RESEARCH FRONT

CSIRO PUBLISHING

Aust. J. Chem. **2015**, *68*, 1810–1814
http://dx.doi.org/10.1071/CH15393

Full Paper

Iridium-Catalyzed Triborylation of 3-Substituted Indoles

Andrew S. Eastabrook[A] *and Jonathan Sperry*[A,B]

[A]School of Chemical Sciences, University of Auckland, 23 Symonds Street, Auckland 1142, New Zealand.
[B]Corresponding author. Email: j.sperry@auckland.ac.nz

Readily available 3-substituted indoles undergo a one-pot iridium-catalyzed triborylation at the C2, C5, and C7 sites. ^{1}H NMR analysis indicates borylation at C2 and C7 occurs first (no monoborylated product is observed), with the third borylation occurring as a separate, distinct step that is sterically directed to C5 by a combination of the substituent at C3 and the boronate at C7. The resulting tetrasubstituted indoles possess a substitution pattern that is cumbersome to prepare using existing methods.

Manuscript received: 1 July 2015.
Manuscript accepted: 29 July 2015.
Published online: 27 August 2015.

Introduction

Advances in C–H functionalization have facilitated access to substituted aromatics and heteroaromatics that were previously cumbersome to prepare using classical methods.[1] A pertinent example is the iridium-catalyzed borylation of the indole heterocycle (Scheme 1), which was initially discovered to occur regioselectively at C2.[2] If the C2 position is substituted, borylation at C7 predominates.[3] In a landmark development, subjecting an indole with a vacant C2 site to an initial *N*-hydrosilylation directs the subsequent borylation to C7.[4] A one-pot C2/C7 diborylation-C2-protodeborylation process can also be used to access 7-borylindoles.[5] When a bulky directing group is placed on the indole nitrogen, steric factors dictate that the C–H activation/borylation occurs at C3.[6–8]

In an interesting result, ethylindole-2-carboxylate undergoes diborylation to give a mixture of the 4,7- and 5,7-diborylated products (Scheme 1).[9] Although a solitary example that results in a regioisomeric mixture, this observation indicates that the iridium-catalyzed borylation could potentially be used to selectively functionalize the indole heterocycle at sites in addition to C2, C3, and C7, further extending the utility of this reaction. In an extension of our ongoing interest in the iridium-catalyzed borylation of indoles,[10,11] we report herein that several 3-substituted indoles undergo a one-pot regioselective, iridium-catalyzed triborylation at the C2, C5, and C7 sites, delivering tetrasubstituted indoles with a substitution pattern that is difficult to prepare using traditional methods.

Results and Discussion

Having recently demonstrated that the ligand 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen) plays a crucial role in the efficient diborylation (C2/C7) of a 3-substituted indole,[11] skatole (3-methylindole) was subjected to the iridium-catalyzed borylation using this ligand and five equivalents of bis(pinacolato)diboron in efforts to effect triborylation. In a satisfying result, the product **1** was isolated in good yield, resulting from triborylation at C2, C5, and C7 sites (confirmed by nuclear Overhauser effect (NOE) analysis), with no other products observed (Scheme 2).

