.31 (2H, m, CH$_2$-CH$_3$), 0.92 (3H, t, $J$ = 7.5 Hz, CH$_3$); $\delta_{C}$ (75 MHz, CDCl$_3$) 162.7, 162.5 162.4, 162.2, 147.7, 147.6, 140.4, 139.9, 138.0, 136.3, 135.7, 130.1, 128.9, 128.8, 128.4, 128.3, 128.1, 127.9, 127.8, 127.4, 127.3, 127.0, 125.7, 125.7, 123.5, 59.7, 40.8, 30.0, 20.3, 13.8; IR $\nu_{\text{max}}$ 3059, 3029, 2958, 2871, 1707, 1666, 1436, 1301, 1205, 765, 696, cm$^{-1}$; UV-Vis $\nu_{\text{max}}$ 251 ($\varepsilon$ 11830 L mol$^{-1}$ cm$^{-1}$), 359 ($\varepsilon$ 5430 L mol$^{-1}$ cm$^{-1}$), 377 ($\varepsilon$ 6180 L mol$^{-1}$ cm$^{-1}$) nm; TOF-MS (ESI+) $m/z$ calcd for [C$_{43}$H$_{32}$N$_2$O$_4$+Na]$^+$ 663.2260; found 663.2266.
COSY
(300 MHz, CDCl₃)
HSQC (300 MHz, CDCl$_3$)

HMBC (300 MHz, CDCl$_3$)
HMBC (300 MHz, CDCl₃)
NOESY (500 MHz, CDCl₃
– nOe peaks in red)
COSY (500 MHz, CDCl₃)
COSY (300 MHz, CDCl₃)
HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl₃)
HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl₃)
HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl₃)
COSY (300 MHz, CDCl₃)
HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl₃)
HMBC enlargement (300 MHz, CDCl₃)
COSY (300 MHz, CDCl₃)
HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl$_3$)
HMBC enlargement (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl₃)
HMBC enlargement (300 MHz, CDCl$_3$)
PENDANT (100 MHz, CDCl$_3$ - CH/CH$_3$ up, C/CH$_2$ down)

COSY (400 MHz, CDCl$_3$)
HSQC (400 MHz, CDCl₃)
HMBC (400 MHz, CDCl₃)
COSY (500 MHz, CDCl₃)
PENDANT (125 MHz, CDCl$_3$ - CH/CH$_3$ up, C/CH$_2$ down)

COSY (500 MHz, CDCl$_3$)
HSQC (500 MHz, CDCl₃)
HMBC (500 MHz, CDCl₃)
PENDANT (100 MHz, 
CDCl₃ - CH/CH₃ up, 
C/CH₂ down)
COSY (400 MHz, CDCl₃)
HSQC (400 MHz, CDCl₃)
HMBC (400 MHz, CDCl₃)
$^{19}$F (376 MHz, CDCl$_3$)

COSY (400 MHz, CDCl$_3$)
HSQC (400 MHz, CDCl₃)
HMBC (400 MHz, CDCl₃)
HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl₃)
HMBC enlargement (300 MHz, CDCl₃)
Note: for compounds 22 and 26, extinction coefficients were calculated over a more limited range of concentrations due to availability and solubility issues.