

# New Route to a [5,5] Carbon Nanotube End-Cap via Direct Borylation of Corannulene

Author: Maria N. Eliseeva

Persistent link: <http://hdl.handle.net/2345/2752>

This work is posted on [eScholarship@BC](#),  
Boston College University Libraries.

---

Boston College Electronic Thesis or Dissertation, 2011

Copyright is held by the author, with all rights reserved, unless otherwise noted.

Boston College

The Graduate School of Arts and Sciences

Department of Chemistry

NEW ROUTE TO A [5,5] CARBON NANOTUBE END-CAP VIA DIRECT  
BORYLATION OF CORANNULENE

a thesis

by

MARIA N. ELISEEVA

submitted in partial fulfillment of the requirements

for the degree of

Master of Science

December 2011

© copyright by MARIA N. ELISEEVA

2011

NEW ROUTE TO A [5,5] CARBON NANOTUBE END-CAP VIA DIRECT  
BORYLATION OF CORANNULENE

Maria N. Eliseeva

Dissertation Advisor: Dr. Lawrence T. Scott

**Abstract**

The Scott lab is interested in the functionalization of corannulene as a building block for large polycyclic aromatic hydrocarbons and carbon nanotube end-cap precursors. Toward that end, a new approach to the direct five-fold borylation of corannulene with iridium (I) catalysts via C-H activation has been explored. It has been discovered that the addition of catalytic amounts of base to the reaction mixture promotes the formation of symmetrical penta-borylated corannulene in a good yield on a sizable scale. All byproducts can be easily removed with iterative methanol washes. The present work also provides proof of the reversibility of the direct borylation reaction under the conditions used. Furthermore, modified Suzuki-Miyaura conditions have been employed to synthesize *pentakis*(2,6-dichlorophenyl)corannulene, a precursor for a [5,5] carbon nanotube end-cap. The reported reactions provide good yields and are scalable.

## Table of Contents

Acknowledgements	ii
<b>Chapter 1. Introduction</b>	<b>1</b>
<b>Chapter 2. Borylation reaction</b>	<b>8</b>
Direct C-H activation borylation	9
Deborylation of corannulene	36
Conclusions	38
<b>Chapter 3. Suzuki-Miyaura cross-coupling reaction</b>	<b>39</b>
<b>Chapter 4. Experimental</b>	<b>43</b>
General Procedure	44
Direct borylation of corannulene ( <b>4</b> ) under standard conditions	45
General procedure for 1,3,5,7,9-pentakis(Bpin)corannulene ( <b>5</b> ) (300 mg scale)	47
1,3,5,7,9-Pentakis(Bpin)corannulene ( <b>5</b> ) (100 mg scale)	52
1,3,5-Tris(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene ( <b>14</b> ) from benzene	54
4,4',5,5'-Tetramethyl-2,2'-bipyridine	57
1,4-Bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene ( <b>13</b> )	58
1,3,5-Tris(Bpin)benzene ( <b>14</b> ) from 1,4-bis(Bpin)benzene ( <b>13</b> )	59
Corannulene recovery from a mixture of borylated corannulene	61
1,3,5,7,9-Pentakis(2,6-dichlorophenyl)corannulene (50 mg scale)	62
1,3,5,7,9-Pentakis(2,6-dichlorophenyl)corannulene (250 mg scale)	64
Appendix 1. NMR analysis of corannulene borylation product mixtures	66
Appendix 2. Details for the borylation reaction set up	68

## Acknowledgments

First, I would like to thank my adviser, Dr. Lawrence Scott. I am extremely grateful to you for having had the chance to be a part of your group. I cannot express in words how lucky I am that you were my adviser. Thank you for all the discussions we had, for your wise advice concerning chemistry, your constant encouragement. Your extraordinary passion to chemistry was inspiring me and I was happy with what I was doing. You are a great teacher and I have learned a lot from you. I will always appreciate that.

I extend gratitude to Boston College and Chemistry department Staff for the great time I had during these three years and to the Professors I have ever had a fortune of learning from.

To the rest of the Scott group, past and present, thank you for providing the opportunity to learn chemistry in such a friendly, exciting, and smart environment. Especially to Allison Greene, Michel Rickhaus and Natalie Smith – thank you guys for all your support, help, chemistry talks, coffee walks, and proofreading.

Thanks to Alena Carlson for many lunch trips to commiserate and discuss something besides chemistry.

I am thankful to my friends back in Russia for their love, encouragement and letters.

I am grateful to my undergraduate adviser Vladimir Zaitsev for the fundamental synthetic skills in the lab. That knowledge helped me a lot in my grown-up line.

Finally I would like to thank My Family for all the love, support and inspiration they have given me over the years. Uncle Alexey and Aunt Maria, this all would have been impossible without you. I am very grateful for everything you did for me, thank you so much. Julia, Anna and Alesha, thank you for the fun time and being there for me during crises.

Mom and Dad, thank you for letting me go so far from you, your sacrifice and faith in me. I love you.

# ***Chapter 1***

## ***Introduction***

The discovery of carbon nanotubes<sup>1</sup> (CNTs) holds promise to be among the most significant achievements of modern science. These diminutive long tubes draw a lot of attention due to a variety of properties they possess. Hardly any other material with such a simple chemical composition can have properties comparable with carbon nanotubes. First, nanotubes appear to be very strong materials in terms of tensile strength<sup>2</sup> and superlative resilience. Second, they demonstrate thermal stability and unique electronic properties.<sup>3</sup> Furthermore, there are a variety of forms: nanotubes can have different diameters and chiralities, can be monolayer or multilayered.

The structure of a nanotube strongly affects its electrical properties, and calculations predict that armchair nanotubes are metallic, whereas most others are semiconductive.<sup>4</sup> The problem is that all of the current methods produce inseparable mixtures of CNTs with a variety of diameters and chiralities.<sup>5</sup>

The Scott lab has been interested in carbon nanotubes for almost a decade and has worked out a strategy for controlled selective synthesis of a single chirality carbon nanotube utilizing classical synthetic chemistry techniques (Figure 1).<sup>6</sup> We proposed to use a template, such as a CNT end-cap, which predefines the diameter and chirality of a desired carbon nanotube. The end-cap has bay-regions, which can be utilized for the elongation using a method proposed by Dr. Eric Fort, a former student of the Scott lab.<sup>7</sup>

---

<sup>1</sup> Iijima, S. *Nature* **1991**, *354*, 56 – 58.

<sup>2</sup> Yu, M.; Lourie, O.; Dyer, M. J.; Moloni, K.; Kelly, T. F.; Ruoff, R. S. *Science* **2000**, *287*, 5453, 637–640.

<sup>3</sup> Collins, P. G.; Avouris, P. *Sci. Am.* **2000**, *283*, 62-69.

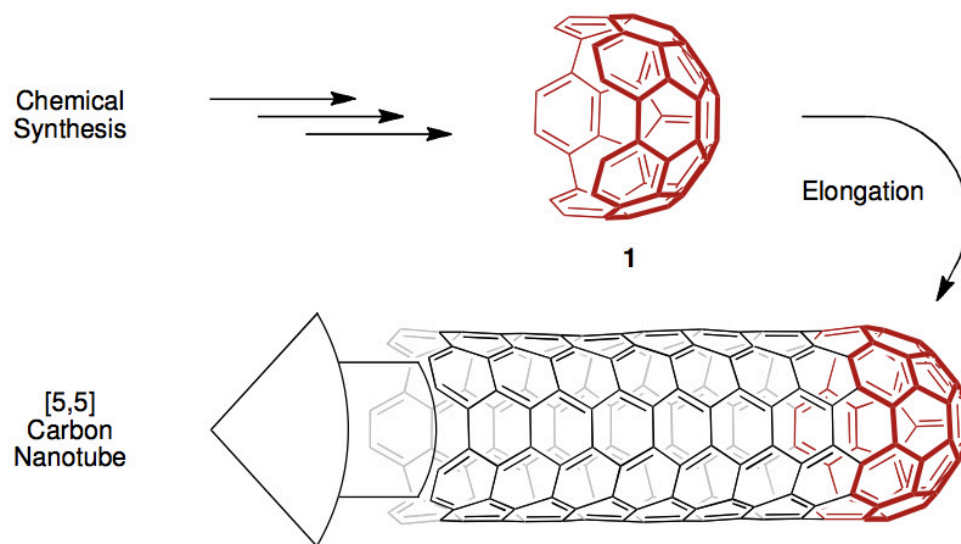
<sup>4</sup> Lu, X.; Chen, Z. *Chem. Rev.* **2005**, *105*, 10, 3643–3696.

<sup>5</sup> Wang, F.; Komatsu, N. *Materials* **2010**, *3*, 3818-3844.

<sup>6</sup> Scott, L. T.; Jackson, E. A.; Zhang, Q.; Steinberg, B. D.; Bancu, M.; Li, B. *J. Am. Chem. Soc.* **2011** DOI: 10.1021/ja209461g

<sup>7</sup> Fort, E. H. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2010.

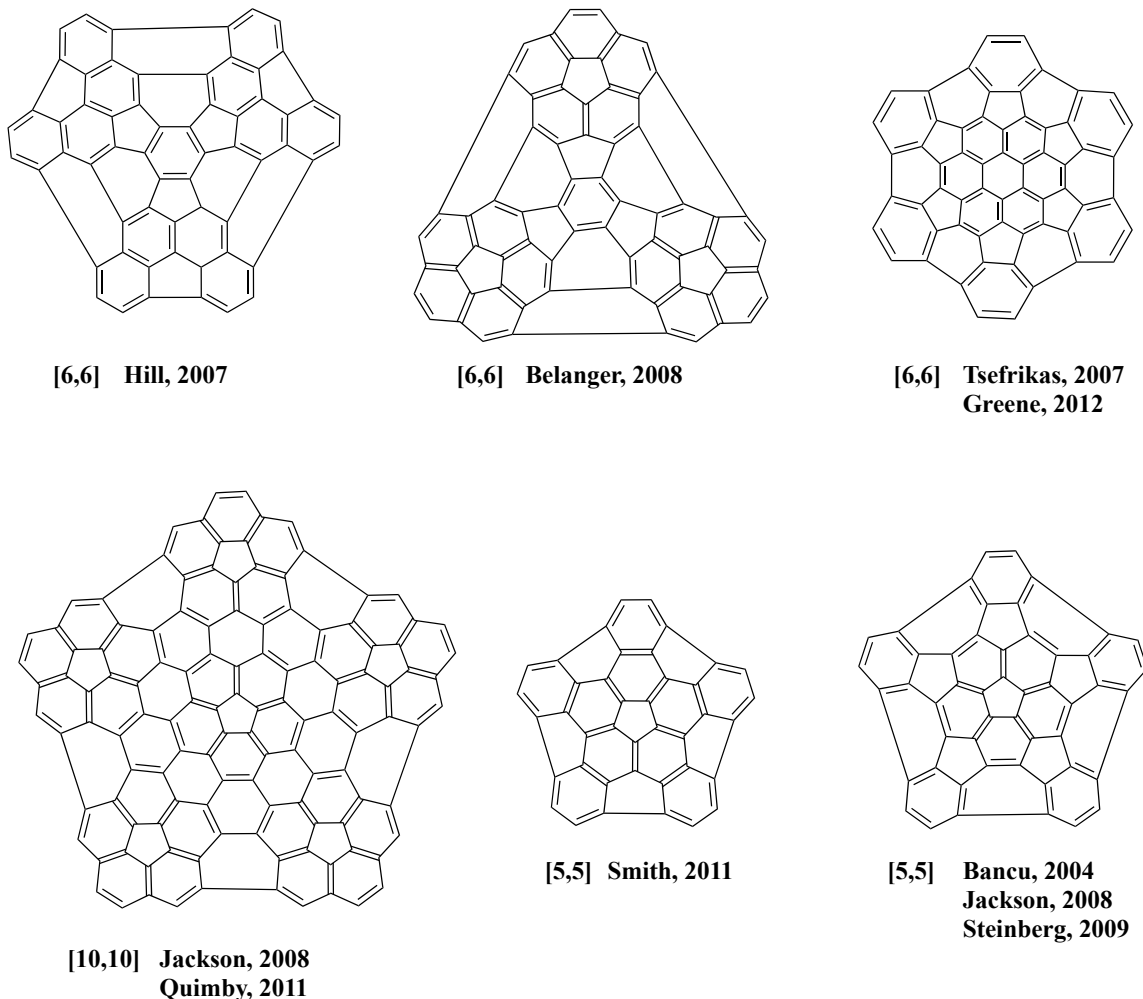




**Figure 1.** Strategy for the synthesis of uniform diameter, single chirality [5,5] CNT<sup>6</sup>

There have been several projects ongoing in the Scott lab in which different diameters CNT end-caps were the targets (Figure 2).<sup>8</sup>

<sup>8</sup> (a) [5,5] end-cap: Bancu, M. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2004. Jackson, E. A. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2008. Steinberg, B. D. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2009. (b) [10,10] end-cap: Jackson, E. A. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2008. Quimby J. M. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2011. (c) [6,6] end-cap: Hill, T. J. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2007. (d) Tsefrikas, V. M. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2007. (e) Belanger, A. P. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2008.