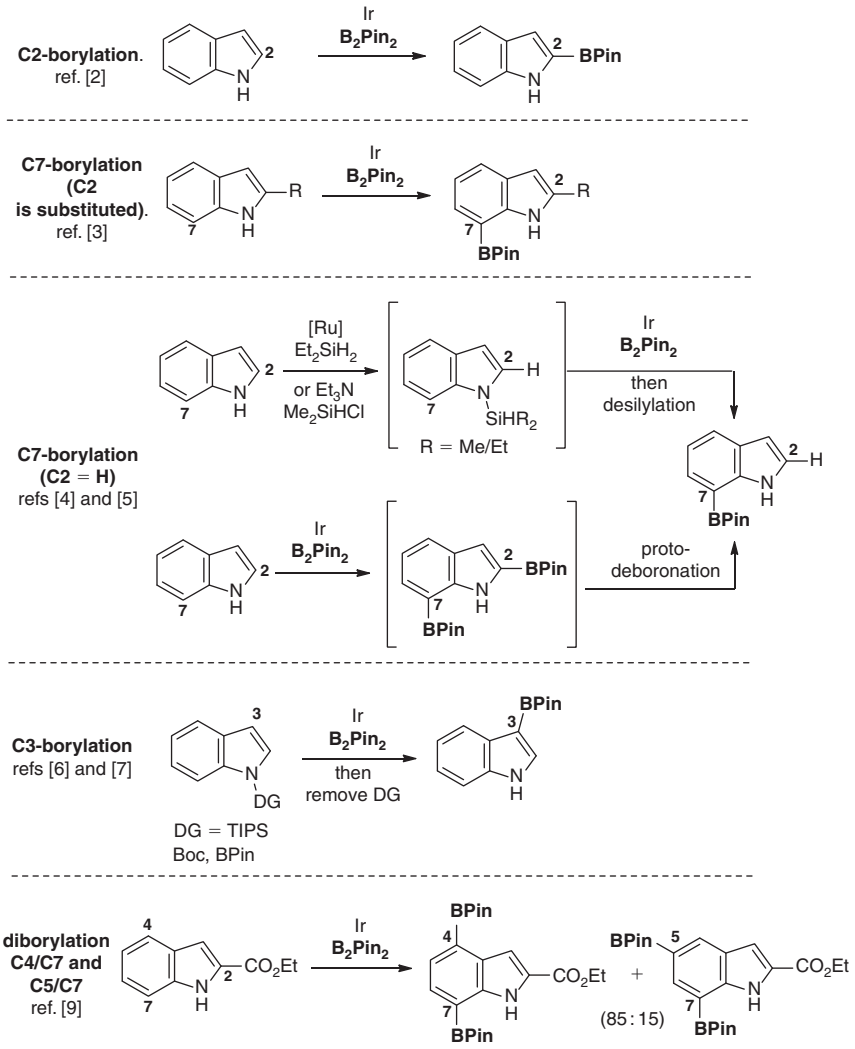
To examine the scope of this triborylation, several 3-substituted indoles were trialled in this process. 3-Chloroindole underwent smooth triborylation to the product **2**. The triborylated tryptophol **3** was also readily obtained. Protected derivatives of indole-3-acetic acid, -propanoic acid, and -butanoic acid were all viable substrates for the triborylation, giving the products **4**–**6**. Triborylated tryptamine **7** and tryptophan **8** are readily available using this process. The building block **8** could potentially be used to access the tryptophan-derived echinulin alkaloids that possess substituents at the 2-, 5-, and 7-positions.[12] In all of the triborylations shown in Scheme 2, thin-layer chromatography and ^{1}H NMR analysis indicates borylation at C2 and C7 occurs first (no monoborylated product is observed), with the third borylation occurring as a separate, distinct step that is sterically directed to C5 by a combination of the substituent at C3 and the boronate at C7. No other regioisomers were detected in any of the examples shown.

Conclusions

Readily available 3-substituted indoles undergo a one-pot, regioselective iridium-catalyzed triborylation at the C2, C5, and C7 sites, providing tetrasubstituted indoles possessing a substitution pattern that is otherwise difficult to access.

Experimental

All reactions were carried out in oven-dried glassware under a nitrogen atmosphere unless otherwise stated. Analytical thin-layer chromatography was performed using 0.2 mm silica plates and compounds were visualized under 365 nm ultraviolet irradiation followed by staining with either alkaline permanganate or ethanolic vanillin solution. Infrared spectra were obtained as thin films between sodium chloride plates. Absorption maxima are expressed in wavenumbers (cm^{-1}). Melting points were recorded on a melting point apparatus and are uncorrected.



Scheme 1. Iridium-catalyzed borylation of indoles.

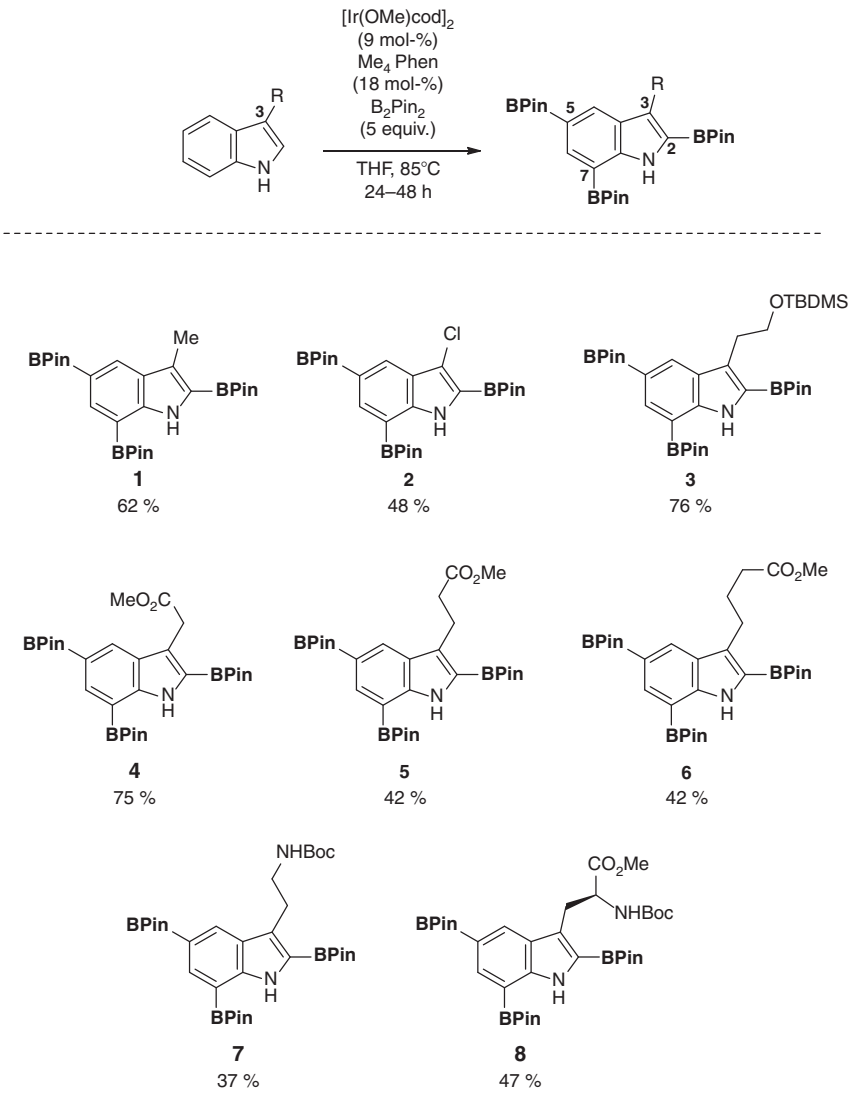
NMR spectra were recorded as indicated on an NMR spectrometer operating at either 500 or 400 MHz for ^{1}H nuclei and 125 or 100 MHz for ^{13}C nuclei. Chemical shifts are reported in parts per million (ppm) relative to the tetramethylsilane (TMS) peak recorded as 0.00 ppm in $CDCl_3$, or the residual chloroform (7.24 ppm) peak. The ^{13}C NMR values were referenced to the residual chloroform (77.1 ppm) peaks. ^{13}C NMR values are reported as chemical shift (δ) and assignment. ^{1}H NMR shift values are reported as chemical shift (δ), relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (J in Hz) and assignment. Assignments were made with the aid of DEPT 90, DEPT 135, COSY, NOESY, and HSQC experiments. High resolution mass spectra were obtained using electrospray ionization in positive ion mode at a nominal accelerating voltage of 70 eV on a microTOF mass spectrometer.

General Procedure

A catalyst solution was prepared by suspending bis(pinacolato) diboron (B_2Pin_2) (5 equivalents), $[Ir(OMe)cod]_2$ (9 mol-%), and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen) (18 mol-%) in THF (1 mL) in a sealed tube with stirring for 1 min. 3-Substituted indole (50 mg) was added and the mixture was heated to 85°C for 24–48 h. The reaction mixture was cooled to room temperature, quenched with one drop of methanol, and then concentrated under vacuum. The crude residue was purified by flash chromatography on silica gel eluting with petroleum ether and ethyl acetate to give the triborylated product.