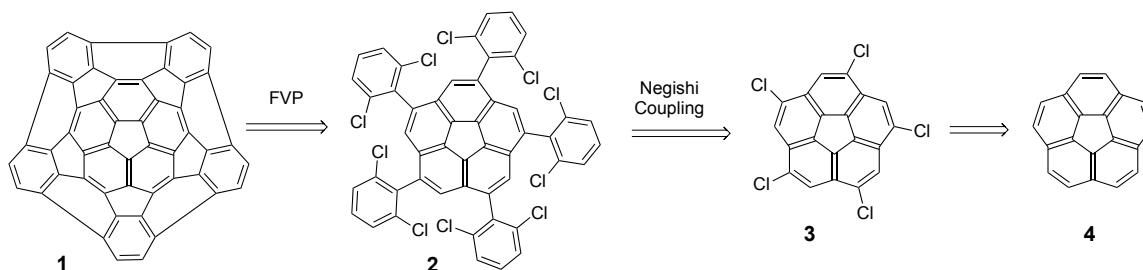


**Figure 2.** Variety of CNT end-caps chosen as synthetic targets in the Scott lab

The work detailed herein will focus on the [5,5] CNT end-cap synthesis.<sup>9</sup> Recent studies carried out by Jackson and Steinberg in our lab have shown that 1,3,5,7,9-*pentakis*(2,6-dichlorophenyl)corannulene **2** can be subjected to Flash Vacuum Pyrolysis to form [5,5]SWNT end-cap **1**.<sup>6</sup> The retrosynthetic analysis that led to the first successful proof of principle is represented in Scheme 1. Using that route, Edward Jackson was the

<sup>9</sup> For detailed discussion of previous attempted syntheses of the [5,5] end-cap see references cited in 8 (a).

first to isolate the desired C<sub>50</sub>H<sub>10</sub> [5,5] SWNT end-cap (**1**), and later Dr. Qianyan Zhang, a postdoc in the Scott lab, grew a crystal of it. Unfortunately, that method is low yielding, and for utilizing **1** in the nanotube growth process we had to look for more efficient ways to obtain **1**.

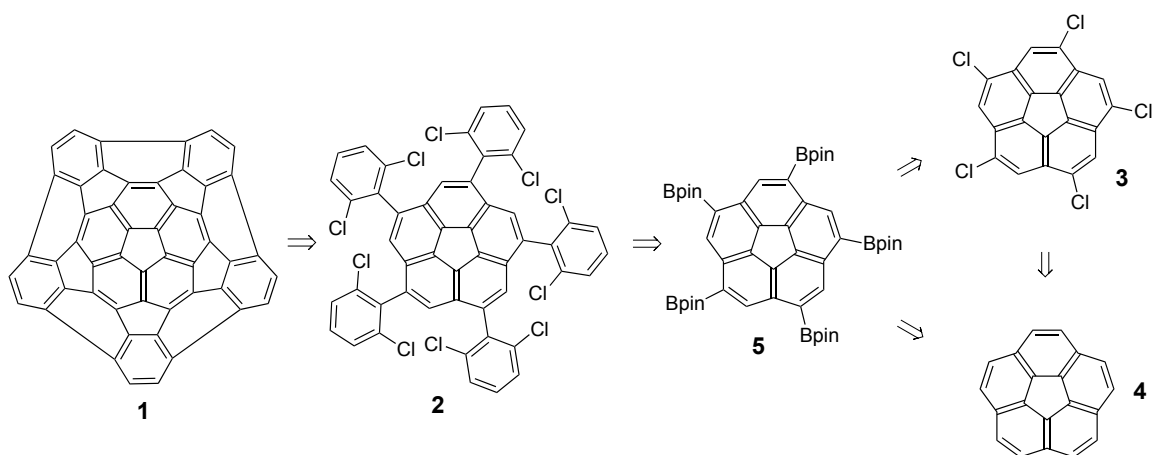


**Scheme 1.** Retrosynthetic analysis of a [5,5] end-cap back to corannulene (**4**)

Brian Steinberg proposed another method to reach **1**, utilizing a Suzuki-Miyaura cross-coupling reaction.<sup>10</sup> The route involved direct chlorination of corannulene<sup>11</sup> using iodine monochloride, followed by palladium mediated cross-coupling of B<sub>2</sub>pin<sub>2</sub> with pentachlorinated corannulene **3**. Finally five-fold Suzuki-Miyaura coupling of pentachlorinated corannulene **3** with 2-bromo-1,3-dichlorobenzene incorporates the remaining 30 carbons to **1** (Scheme 2).

<sup>10</sup> Steinberg, B. D. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2009.

<sup>11</sup> For the detailed synthesis of corannulene see Smith, N. J. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2011.



**Scheme 2.** Alternative retrosynthetic analysis of a [5,5] end-cap back to corannulene (**4**)

Unfortunately, that pathway also had some disadvantages. First, the yield of **3** is usually no more than 40%. Second, pentaborylated corannulene **5** is difficult to separate from excess  $B_2pin_2$ , and under the Suzuki-Miyaura conditions **5** was experiencing substantial deborylation, which led to a mixture of the desired 1,3,5,7,9-*pentakis*(2,6-dichlorophenyl)corannulene **2** with various tetra- and tri-arylated byproducts. The more direct synthetic route outlined in Scheme 2, proposes a 2-step synthesis of 1,3,5,7,9-*pentakis*(2,6-dichlorophenyl)corannulene **2** from **4**. The first step involves direct borylation of corannulene **4**, followed by a modified Suzuki coupling of **5** with 2-bromo-1,3-dichlorobenzene.

It is noteworthy, that the new improved route to 1,3,5,7,9-*pentakis*(pinacolboryl)corannulene gives a new life to this compound, which is envisioned to be a useful precursor for many synthetic groups.<sup>12</sup>

---

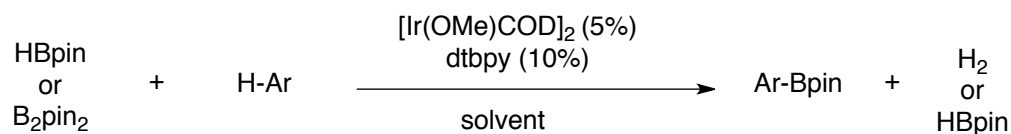
<sup>12</sup> Pappo, D.; Mejuch, T.; Reany, O.; Solel, E.; Gurrarn, M.; Keinan, E. *Org. Lett.* **2009**, *11*, 1063-1066. For potential applications of 1,3,5,7,9-*pentakis*(pinacolboryl)corannulene in the Scott lab see: Quimby J. M. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2011.

## ***Chapter 2***

### ***Borylation reaction***

## Direct C-H activation borylation

Encouraged by the results Brian Steinberg reported in his thesis<sup>13</sup> (Scheme 2, chapter 1), we started to think how to improve the yield for the borylation step. By happy coincidence around that time Professor Milton Smith, one of the discoverers of the direct C-H activation borylation reaction, gave a talk on that topic in our department.<sup>14</sup> The interesting thing was that most of the presented reactions were run in neat pinacol borane, not with a *bis*(pinacolato)diboron.<sup>15</sup> So, we hoped that by using that trick, we could eliminate the problem of separation of the desired product from the leftover B<sub>2</sub>pin<sub>2</sub>, because the excess of HBpin should be easily removed under reduced pressure.<sup>16</sup> Another nice thing about pinacol borane is that it is much cheaper than *bis*(pinacolato)diboron. Also, if this reaction were to work on corannulene we could shorten the route towards the end-cap by one step (see Scheme 2 in chapter 1). The general scheme for the direct borylation is presented in Figure 3.



**Figure 3.** Iridium-catalyzed aromatic borylation

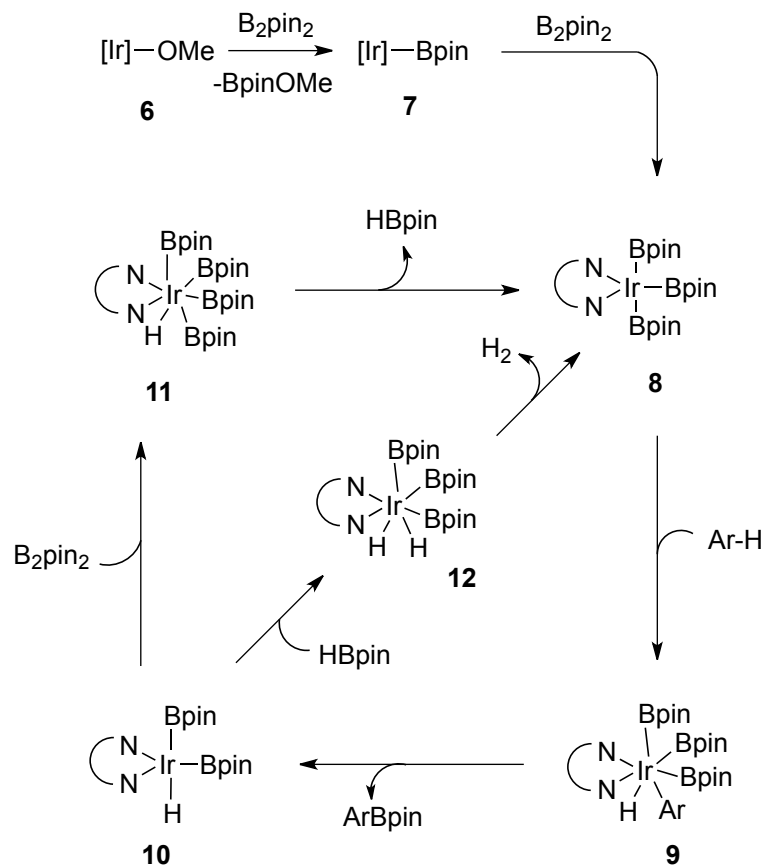
<sup>13</sup>See introduction chapter, also Steinberg, B. D. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2009.

<sup>14</sup>Inversion, C. N.; Smith, M. R. *J. Am. Chem. Soc.* **1999**, *121*, 7696–7697. Radano, C. P.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1552-1553. Cho, J. Y.; Iverson, C. N.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 12868-12869.

<sup>15</sup>Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III *Science* **2002**, *295*, 305-308.

<sup>16</sup>B.p. of pinacol borane is 42-43 °C/50 mmHg according to the Sigma-Aldrich website.

The mechanism of the direct borylation of aromatic compounds has been extensively studied by Hartwig, Smith, Ishiyama and others.<sup>17</sup> The proposed catalytic cycle is shown in Figure 4.<sup>18</sup>



**Figure 4.** Proposed catalytic cycle for Ir(I)-catalyzed borylation of arenes

Mechanistic studies by Hartwig's group have shown that *tris*(boryl)Ir(III) intermediate (**8**) is an active component involved in the catalytic cycle. It can be produced by oxidative addition of  $\text{B}_2\text{pin}_2$  to a (Bpin)Ir(I) complex (**7**) generated by  $\sigma$ -

<sup>17</sup> Mkhalid, I. A.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890-931.