*3-Methyl-2,5,7-tris(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-indole (**1**)*

The general procedure was performed using 3-methylindole (50 mg, 0.38 mmol), $[Ir(OMe)cod]_2$ (25 mg), Me_4Phen (16 mg), and B_2Pin_2 (484 mg) at 60°C for 96 h. The reaction mixture was cooled to room temperature, concentrated under vacuum, and the crude residue purified by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (9 : 1). The *title compound* (121 mg, 0.24 mmol, 62 %) was obtained as a pale brown solid. Mp 269.3–274.5°C. ν_{max} (neat)/cm^{-1} 3457, 2979, 2927, 1594, 1552, 1475, 1372, 1297, 1254, 1204, 1137, 1115, 1042, 964, 902, 850, 827, 679. δ_H (400 MHz, $CDCl_3$) 9.10 (1H, br s, NH), 8.23 (1H, s, ArH), 8.15 (1H, d, J 1.0, ArH), 2.54 (3H, s, Me), 1.38 (12H, s, 4 × Me), 1.35 (12H, s, 4 × Me), 1.34 (12H, s, 4 × Me). δ_C (100 MHz, $CDCl_3$) 144.9 (C), 137.6 (CH), 131.2 (CH), 127.7 (C), 125.2 (C), 83.7 (2 × C), 83.6 (2 × C), 83.4 (2 × C), 25.0 (4 × Me), 24.9 (8 × Me), 10.2 (Me), 3 × C not



Scheme 2. Iridium-catalyzed triborylation of 3-substituted indoles. All reactions were conducted in a sealed tube with 50 mg of indole. Products **1**–**8** all showed clear NOE correlations between the indole N–H and the boronates at C2 and C7. The products **1** and **3**–**8** all showed NOE correlations between the C3 substituent and the C4–H. In the chlorinated product **2**, the distinctive chemical shifts and splitting pattern of C4–H and C6–H was used to assign the site of the boronate at C5.

observed. *m*/*z* (HRMS ESI) 532.3187; $[C_{27}H_{42}B_3NO_6 + Na]^+$ requires 532.3197.

*3-Chloro-2,5,7-tris(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-indole (**2**)*

The general procedure was performed using 3-chloroindole, $[Ir(OMe)cod]_2$ (20 mg), Me_4Phen (14 mg), and B_2Pin_2 (419 mg) for 24 h. Purification using petroleum ether/ethyl acetate (9 : 1) gave the *title compound* (84 mg, 0.16 mmol, 48 %) as a colourless solid. Mp 244.3–252.1°C. ν_{max} (neat)/cm^{-1} 3452, 2979, 2930, 1592, 1536, 1479, 1371, 1323, 1300, 1253, 1135, 1093, 964, 901, 849, 677. δ_H (400 MHz, $CDCl_3$) 9.26 (1H, br s, NH), 8.29 (1H, s, ArH), 8.18 (1H, d, *J* 1.0, ArH), 1.38 (12H, s, 4 × Me), 1.37 (12H, s, 4 × Me), 1.34 (12H, s, 4 × Me). δ_C (100 MHz, $CDCl_3$) 143.6 (C), 138.4 (CH), 130.5 (CH), 129.4 (C), 125.0 (C), 84.2 (2 × C), 83.9 (2 × C), 83.6 (2 × C), 25.0 (4 × Me), 24.91 (4 × Me), 24.88 (4 × Me), 3 × C not observed. *m*/*z* (HRMS ESI) 552.2630; $[C_{26}H_{39}B_3^{35}ClNO_6 + Na]^+$ requires 552.2643.

*3-(2-(*tert*-Butyldimethylsiloxyethyl))-2,5,7-tris(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-indole (**3**)*

The general procedure was performed using *tert*-butyldimethylsilyltryptophol[13] (50 mg, 0.18 mmol), $[Ir(OMe)cod]_2$ (11 mg), Me_4Phen (8 mg), and B_2Pin_2 (230 mg) for 40 h. Purification using petroleum ether/ethyl acetate (9 : 1) gave the *title compound* (90 mg, 0.14 mmol, 76 %) as a colourless oil. ν_{max} (neat)/cm^{-1} 3453, 2978, 2929, 2857, 1592, 1549, 1472, 1372, 1315, 1257, 1141, 1115, 966, 852, 834, 775, 682. δ_H (400 MHz, $CDCl_3$) 9.19 (1H, br s, NH), 8.33 (1H, s, ArH), 8.13 (1H, d, *J* 0.8, ArH), 3.79 (2H, t, *J* 8.0, CH_2), 3.26 (2H, t, *J* 8.0, CH_2), 1.37 (12H, s, 4 × Me), 1.34 (24H, s, 8 × Me), 0.89 (9H, s, 3 × Me), 0.05 (6H, s, 2 × Me). δ_C (100 MHz, $CDCl_3$) 144.8 (C), 137.6 (CH), 131.6 (CH), 127.3 (C), 125.7 (C), 83.7 (4 × C), 83.4 (2 × C), 65.1 (CH_2), 29.2 (CH_2), 26.1 (3 × Me), 25.0 (4 × Me), 24.92 (4 × Me), 24.89 (4 × Me), 18.4 (C), −5.1 (2 × Me), 3 × C not observed. *m*/*z* (HRMS ESI) 676.4135; $[C_{34}H_{58}B_3NO_7Si + Na]^+$ requires 676.4171.

*Methyl 2,5,7-Tris(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-indole-3-acetate (**4**)*

The general procedure was performed using methyl indole-3-acetate (50 mg, 0.26 mmol), $[Ir(OMe)cod]_2$ (16 mg), Me_4Phen (11 mg), and B_2Pin_2 (336 mg) for 24 h. Purification using petroleum ether/ethyl acetate (4 : 1) gave the *title compound* (113 mg, 0.20 mmol, 75 %) as a colourless solid. Mp 101.0–104.3°C. ν_{max} (neat)/cm^{-1} 3452, 2979, 1737, 1594, 1554, 1476, 1372, 1315, 1257, 1138, 1110, 965, 901, 851, 829, 679. δ_H (500 MHz, $CDCl_3$) 9.30 (1H, br s, NH), 8.21 (1H, s, ArH), 8.15 (1H, s, ArH), 4.10 (2H, s, CH_2), 3.64 (3H, s, Me), 1.38 (12H, s, 4 × Me), 1.34 (12H, s, 4 × Me), 1.33 (12H, s, 4 × Me). δ_C (125 MHz, $CDCl_3$) 172.7 (C=O), 144.8 (C), 137.8 (CH), 131.0 (CH), 126.9 (C), 121.0 (C), 83.8 (2 × C), 83.7 (2 × C), 83.4 (2 × C), 51.7 (Me), 30.9 (CH_2), 25.0 (4 × Me), 24.94 (4 × Me), 24.88 (4 × Me), 3 × C not observed. *m/z* (HRMS ESI) 590.3237; $[C_{29}H_{44}B_3NO_8 + Na]^+$ requires 590.3253.

*Methyl 2,5,7-Tris(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-indole-3-propionate (**5**)*