<sup>18</sup> Ishiyama, T.; Miyaura, N. *Pure Appl. Chem.* **2006**, *78*, 1369-1375.



bond metathesis between [Ir]-OMe (**6**) and B<sub>2</sub>pin<sub>2</sub>, or by an oxidative addition/reductive elimination sequence. Then oxidative addition of an arene to a *tris*(boryl)Ir(III) intermediate (**8**) yields an Ir(V) species (**9**) that reductively eliminates an arylboronate. Oxidative addition of B<sub>2</sub>pin<sub>2</sub> to **10** can be followed by reductive elimination of HBpin to regenerate **8**. The resulting HBpin participates in the catalytic cycle via a sequence of oxidative addition to **10** and hydrogen reductive elimination from an 18-electron Ir(V) intermediate (**12**). Borylation of arenes with HBpin may occur after consumption of B<sub>2</sub>pin<sub>2</sub>, since the catalytic reaction shows a two- step process: fast borylation by B<sub>2</sub>pin<sub>2</sub> followed by slow borylation by HBpin.<sup>7a</sup> Along this catalytic cycle, electron donation to the metal center by two nitrogen atoms of a planar bipyridine ligand, as well as its small steric hindrance allows oxidative addition of an arene C–H bond, giving intermediate **9**. The small steric influence of the planar dioxaboryl rings (Bpin) can also be critical for the formation of such a sterically hindered hepta-coordinated Ir(V) intermediate as **9**.

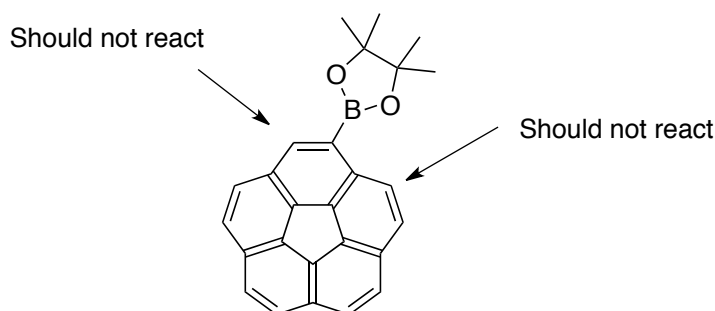
Since corannulene was a valuable starting material, we decided to use pyrene as a test system. In most of the papers we were looking through, arenes were used in a big excess compare to the borylating agent, which was not applicable to our case. So we had to figure out how many equivalents of HBpin we needed per one C-H bond. The second problem we encountered was that we could not run our reactions in neat HBpin, because the starting material was not soluble enough in it. Though we tried a couple of reactions in neat pinacol borane, both at room<sup>19</sup> and elevated temperature, they never went to completion, and a lot of starting material was still presented in the mixtures.

---

<sup>19</sup> Ishiyama, T.; Nobuta, Y.; Hartwig, J. F.; Miyara, N. *Chem. Commun.* **2003**, 2924-2925.

The most popular reported solvents for the reaction are hexane and cyclohexane. Since anhydrous solvent is required for this reaction, and neither of these solvents was available at that time, we used tetrahydrofuran from our anhydrous solvent system. Running the reactions at room temperature did not give positive results. Reaction occurred very slowly, was inconsistent, and never went to completion. Increasing the temperature to 60 °C speeded the reaction up, and no starting material was usually observed, but the reaction still gave a mixture of di- and tri-borylated pyrene. The preliminary results also showed that we needed approximately 2.5 equivalents of HBpin per bond.

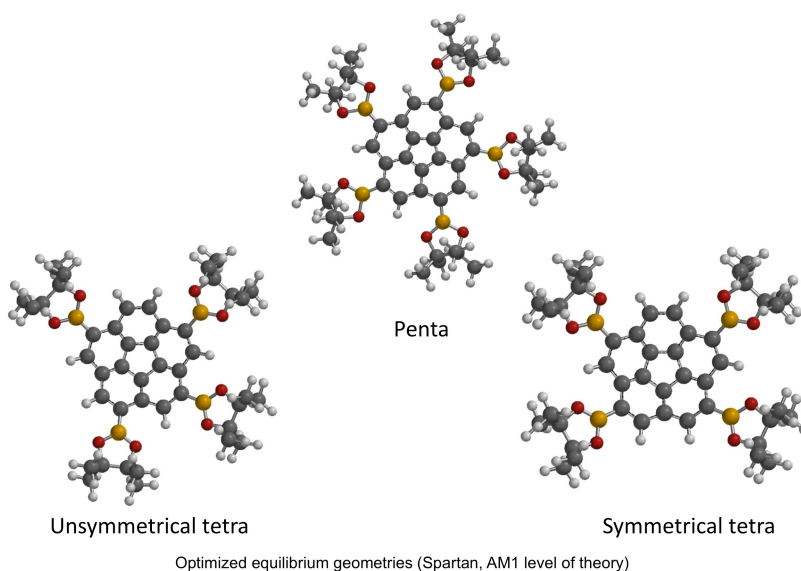
Having those conditions in hand, we employed them with corannulene, but before we turn to the discussion of the results, we should elaborate what we expected to see. We hoped, that due to sterics, the borylation should not occur *ortho* to the already borylated C-H bond on the same ring or in the *peri*-position on the adjacent ring<sup>20</sup> (Figure 5).



**Figure 5.** Site selectivity for the direct borylation of corannulene

<sup>20</sup> Coventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B.; Perutz, R. N. *Chem. Commun.* **2005**, 2172-2174.

According to that rule, statistics predict a 32.4% yield of symmetrical penta-substituted corannulene. But as found with penta-chlorination of corannulene, statistics can be overcome due to electronic directing effects.<sup>21</sup> Also, there should not be any tri-borylated products; that would always leave an open position, which could be borylated a fourth time. So, considering all of the above, we expected to get a mixture of tetra- and penta-substituted corannulenes (Figure 6).



**Figure 6.** Major products – penta & tetra-borylated corannulenes

The initial results obtained from application of the tested conditions to corannulene were disappointing. The results were inconsistent; the reaction never went to the expected mixture, unless additional amounts of catalyst and borylating agent were

---

<sup>21</sup> Jackson, E. A. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2008.

added. Also, solvent evaporated over time, since the reaction setup involved a condenser and small volumes of solvent were used. In addition to that, we also observed some deborylation of the product, if the reaction was run for several days. The only explanation we could come up with for this strange observation was that water from the air (since it was humid in the lab at that period) somehow promoted deborylation and probably prevented completion of the reaction.

After a thorough literature search, we found that Hartwig *et al.* used tetrahydrofuran at 80 °C as a solvent for the borylation of arenes, which implied the use of a pressure vessel.<sup>22</sup> We thought this might solve our problems, but we still encountered some inconsistency problems. Pinacol borane is known to be very sensitive to moisture and is difficult to store for any period of time.<sup>23</sup> That could be another reason for our misfortunes, since all our chemistry was bench-top, and we did not use a glove box. After distilling HBpin before every other set up and using 10 equivalents of it, we finally achieved a mixture of the expected products in 24 hours. But the idea of distilling the reagent before every single run was not inspiring, so we decided to switch to B<sub>2</sub>pin<sub>2</sub>.<sup>24</sup> By that time we also found out that many Bpin derivatives and even some B<sub>2</sub>pin<sub>2</sub> are formed during the reaction, so the biggest argument against using *bis*(pinacolato)diboron vanished.

---

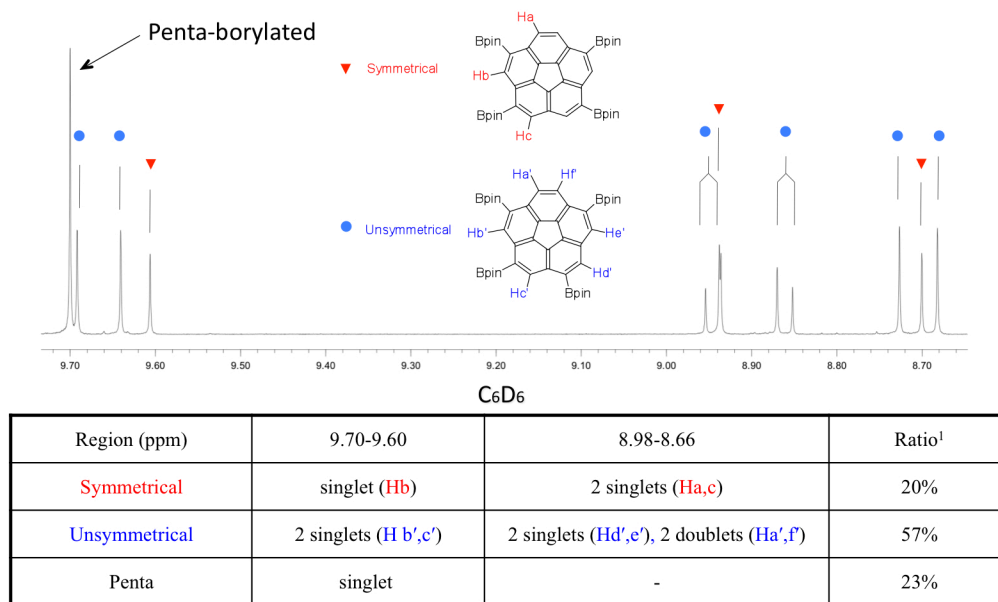
<sup>22</sup> Murphy, J. M.; Liao, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 15434-15435. Boebel, T. A.; Hartwig, J. S. *J. Am. Chem. Soc.* **2008**, *130*, 7534-7535.

<sup>23</sup> Ishiyama, T.; Takagi, J.; Nobuta, Y.; Miyaura, N. *Org. Synth.* **2005**, *82*, 126.

<sup>24</sup> We thank Frontier Scientific, Inc. for gifts of B<sub>2</sub>pin<sub>2</sub>.

Marder *et al.* studied Ir-catalyzed borylation of aromatic hydrocarbons such as naphthalene, pyrene and perylene and found out that the reaction proceeds to completion with 1.1 molar equivalents of B<sub>2</sub>pin<sub>2</sub> per bond.<sup>3</sup>

During the optimizing conditions, we solved the puzzle of the product mixture content by analyzing NMRs and mass spectra at different stages of the reaction. When the reaction went to completion, we always observed identical mixtures of products. Figure 6 shows the three major compounds of the resulting mixture. The decryption of the representative mixture by NMR is introduced in Figure 7.



<sup>1</sup> ratio based on NMR integration. Conditions: 5% [Ir(OMe)COD]<sub>2</sub>, 10% dtbpy, 5.5 eq B<sub>2</sub>pin<sub>2</sub>, 0.4M

**Figure 7.** Analysis of representative corannulene borylation mixture<sup>25</sup>

<sup>25</sup> For explanation of integration method see Appendix 1.

When a proton is located between two Bpin groups, the chemical shift is moved to the 9.7-9.6 ppm range. When the hydrogen is adjacent to only one Bpin group, either *ortho* or *peri*, the signals appear in the 9.0-8.6 ppm area.

Having established the components of the mixture, we had to find a way of separating the borylated corannulenes from the various Bpin reagents and side products.<sup>26</sup> B<sub>2</sub>pin<sub>2</sub> was found to be soluble in most solvents, so the idea was to find a solvent or a system of solvents in which the products were not soluble. After screening most of common solvents (pentane, diethyl ether, ethanol, hexane), methanol was found to be the most useful. The best thing about that solvent was that to our great surprise and excitement it precipitated mostly the penta-substituted product, whereas the two tetra-substituted isomers, for some reason, were more soluble in it. So we were able to isolate 10% of pure penta-Bpin product with methanol precipitation.