The general procedure was performed using methyl indole-3-propionate (50 mg, 0.25 mmol), $[Ir(OMe)cod]_2$ (15 mg), Me_4Phen (10 mg), and B_2Pin_2 (312 mg) for 42 h. Purification using petroleum ether/ethyl acetate (4 : 1) gave the *title compound* (60 mg, 0.10 mmol, 42 %) as a colourless oil. ν_{max} (neat)/cm^{-1} 3451, 2979, 1738, 1592, 1549, 1475, 1372, 1314, 1257, 1214, 1166, 1138, 1111, 1045, 965, 901, 851, 830, 731, 681. δ_H (500 MHz, $CDCl_3$) 9.21 (1H, br s, NH), 8.25 (1H, s ArH), 8.15 (1H, d, *J* 1.0, ArH), 3.66 (3H, s, Me), 3.34 (2H, t, *J* 8.1, CH_2), 2.65 (2H, t, *J* 8.1, CH_2), 1.37 (12H, s, 4 × Me), 1.34 (24H, s, 8 × Me). δ_C (125 MHz, $CDCl_3$) 173.9 (C=O), 144.8 (C), 137.7 (CH), 130.9 (CH), 128.0 (C), 126.6 (C), 83.7 (4 × C), 83.4 (2 × C), 51.4 (Me), 36.6 (CH_2), 25.0 (4 × Me), 24.93 (4 × Me), 24.89 (4 × Me), 20.7 (CH_2), 3 × C not observed. *m/z* (HRMS ESI) 604.3382; $[C_{30}H_{46}B_3NO_8 + Na]^+$ requires 604.3410.

*Methyl 2,5,7-Tris(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-indole-3-butyrate (**6**)*

The general procedure was performed using methyl indole-3-butyrate (50 mg, 0.23 mmol), $[Ir(OMe)cod]_2$ (14 mg), Me_4Phen (8 mg), and B_2Pin_2 (292 mg) for 48 h. Purification using petroleum ether/ethyl acetate (4 : 1) gave the *title compound* (57 mg, 0.10 mmol, 42 %) as a colourless oil. ν_{max} (neat)/cm^{-1} 3454, 2979, 2930, 1738, 1592, 1550, 1473, 1372, 1314, 1257, 1214, 1165, 1138, 1111, 1006, 966, 902, 851, 732, 683. δ_H (400 MHz, $CDCl_3$) 9.18 (1H, br s, NH), 8.22 (1H, s, ArH), 8.14 (1H, d, *J* 1.2, ArH), 3.60 (3H, s, Me), 3.07 (2H, t, *J* 7.1, CH_2), 2.30 (2H, t, *J* 7.8, CH_2), 2.03–1.96 (2H, m, CH_2), 1.37 (12H, s, 4 × Me), 1.34 (24H, s, 8 × Me). δ_C (100 MHz, $CDCl_3$) 174.5 (C=O), 145.0 (C), 137.7 (CH), 131.1 (CH), 128.7 (C), 126.8 (C), 83.71 (2 × C), 83.67 (2 × C), 83.4 (2 × C), 51.3 (Me), 33.6 (CH_2), 26.8 (CH_2), 25.0 (4 × Me), 24.94 (4 × Me), 24.90 (4 × Me), 24.3 (CH_2), 3 × C not observed. *m/z* (HRMS ESI) 596.3722; $[C_{31}H_{48}B_3NO_8 + H]^+$ requires 596.3747.

*2,5,7-Tris(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*10-(*tert*-butoxycarbonyl)tryptamine (**7**)*

The general procedure was performed using *N*10-(*tert*-butoxycarbonyl)tryptamine (50 mg, 0.19 mmol), $[Ir(OMe)cod]_2$ (11 mg), Me_4Phen (8 mg), and B_2Pin_2 (244 mg) for 40 h. Purification using petroleum ether/ethyl acetate (4 : 1) gave the *title compound* (45 mg, 0.07 mmol, 37 %) as a colourless oil. ν_{max} (neat)/cm^{-1} 3451, 2977, 2930, 1701, 1592, 1549, 1511, 1477, 1372, 1316, 1257, 1166, 1138, 1112, 965, 903, 851, 731, 683. δ_H (500 MHz, $CDCl_3$) 9.22 (1H, br s, NH), 8.23 (1H, s, ArH), 8.16 (1H, d, *J* 0.7, ArH), 5.08 (1H, br s, NH), 3.41 (2H, t, *J* 5.5, CH_2), 3.19 (2H, t, *J* 6.0, ArH), 1.38 (12H, s, 4 × Me), 1.37 (12H, s, 4 × Me), 1.34 (9H, s, 3 × Me), 1.33 (12H, s, 4 × Me). δ_C (100 MHz, $CDCl_3$) 156.0 (C=O), 145.0 (C), 137.9 (CH), 131.0 (CH), 126.8 (C), 126.6 (C) 84.1 (2 × C), 83.8 (2 × C), 83.4 (2 × C), 77.2 (C, partially obscured by $CDCl_3$), 42.1 (CH_2), 28.5 (3 × Me), 25.0 (4 × Me), 24.91 (4 × Me), 24.87 (4 × Me), 24.7 (CH_2), 3 × C not observed. *m/z* (HRMS ESI) 639.4174; $[C_{33}H_{53}B_3N_2O_8 + H]^+$ requires 639.4170.

*2,5,7-Tris(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(tert-butoxycarbonyl)-L-tryptophan Methyl Ester (**8**)*

General procedure was performed using *N*-Boc-L-tryptophan methyl ester (50 mg, 0.16 mmol), $[Ir(OMe)cod]_2$ (9 mg), Me_4Phen (7 mg), and B_2Pin_2 (199 mg) for 40 h. Purification using petroleum ether/ethyl acetate (4 : 1) gave the *title compound* (51 mg, 0.07 mmol, 47 %) as a colourless solid. Mp 115.1–118.7°C. $[\alpha]_D$ −15.7 (*c* 1.0 in MeOH). ν_{max} (neat)/cm^{-1} 3451, 2979, 1717, 1594, 1372, 1316, 1258, 1140, 1111, 965, 902, 852, 731, 682. δ_H (400 MHz, $CDCl_3$) 9.27 (1H, br s, NH), 8.22 (1H, s, ArH), 8.15 (1H, s, ArH), 5.91 (1H, d, *J* 7.0, NH), 4.41–4.36 (1H, m, CH), 3.73 (3H, s, Me), 3.49–3.33 (2H, m, CH_2), 1.37 (24H, s, 8 × Me), 1.34 (12H, d, *J* 1.7, 4 × Me), 1.32 (9H, s, 3 × Me). δ_C (100 MHz, $CDCl_3$) 173.3 (C=O), 155.7 (C=O), 144.9 (C), 138.0 (CH), 130.8 (CH), 126.6 (C), 123.4 (C), 84.4 (2 × C), 83.8 (2 × C), 83.5 (2 × C), 79.1 (C), 55.0 (CH), 52.1 (Me), 28.3 (3 × Me), 27.0 (CH_2), 24.9 (12 × Me), 3 × C not observed. *m/z* (HRMS ESI) 719.4015. $[C_{35}H_{55}B_3N_2O_{10} + Na]^+$ requires 719.4045.

Supplementary Material

^1H and ^{13}C NMR spectra for compounds **1–8** are available on the Journal's website.

Acknowledgements

The authors thank the Royal Society of New Zealand for funding through the Rutherford Discovery Fellowship Scheme.

References

[1] (a) J. Yang, *Org. Biomol. Chem.* **2015**, *13*, 1930. doi:10.1039/C4OB02171A
(b) I. V. Seregin, V. Gevorgyan, *Chem. Soc. Rev.* **2007**, *36*, 1173. doi:10.1039/B606984N
(c) Y. Nakao, *Synthesis* **2011**, *2011*, 3209. doi:10.1055/S-0030-1260212
(d) J. F. Hartwig, *Chem. Soc. Rev.* **2011**, *40*, 1992. doi:10.1039/C0CS00156B
(e) F. Zhang, D. R. Spring, *Chem. Soc. Rev.* **2014**, *43*, 6906. doi:10.1039/C4CS00137K
(f) G. Shi, Y. Zhang, *Adv. Synth. Catal.* **2014**, *356*, 1419. doi:10.1002/ADSC.201400028
(g) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 10236. doi:10.1002/ANIE.201203269

[2] (a) T. Ishiyama, J. Takagi, J. F. Hartwig, N. Miyaura, *Angew. Chem. Int. Ed.* **2002**, *41*, 3056. doi:10.1002/1521-3773(20020816)41:16<3056::AID-ANIE3056>3.0.CO;2-#
(b) J. Takagi, K. Sato, J. F. Hartwig, T. Ishiyama, N. Miyaura, *Tetrahedron Lett.* **2002**, *43*, 5649. doi:10.1016/S0040-4039(02)01135-8
(c) T. Ishiyama, Y. Nobuta, J. F. Hartwig, N. Miyaura, *Chem. Commun.* **2003**, 2924. doi:10.1039/B311103B