Despite the fact that we were able to synthesize and isolate the desired product, the yield was not great, and we wanted to find conditions that would furnish the penta-Bpin product in higher quantities, keeping in mind, that statistics predict that 32% was possible.

Hartwig,<sup>27</sup> Smith<sup>14</sup> and Miyara<sup>18</sup> have reported that ligands can have a great effect on catalyst activity and thereby change the course of the reaction. So our next idea was to screen a variety of ligands, catalysts and reaction conditions to see if we could change the ratio among the products in the mixture (see Table 1). Since Bpin substituents are not

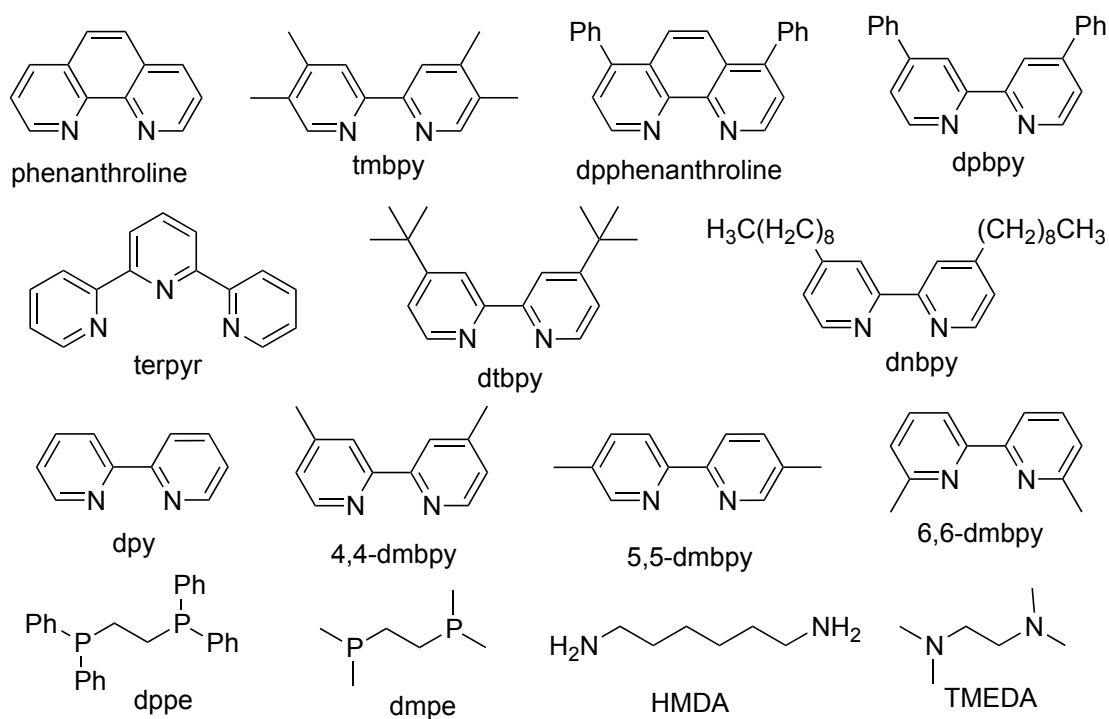
---

<sup>26</sup> See crude NMR in the experimental part. One of the peaks corresponds to O(Bpin)<sub>2</sub>: Hawkeswood, S.; Stephan, D. W. *Dalton Trans.* **2005**, 2182-2187.

<sup>27</sup> Ishiyama, T.; Takagi, J.; Hartwig, J. F.; Miyara, N. *Angew. Chem. Int. Ed.* **2002**, *41*, 3056-3058.

expected to exert any long-range directing effect, we did not anticipate any significant deviation from the statistical mixture, under conditions of kinetic control.

Figure 8 shows most of the screened ligands. As seen from Table 1 neither (Ind)Ir(COD) nor [IrCl(COD)]<sub>2</sub> gave any improvements (entries 1-10). Temperature and time variations also did not affect the ratio. Phosphine ligands are reported to give very high yields,<sup>14</sup> but in our case, they were the slowest and never went beyond tri-borylated products. We tried to reduce the amount of consumed B<sub>2</sub>pin<sub>2</sub> and discovered that 5.0 equivalents are not enough for full 5-fold borylation, but the amount can be lowered down to 5.2 equivalents for 5 bonds.



**Figure 8.** Structures of the screened ligands with abbreviations

So, screenings revealed four 'hits': dtbpy (Table 1, entry 14), 5,5'-dmbpy (Table 1, entry 32), 4,4'-dmbpy (Table 1, entry 37), and tmbpy (Table 1, entry 38). None of those ligands gave better results, but we hoped, that utilizing them at higher loadings of catalyst and/or higher concentrations could push the reaction in the desired direction.



**Table 1.** Screening of catalysts, ligands, solvents and reaction time

Entry	Catalyst(%)	Ligand <sup>a</sup>	B <sub>2</sub> pin <sub>2</sub> (eq)	Solvent	Temp (°C)	Time	Conc.	Yield of penta <sup>c</sup>
(Ind)Ir(COD)								
1	10	dppe <sup>b</sup>	6	1,4-dioxane	130	5 days	0.2	0 <sup>d</sup>
2	10	dmpe <sup>b</sup>	6	1,4-dioxane	150	4 days	0.4	0 <sup>d</sup>
3	30	dmpe <sup>b</sup>	6	1,4-dioxane	150	4 days	0.4	0 <sup>d</sup>
[IrClCOD] <sub>2</sub>								
4	10	dppe	6	THF	100	3 days	0.4	0 <sup>d</sup>
5	10	dpy	6	THF	100	3 days	0.4	<10
6	5	dtbpy	6	THF	85	2 days	0.27	23
7	5	phenanthroline	6	THF	85	3 days	0.27	12
8	5	4,4'-dmbpy	6	THF	85	2 days	0.2	<10
9	10	tmbpy	6	THF	85	1 day	0.5	18

[Ir(OMe)COD] <sub>2</sub>										
10	5	dtbpy	10.5	THF	70	2 days	0.2	23		
11	5		8	THF	80	36 h	0.2	23		
12	5		7	THF	80	36 h	0.2	23		
13	5		7	THF	100	16 h	0.2	23		
14	5		5.5	THF	80	18 h	0.2	23		
15	5		5.5	THF	80	18 h	0.4	23		
16	5		5.5	cyclohexane	80	24 h	0.26	19		
17	5		5	THF	80	2 days	0.2	<23		
18	5		5	THF	100	3 days	0.2	<23		
19	5		4.5	THF	100	3 days	0.2	<23		
20	5		5.5	THF	120	2 days	0.2	23		
21	5		5.5	1,4-dioxane	120	2 days	0.2	23		
22	5		5.2	THF	85	18 h	0.2	23		

23	5	dppe	6	THF	80	2 days	0.2	0 <sup>d</sup>
24	5	dppe	6	1,4-dioxane	150	4 days	0.4	0 <sup>d</sup>
25	5	dpy	6	THF	85	2 days	0.27	18
26	20	dmpe	6	1,4-dioxane	150	4 days	0.4	0 <sup>d</sup>
27	5	phenanthroline	6	THF	85	3 days	0.27	16
28	15	HMDA	6	THF	80	36 h	0.4	0 <sup>d</sup>
29	15	TMEDA	6	THF	80	36 h	0.4	0 <sup>d</sup>
30		dp-phenanthroline	6	THF	80	1 day	0.4	15
31	10	dpbpy	7	THF	110	3 days	0.2	<1
32	10	5,5'-dmppy	6	THF	85	16 h	0.2	23
33	10	dndpy	7	THF	85	3 days	0.2	13
34	10	dnbpy	6	THF	85	1 day	0.5	18
35	10	terpyr	6	THF	80	2 days	0.2	<1

36	10	6,6'-dpy	6	THF	85	3 days	0.2	<1
37	10	4,4'-dmbpy	6	THF	85	16 h	0.2	23
38	10	tmbpy	6	THF	85	17 h	0.8	22

<sup>a</sup>[Ir]:[lig]=1:2. <sup>b</sup>[Ir]:[lig]=1:1. <sup>c</sup>Yield is based on NMR integrated ratio of penta(Bpin)corannulene to the mixture of tetra-borylated isomers.

<sup>d</sup>Partial borylation is occurring, but does not go to penta(Bpin)corannulene

And finally our hopes were justified! Making the reaction very concentrated and increasing the loading of the catalyst to 30 mol %, we were able to reach 31 % of penta-Bpin in the mixture by utilizing 5,5'-dmbpy (Table 2, entry 4) and 48 % of penta-Bpin by employing 4,4'-dmbpy (Table 2, entry 7) in the reaction. Tmbpy (Table 2, entry 9-11) did not give that encouraging results, but evidence of increasing yield was present. Surprisingly, dtbpy (Table 2, entry 12-13) did not show any improvement in the reaction, and the yields were even diminished.

All of the reactions were run in pressure vessels, which were usually left overnight for cleaning purposes in a base bath, contained potassium hydroxide. Sometimes the yield of penta-product was slightly higher than the normal 23%, which made us speculate that the leftover traces of base on the walls of the vessels (or somehow the glass was becoming more basic, while being in the basic environment) could promote the preference for forming the desired penta-product. Fagnou *at al.* reported something similar to what we observed, when addition of pivalic acid resulted in high regioselectivity of a product.<sup>28</sup>

So we again conducted screening with the 'hits' (see Table 3). The results we observed were astonishing. For example, the reaction, utilizing 4,4'-tmbpy for 1 day at 20 mol % catalyst loading without base gave 32% penta-Bpin (Table 3, entry 1), but with 10% of sodium methoxide additive, the amount of penta-Bpin in the mixture increased to 45% (Table 3, entry 2).

---

<sup>28</sup> Stuart, D. R.; Fagnou, K. *Science* **2007**, *316*, 1172-1174.

**Table 2.** Effect of the catalyst loading and concentration

Entry	[Ir(OMe)COD] <sub>2</sub> (%)	Ligand (%)	B <sub>2</sub> pin <sub>2</sub> (eq)	time	Conc.	Yield of penta
5,5'-dmbpy						
1	5	10	6	1 day	1	22
2	10	20	6	1 day	1	24
3	20	40	5.5	1 day	1	26
4	30	60	5.5	1 day	1	31
4,4'-dmbpy						
5	10	20	6	1 day	0.8	23
6	20	40	5.5	1 day	1	32
7	30	60	5.5	1 day	1	48
8	40	80	5.5	1 day	0.8	50

tmbpy						
9	5	10	5.5	1 day	1	18
10	10	20	6	1 day	0.8	22
11	20	40	5.5	1 day	1	26
dtbpy						
12	10	20	6	1 day	1	21
13	20	40	5.5	1 day	1	21

**Table 3.** Effect of a base

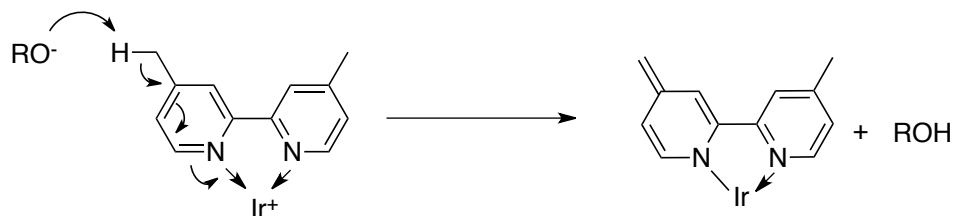
Entry	[Ir(OMe)COD](%)	Ligand (%)	B <sub>2</sub> pin <sub>2</sub> (eq)	Base(%)	time	Conc.	Yield of penta
1	20	40	5.5	-	1 day	1	32
2	20	40	5.5	10	1 day	1	45
3	20	40	5.5	10	2 days	1	55
4	20	40	5.2	10	3 days	1	74
5	20	40	5.2	10	4 days	1	85
6	20	40	5.5	-	4 days	1	41
7	20	40	5.5	45	1 day	1	40
8	20	40	5.5	45	1 day	0.4	<1
9	40	80	5.5	10	1 day	0.8	63
10	40	80	5.5	-	1 day	0.8	50
11	10	20	5.5	10	4 days	1	27



tmbpy							
12	20	40	5.5	10	3 days	0.8	90
13	20	40	5.5	-	3 days	0.8	48
5,5'-dmbpy							
14	20	40	5.5	10	3 days	0.8	35
15	20	40	5.5	-	3 days	0.8	26
dtbpy							
16	20	40	5.5	10	2 days	0.8	24
17	20	40	5.5	-	2 days	0.8	23
4,4'-dmbpy KOtBu							
19	20	40	5.2	10	1 day	1.3	50
20	20	40	5.2	10	3 days	1.3	80
21	20	40	5.2	10	4 days	1.3	90

	bpy	KOtBu				
22	40	5.2	10	4 days	1.3	26
	bpy	Cs <sub>2</sub> CO <sub>3</sub>				
23	40	5.2	10	4 days	1.3	85