(d) T. Ishiyama, J. Takagi, Y. Yonekawa, J. F. Hartwig, N. Miyaura, *Adv. Synth. Catal.* **2003**, *345*, 1103. doi:10.1002/ADSC.200303058
(e) K. Mertins, A. Zapf, M. Beller, *J. Mol. Catal. A: Chem.* **2004**, *207*, 21. doi:10.1016/S1381-1169(03)00470-9

[3] (a) S. Paul, G. A. Chotana, D. Holmes, R. C. Reichle, R. E. Maleczka, Jr, M. R. Smith, III, *J. Am. Chem. Soc.* **2006**, *128*, 15552. doi:10.1021/JA0631652
(b) F.-M. Meyer, S. Liras, A. Guzman-Perez, C. Perreault, J. Bian, K. James, *Org. Lett.* **2010**, *12*, 3870. doi:10.1021/OL1015674

[4] D. W. Robbins, T. A. Boebel, J. F. Hartwig, *J. Am. Chem. Soc.* **2010**, *132*, 4068. doi:10.1021/JA1006405

[5] (a) R. P. Loach, O. S. Fenton, K. Amaike, D. S. Siegel, E. Ozkal, M. Movassaghi, *J. Org. Chem.* **2014**, *79*, 11254. doi:10.1021/JO502062Z
(b) 7-Borylindoles are also available by subjecting a 2-trimethylsilylindole to borylation followed by desilylation; see ref. [3a].

[6] V. A. Kallepalli, F. Shi, S. Paul, E. N. Onyeozili, R. E. Maleczka, Jr, M. R. Smith, III, *J. Org. Chem.* **2009**, *74*, 9199. doi:10.1021/JO901822B

[7] For use of a traceless directing group, see: S. M. Preshlock, D. L. Plattner, P. E. Maligres, S. W. Krska, R. E. Maleczka, Jr, M. R. Smith, III, *Angew. Chem. Int. Ed.* **2013**, *52*, 12915. doi:10.1002/ANIE.201306511

[8] For an ester directed C3-borylation of methylindole-2-carboxylate using a silica supported iridium complex, see: S. Kawamorita, H. Ohmiya, M. Sawamura, *J. Org. Chem.* **2010**, *75*, 3855. doi:10.1021/JO100352B

[9] W. F. Lo, H. M. Kaiser, A. Spannenberg, M. Beller, M. K. Tse, *Tetrahedron Lett.* **2007**, *48*, 371. doi:10.1016/J.TETLET.2006.11.083

[10] A. S. Eastabrook, C. Wang, E. K. Davison, J. Sperry, *J. Org. Chem.* **2015**, *80*, 1006. doi:10.1021/JO502509S

[11] J. A. Homer, J. Sperry, *Tetrahedron Lett.* **2014**, *55*, 5798. doi:10.1016/J.TETLET.2014.08.104

[12] (a) A. Quilico, L. Panizzi, *Chem. Ber.* **1943**, *76*, 348. doi:10.1002/CBER.19430760408
(b) R. Nakashima, G. P. Slater, *Tetrahedron Lett.* **1971**, *12*, 2649. doi:10.1016/S0040-4039(01)96941-2
(c) H. Fujimoto, T. Fujimaki, E. Okuyama, M. Yamazaki, *Chem. Pharm. Bull.* **1999**, *47*, 1426. doi:10.1248/CPB.47.1426
(d) X. Zou, Y. Li, X. Zhang, Q. Li, X. Liu, Y. Huang, T. Tang, S. Zheng, W. Wang, J. Tang, *Molecules* **2014**, *19*, 17839. doi:10.3390/MOLECULES191117839

[13] Y. Du, H.-Y. Huang, H. Liu, Y.-P. Ruan, P.-Q. Huang, *Synlett* **2011**, 565. doi:10.1055/S-0030-1259521