Even better results were obtained with tmbpy - 90% of penta-Bpin after 3 days with 10% sodium methoxide (Table 3 entry 12), but that ligand is not commercially available and is less useful in terms of general accessibility.<sup>29</sup> The di-*tert*-butylbipyridine reaction was not affected by catalyst loading, concentration, or the presence of base (Table 2, entry 12 and 13, Table 3, entry 16 and 17), which did not really make sense to us. It was also not obvious why the ligand, which had methyl groups in the 4,4' positions in bipyridine would be so superior to others. One of the possible explanations is that a base deprotonates the methyl group, which makes the nitrogen on the ligand more nucleophilic (Scheme 3). The acidity of the methyl C-H would be enhanced by coordination with Ir(I).

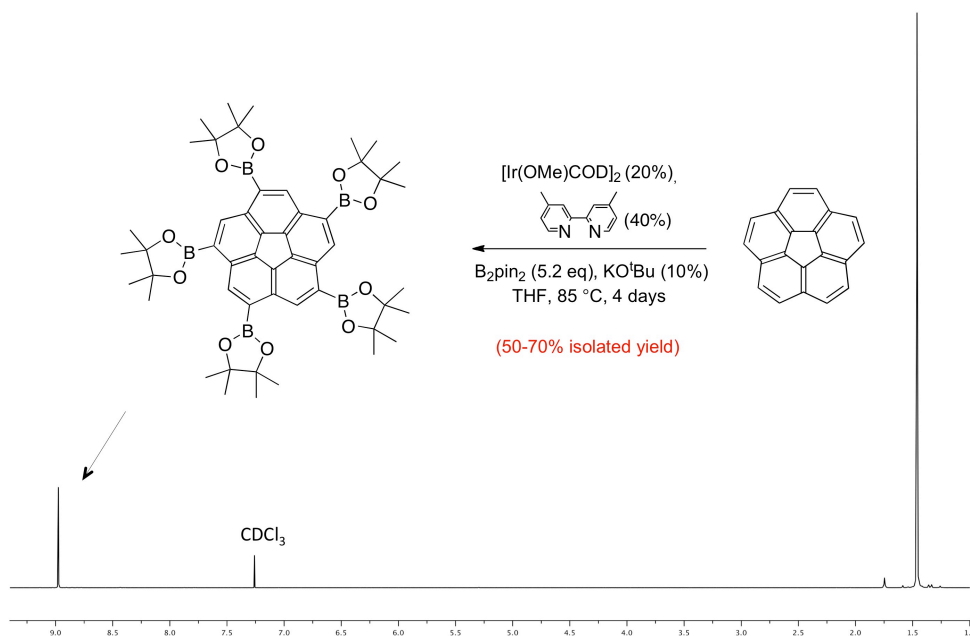


**Scheme 3.** Deprotonation of methyl group in 4,4'-dmbpy

Several bases were tried, and all showed similar good results (Table 3, entry 5, 21 and 23). Hydroxides were also tried but did not give good results due to the fact that they are highly hygroscopic.

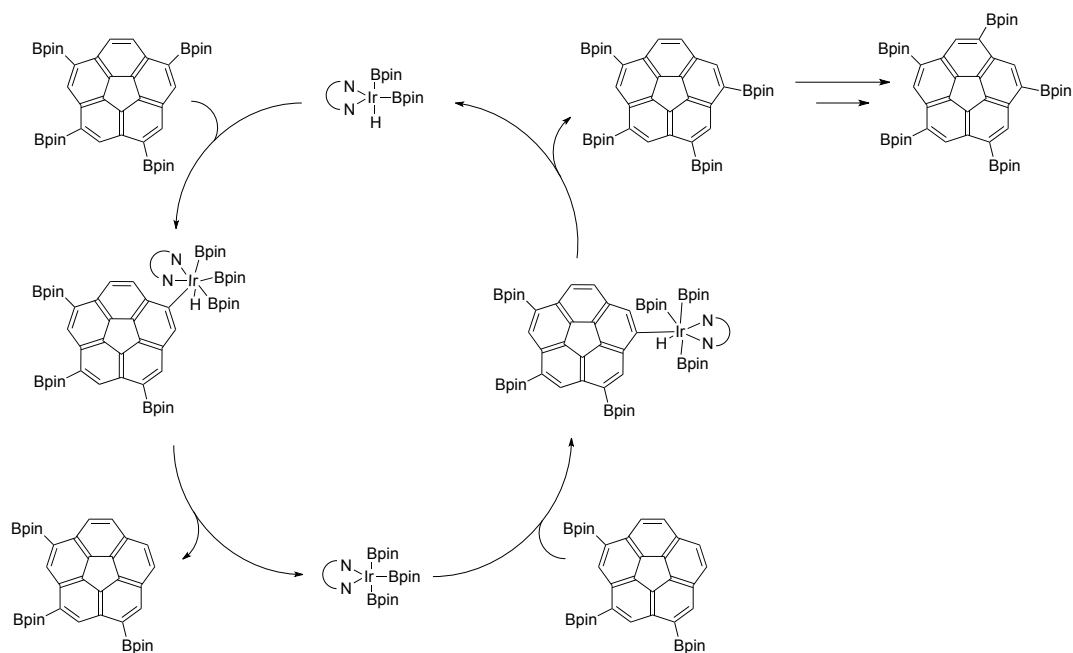
<sup>29</sup> Tmbpy was synthesized from 3,4-lutidine, see Experimental Chapter for details.

It is noteworthy that when the reaction was monitored for several days, the ratio of the penta-Bpin rose every day until penta-Bpin became the dominant product (Figure 9). There were no tri- or tetra-Bpin isomers (which could lead to the formation of penta-Bpin) left, however, after the first day.



**Figure 9.**  $^1\text{H}$  NMR of *pentakis*(Bpin)corannulene in  $\text{CDCl}_3$

This fact made us believe that the reaction is reversible and that the desired penta-Bpin is formed predominantly by consuming the tetra-Bpin isomers. Our proposed reversible mechanism is shown in Figure 10.

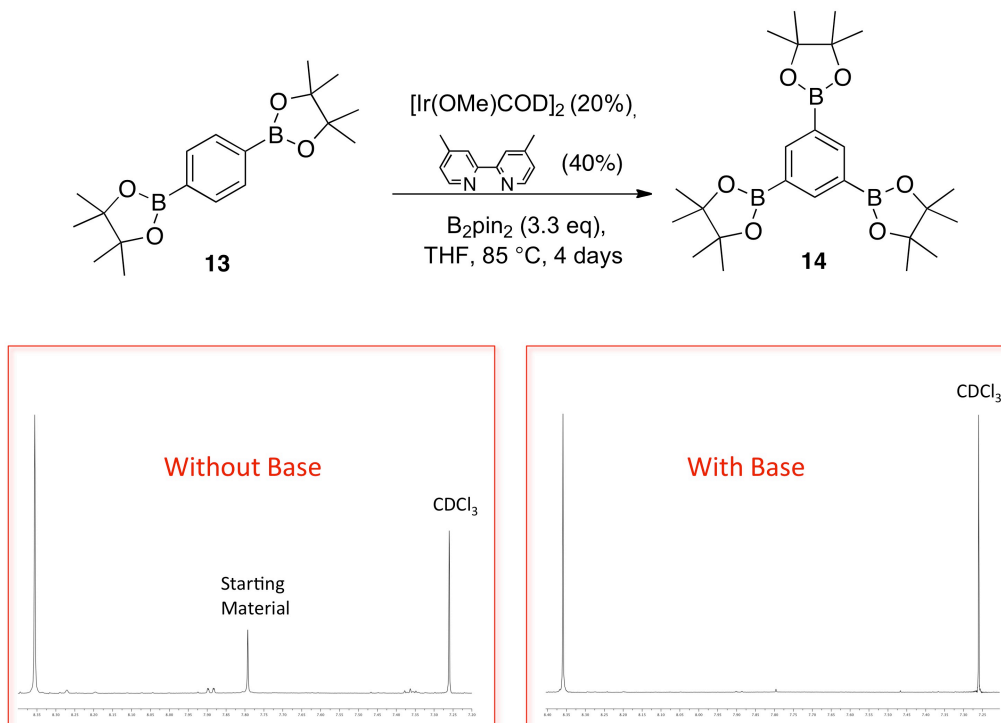


**Figure 10.** Proposed mechanism for reversible borylation of corannulene

To test that hypothesis, we exposed 1,4-*bis*(Bpin)benzene (**13**)<sup>30</sup> to our borylation conditions and observed its complete conversion to 1,3,5-*tris*(Bpin)benzene (**14**) (Figure 11). We also conducted the same experiment without base and found that the reaction does proceed, but at a much slower rate. We also subjected 1,4-*bis*(Bpin)benzene (**13**) to conditions without catalyst and borylating reagent and recovered the starting material unchanged. That study showed that the catalyst plays a critical role in this deborylation/reborylation mechanism. Apparently, the base also accelerates the deborylation process and makes it possible to achieve maximum capacity within 4 days.

<sup>30</sup> Was synthesized from 1,4-phenylenediboronic acid (see Experimental Chapter).

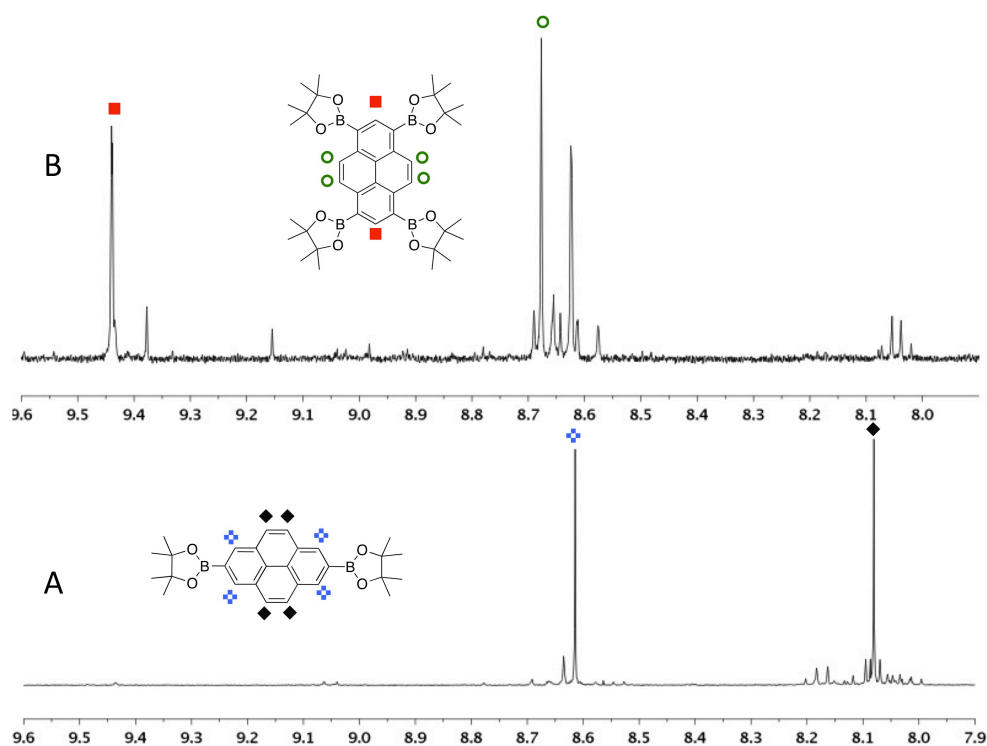
It is likely that the base coordinates the boron on the aryl-Bpin and activates it for the iridium insertion.



**Figure 11.** Studies of reversibility of the direct borylation

This principle of ‘exhaustive borylation’ should work for all aromatic hydrocarbons. Since it is a slow process, however, there should always be an excess of  $\text{B}_2\text{pin}_2$  (for the maintenance of Le Chatlier’s principle) and active catalyst, which has a limited turnover number and ‘dies’ over time.

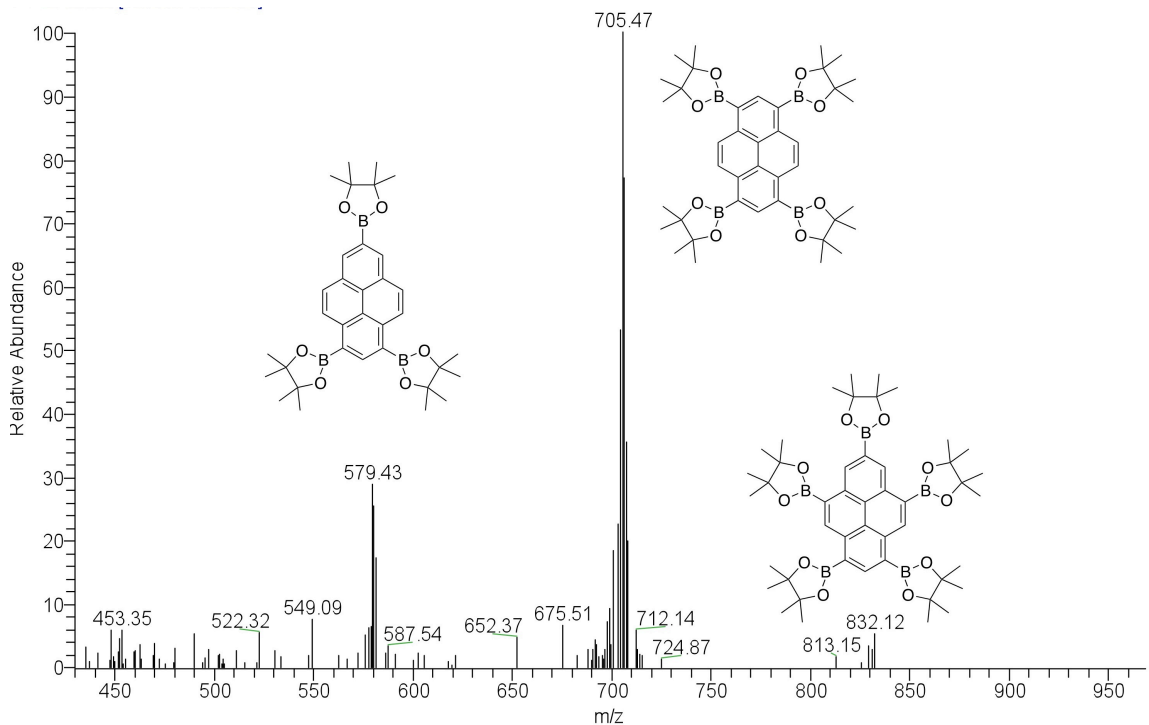
We were curious to try our conditions for other aromatic hydrocarbons. When we subjected pyrene to our conditions and ran the reaction for 6 days, we obtained tetra-borylated pyrene as the major product and tri-borylated pyrene as a minor product.



**Figure 12.** Representative mixtures containing diborylated pyrene (A) and tetra-borylated pyrene (B)

Figure 12 shows the NMR spectrum of diborylated pyrene (A), which was produced under standard conditions, and a mixture of tetra and tri-borylated pyrenes (B), recovered after the new borylation conditions. As in the corannulene case, the signal of a proton between two Bpin groups (■) is shifted to a 9.4 ppm, whereas the one, neighboring only one Bpin group (+) appears at 8.6 ppm. As seen from Figure 13 there is also a trace of penta-borylated pyrene, which starts to form.

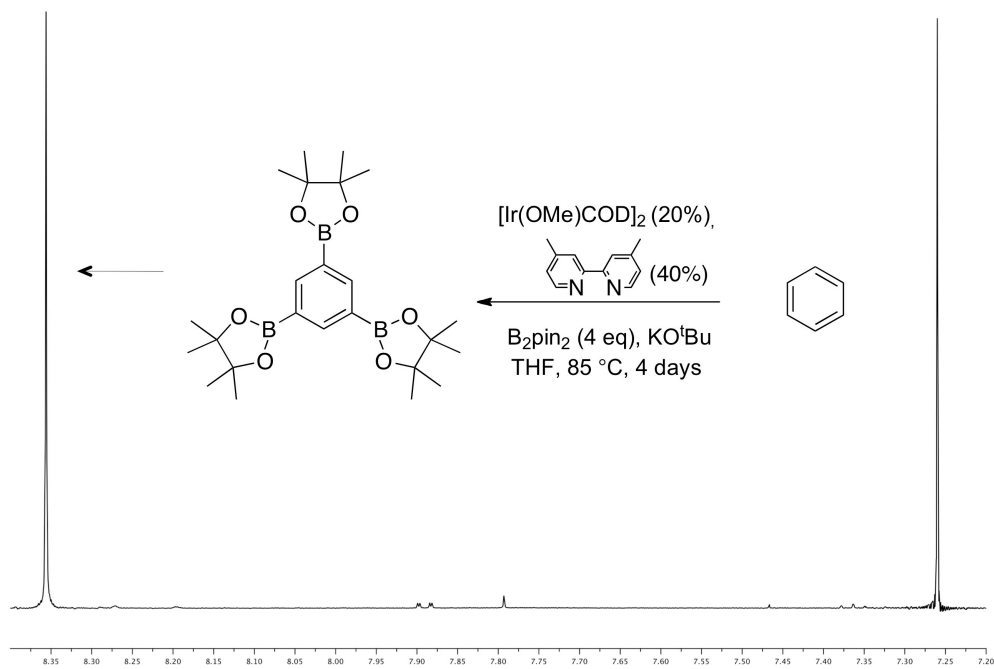
Encouraged by the results, we subjected benzene to our conditions and after 4 days were able to isolate 40% of tri-borylated benzene<sup>31</sup> by methanol precipitation (without optimization) (Figure 14).



**Figure 13.** Mass-spectrum (EI) of the mixture of borylated pyrenes formed under new borylation conditions

<sup>31</sup> For previous synthesis of tryborylated benzene see Geny, A.; Lebauf, D.; Rouquie, G.; Vollhardt, K.P.C.; Malacria, M.; Gandon, V.; Aubert, C. *Chem. Eur. J.* **2007**, *13*, 5408-5425. Bao, B.; Yuwen, L.; Zhan, X.; Wang, L. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 3431-3439.

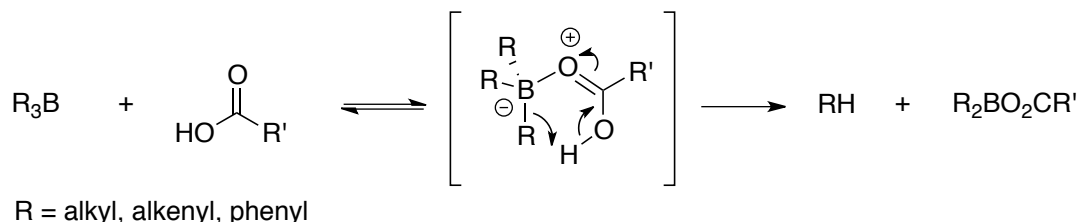




**Figure 14.**  $^1\text{H}$  NMR (CDCl<sub>3</sub>) of crude product mixture from direct borylation of benzene under new conditions

## Deborylation of corannulene

At early stages of our work, when the isolated yield of *pentakis*(Bpin)corannulene (**5**) was only 10%, we wanted to find a way of recycling the corannulene (**4**) that was not converted to **5**. In 1959 Brown *et al.* reported that carboxylic acids cleave the carbon-boron bonds readily.<sup>32</sup> The proposed mechanism is shown in Figure 15. It has been established, that in the protonolysis of organoboranes by carboxylic acids, a coordination of the acid with the boron atom occurs that simultaneously polarizes and weakens the carbon-boron bond and increases the electrophilic character of the proton. The protonolysis thus proceeds through a six-membered transition state, where the nucleophilic and electrophilic sites are in proper geometric relationship to one another.<sup>33</sup>



**Figure 15.** Mechanism for the cleavage of carbon-boron bonds by carboxylic acids

We applied this method to our mixture. When we heated the reaction with acetic acid at 140 °C, we observed deborylation, but it took several days to obtain fully deborylated corannulene. When we tried higher boiling propionic acid, and ran the

<sup>32</sup> Brown, H. C.; Murray, K. J. *J. Am. Chem. Soc.* **1959**, *81*, 4108-4109.

<sup>33</sup> Toporcer, L. H.; Dessy, R. E.; Green, S. I. E. *J. Am. Chem. Soc.* **1965**, *87*, 1236-1240. Brown, H.C.; Molander, G. A. *J. Org. Chem.* **1986**, *51*, 4512-4514.

reaction at 190 °C, we were able to isolate pure corannulene after 24 hours of heating. Utilizing this very simple method, we were able to recover 85% of the unconverted corannulene for recycling.

## Conclusions

Numerous borylation conditions were investigated, and it was found that addition of a base to the standard borylation conditions, together with utilization of iridium catalyst (20%) and 4,4'-dimethylbipyridyl (40%) as a ligand at high concentrations for 3-4 days, affords a five-fold borylated corannulene as the major product, with a 55% consistent isolated yield. The method has already been successfully reproduced by other Scott group members and also by students from the group of Professor Jay Siegel in Switzerland.

These new conditions were also utilized for direct exhaustive borylation of benzene and pyrene.

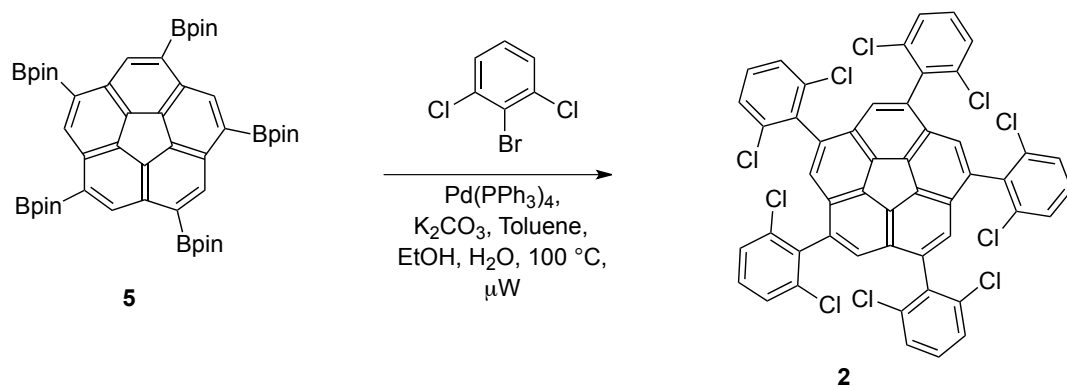
Further application of the compound will be discussed in the next chapter.

## **Chapter 3**

### ***Suzuki-Miyaura cross-coupling reaction***

Palladium-catalyzed cross-coupling reactions have taken a leading role in methods for selective formation of carbon-carbon bonds. The 2010 Nobel Prize in Chemistry was awarded to Suzuki (shared prize) for his discovery and development of the reaction between aryl or vinyl boronic acids and aryl or vinylhalides.<sup>34</sup>

This reaction has been widely used in the Scott lab. A former student in the Scott group previously worked out the conditions shown in Scheme 4.<sup>10</sup> The halide used in this coupling, 2-bromo-1,3-dichlorobenzene, was chosen based on its commercial availability. By exploiting the difference in chemical reactivity of aryl chlorides vs. aryl bromides and applying appropriate reaction conditions, we can prevent additional undesired chemistry.



**Scheme 4.** Previously reported conditions for the Suzuki reaction

Unfortunately, when we attempted to synthesize 1,3,5,7,9-pentakis(2,6-dichlorophenyl)corannulene following Steinberg's conditions, we were unable to achieve the yield he reported. Another disadvantage of this method was the inability to scale it up,

<sup>34</sup> Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *20*, 3437–3440. Miyaura, N.; Suzuki, A. *Chem. Comm.* **1979**, *19*, 866–867.

due to the microwave vessel volume limitations. When we tried to apply the conditions shown above in a hood for scale up purposes, we observed mostly unreacted starting material. If more catalyst was added, significant amounts of undesired byproducts were formed as a result of deborylation.

The original conditions employed toluene, ethanol, and water as a solvent system,<sup>35</sup> which was not very convenient due to the high boiling point of toluene. We tried an alternative system of tetrahydrofuran and water, which worked better and was easier to handle during work up. Taking into account that *tetrakis*(triphenylphosphine)-palladium(0) is sensitive to air, which could be one of the potential problems, we switched to the more stable dichloro[1,1'-*bis*(diphenylphosphino)ferrocene]palladium(II). We also screened different bases, such as cesium carbonate, potassium hydroxide,<sup>36</sup> sodium hydroxide,<sup>4</sup> and potassium phosphate. It is worth noting that when hydroxide was used the reaction suffered from almost complete deborylation. Cesium carbonate showed the best results. When all of these modifications were applied, the yield was improved to 40%, but some deborylation of the starting material was still observed.

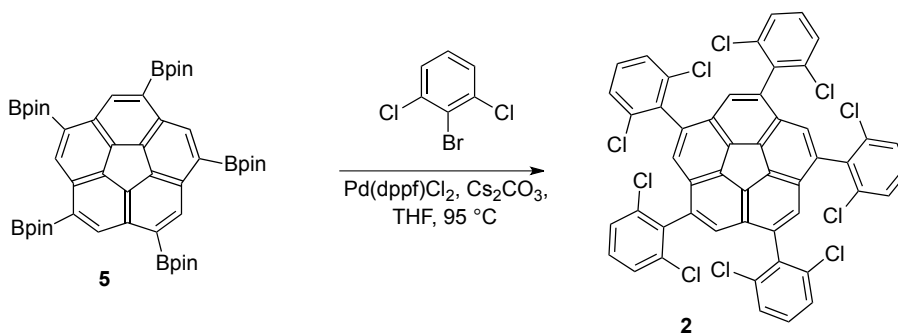
Water has been known to accelerate the Suzuki reaction, but in our case water seemed to be causing the deborylation. When water was eliminated from the reaction conditions we were able to synthesize 1,3,5,7,9-*pentakis*(2,6-dichlorophenyl)corannulene from 1,3,5,7,9-*pentakis*(Bpin)corannulene in 76-82% yield and with a minimal amount of deborylated product. Scheme 5 presents the new conditions.

---

<sup>35</sup> Bahl, A.; Grahn, W.; Stadler, S.; Feiner, F.; Bourhill, G.; Bräuchle, C.; Reisner, A.; Jones, P. G.; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1485-1488.

<sup>36</sup> Morris, J.; Steel, P. G.; Marder, T. B.; *Synlett* **2009**, *1*, 147-150.

We typically ran all reactions (50 mg scale) in 15 mL pressure vessels. When the identical reaction was run on the same scale in a 75 mL pressure vessel, the yield significantly dropped, and NMR showed some tri- and tetraarylated products. We set up two parallel reactions in 15 and 75 mL pressure vessels, and the results were consistent. We still saw products of deborylation of starting material in the reaction run in the 75 mL pressure vessel, while deborylation is pretty minor when run in a 15 mL pressure vessel.



**Scheme 5.** New Suzuki-coupling conditions

Our explanation for this observation is that the reaction is concentration dependent. Since 5 mL of solvent takes less than 1/10 of a 75 mL vessel, at 95 °C a lot of solvent molecules transfer to the gas phase, significantly increasing the concentration, which promotes deborylation.

By modifying a number of variables in the reaction conditions, we have worked out a reliable method for synthesizing this precursor to a [5,5] carbon nanotube end-cap.



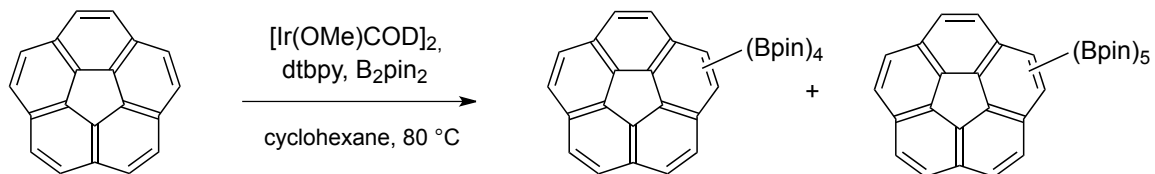
## ***Chapter 4***

### ***Experimental***

## General Procedure

All solvents and commercial chemicals were purchased from commercial sources (Strem, Acros, Fisher, Aldrich, AlfaAesar) and were used without purification, unless otherwise stated. Tetrahydrofuran was obtained from a Glass Contour solvent purification system. Anhydrous cyclohexanes and hexanes were obtained by house vacuum distillation over CaH<sub>2</sub> under N<sub>2</sub>. Column chromatography was carried out using Sorbent Technologies standard grade silica gel (porosity = 60 Å, particle size = 32-63 µm). Preparative thin layer chromatography was carried out using Analtech silica GF. Microwave reactions were conducted using a CEM Corporation Discover microwave reactor. Proton and Carbon NMR spectra were taken with a Varian 500 MHz NMR spectrometer. Chemical shifts are reported in ppm downfield from TMS in chloroform-d (δH = 7.26 ppm, δC = 77.16 ppm), benzene-d<sub>6</sub> (δH = 7.16 ppm). Low resolution mass analyses were performed using a Thermo Electron Corporation Finnigan Trace GC Ultra gas chromatograph unit connected to a Thermo Electron Corporation Finnigan Trace DSQ mass spectrometer with direct insertion capability. High-resolution mass spectrometry was achieved by the Boston College Mass Spectrometry Center using various TOF instruments. X-ray crystallography was performed at the Boston College X-ray Crystallography Center. Elemental analysis was carried out by Robertson Microlit Laboratories. SAFETY NOTE: all pressure vessel reactions were run behind a blast shield.

### Direct borylation of corannulene (**4**) under standard conditions<sup>37</sup>



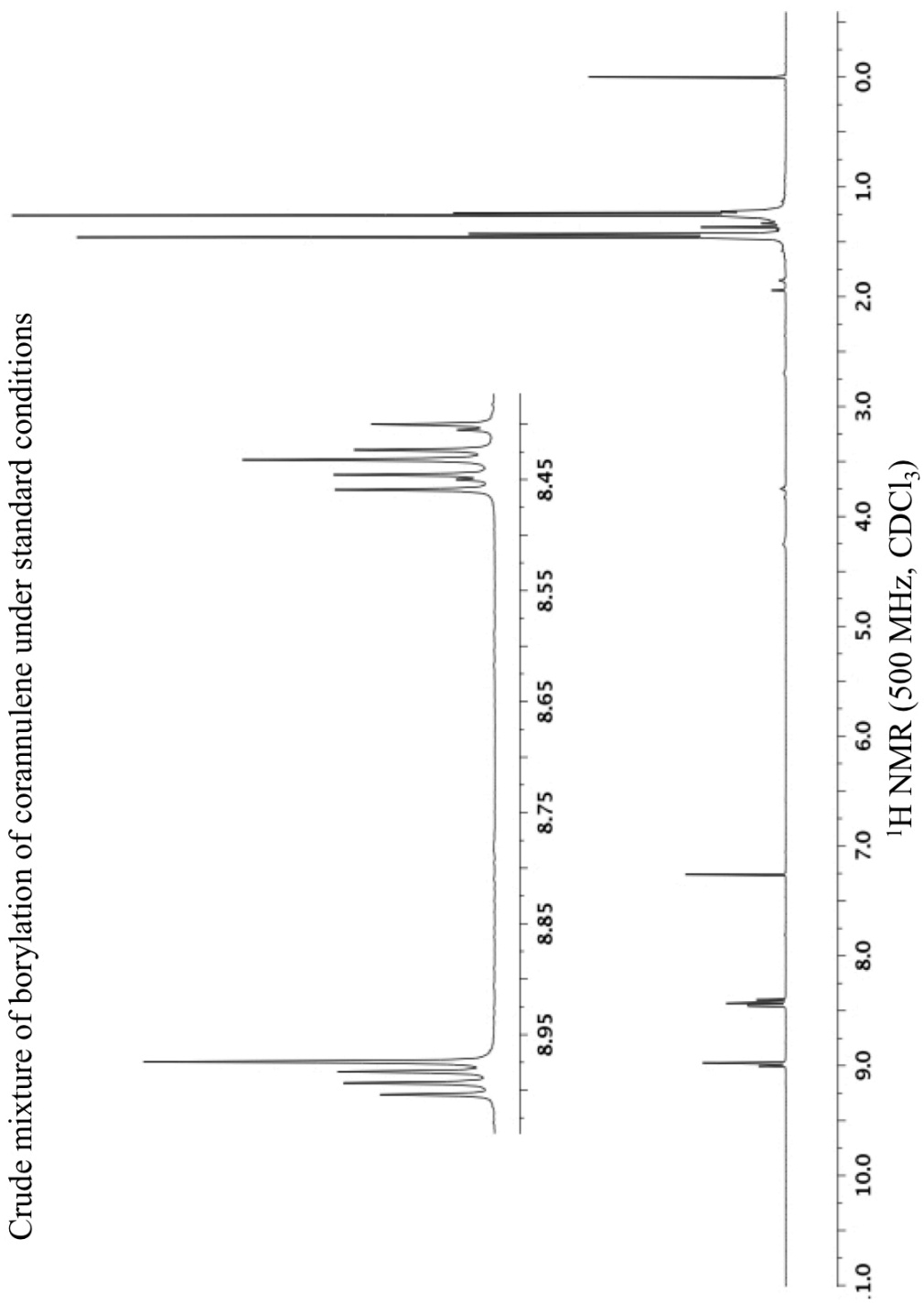
To a 15 mL flame dried pressure vessel equipped with a stirring bar and a septum were added  $[\text{Ir}(\text{OMe})\text{COD}]_2$  (13 mg, 0.02 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (11 mg, 0.04 mmol),  $\text{B}_2\text{pin}_2$  (559 mg, 2.2 mmol), and distilled cyclohexane (1.5 mL) under a nitrogen atmosphere. The mixture was heated at  $50\text{ }^\circ\text{C}$  for 10 min, and the vessel was charged with corannulene (100 mg, 0.40 mmol), then purged with nitrogen, and sealed; the resulting mixture was allowed to stir at  $80\text{ }^\circ\text{C}$  for 24 h. The mixture was removed from the oil bath, cooled, and diluted with dichloromethane ( $\sim 5\text{ mL}$ ). The reaction was quenched by the dropwise addition of 10% HCl ( $\sim 5\text{ mL}$ ).<sup>38</sup> The layers were separated, and the aqueous layer was thoroughly extracted with dichloromethane. The combined organic layers were washed with water (1 $\times$ ) and brine (1 $\times$ ), and dried over magnesium sulfate.<sup>39</sup> The filtrate was concentrated to dryness on a rotary evaporator to give a dark red-brown oily semi-solid mixture, which was analyzed by NMR and found to contain a mixture of tetra(Bpin)corannulenes and penta(Bpin)corannulene (see Figures 6 and 7).

<sup>37</sup> Coventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B.; Perutz, R. N. *Chem. Commun.* **2005**, 2172-2174.

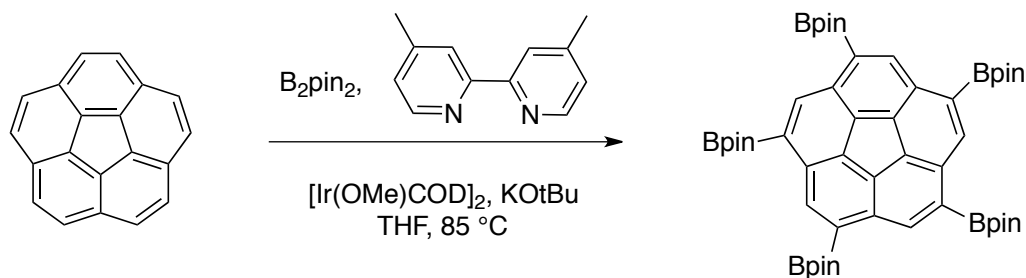
<sup>38</sup> Caution! Gas evolves!

<sup>39</sup> When filtering, the drying agent is washed with dichloromethane several times, but it remains orange.

Crude mixture of borylation of corannulene under standard conditions



### General procedure for 1,3,5,7,9-pentakis(Bpin)corannulene (**5**) (300 mg scale)



A 15 mL flame dried pressure vessel was equipped with a stirring bar and a septum and was purged with nitrogen. The vessel was then charged with  $[Ir(OMe)COD]_2$  (159 mg, 0.24 mmol), 4,4'-dimethyl-2,2'-bipyridyl (88 mg, 0.48 mmol),  $B_2pin_2$  (1.585 g, 6.24 mmol), and potassium *t*-butoxide (14 mg, 0.12 mmol). THF (1.0 mL)<sup>40</sup> was added by syringe, and the mixture was heated at 50 °C for 5-10 min. A dark brown-red solution formed. The vessel was charged with corannulene (300 mg, 1.20 mmol), purged with nitrogen, and sealed, and the resulting mixture was stirred at 85 °C for 4 d. The mixture was removed from the oil bath, cooled, and diluted with dichloromethane (~5 mL). The reaction was quenched by the dropwise addition of 10% HCl (~5 mL).<sup>41</sup> The layers were separated, and the aqueous layer was thoroughly extracted with dichloromethane. The combined organic layers were washed with water (1×) and brine (1×), and dried over magnesium sulfate.<sup>42</sup> The filtrate was concentrated to dryness on a rotary evaporator to give a dark red-brown oily semi-solid mixture, which was left under vacuum for a couple of hours.

<sup>40</sup> Concentration is crucial; important to keep the corannulene concentration at no less than 0.8 M

<sup>41</sup> Caution! Gas evolves!

<sup>42</sup> When filtering, the drying agent was washed with dichloromethane several times, but it remained orange.

Methanol (~30 mL) was added to the flask, and the mixture was sonicated for 5-10 min, until the dark mixture separated into a dark solution and an off-white precipitate.<sup>43</sup> The precipitate was collected by vacuum filtration with a Buchner funnel and a paper filter,<sup>44,45</sup> and the precipitate was washed with methanol until most of the orange color was gone (~15 mL). The purity of the first batch of product was checked by NMR. Usually, it was free of B<sub>2</sub>pin<sub>2</sub>, but it still contained some tetraborylated corannulene. The precipitate collected in the funnel was flushed into a clean side-arm flask with some dichloromethane (~20 mL) under vacuum, and the solution was then transferred to a round-bottom flask. Methanol (~30 mL) was added, and the mixture was concentrated on the rotary evaporator until a lot of precipitate appeared. Some methanol was added if the mixture had evaporated to dryness. The precipitated solid was again collected by vacuum filtration and washed with methanol. The product was white to lightly yellow in color and could be a dry heavy powder or a fluffy<sup>46</sup> solid. Chart 1 summarizes these steps. The yield was usually 528-740 mg (50-70%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.98 (s, 5H), 1.46 (s, 60H); <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 9.75 (s, 5H), 1.01 (s, 60H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 138.9, 137.0, 133.3, 128.6 (broad) 83.8, 25.2; HRMS (MALDI): calcd for C<sub>50</sub>H<sub>65</sub>O<sub>10</sub>B<sub>5</sub>: 880.5038 found 880.5057; elemental analysis calcd for C<sub>50</sub>H<sub>65</sub>O<sub>10</sub>B<sub>5</sub>: C=68.23%, H=7.44%, B=6.14% found C=68.43%, H=7.35%, B=6.28%.

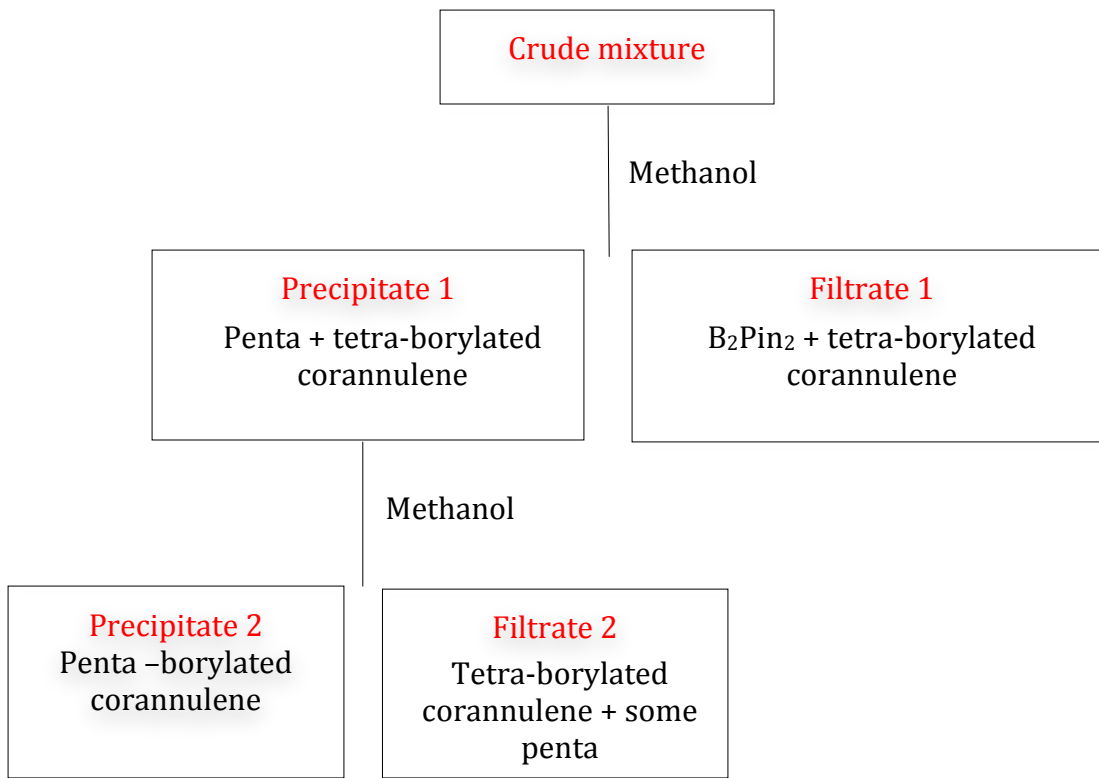
---

<sup>43</sup> A lot of white-pink precipitate accumulated in the flask

<sup>44</sup> The filtration was slow.

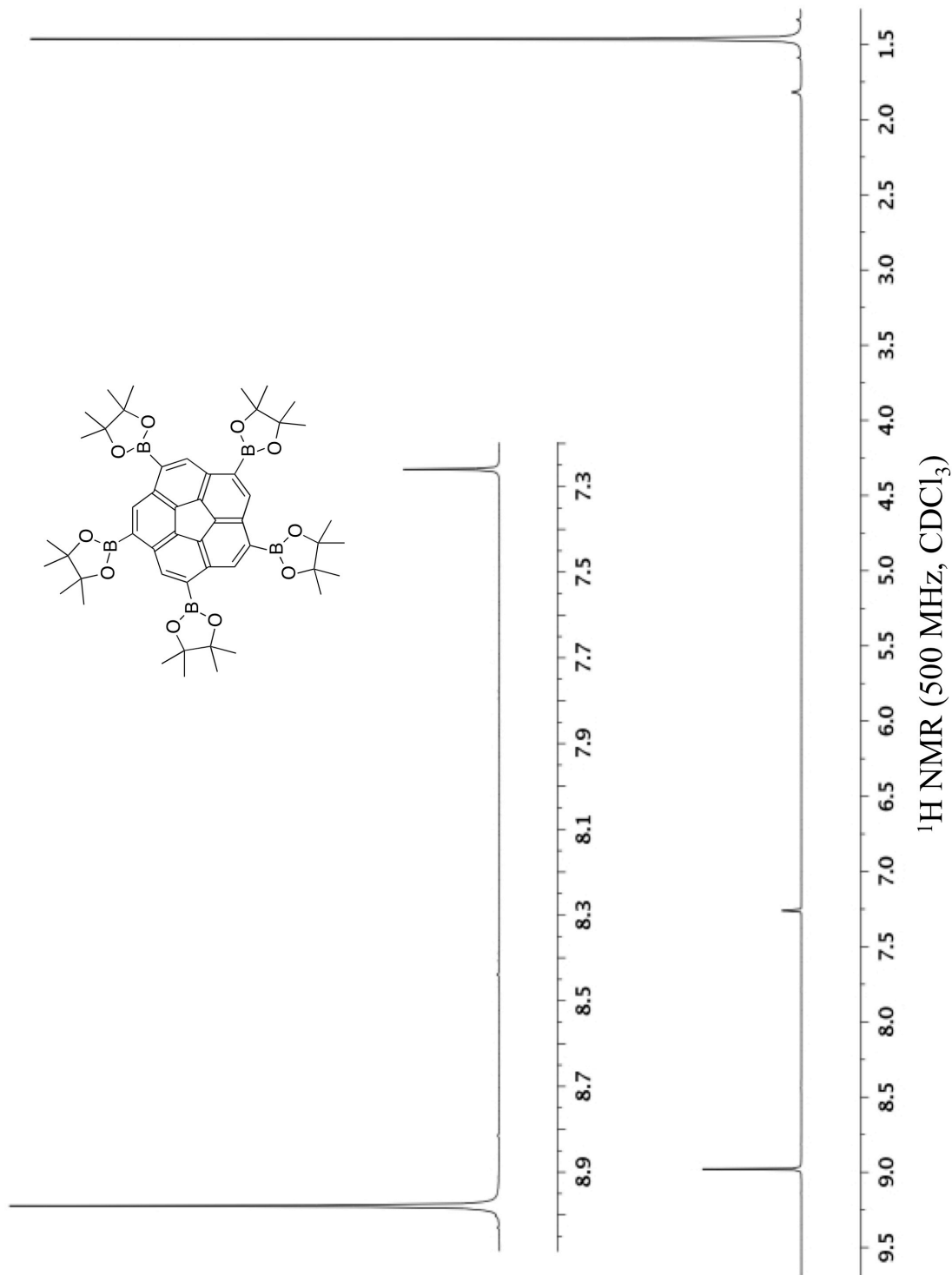
<sup>45</sup> Sometimes, some additional penta-borylated corannulene began to precipitate from the first filtrate. In that case, the filtrate was transferred from the side arm filter flask to a round-bottom flask with the help of dichloromethane, and the mixture was concentrated on the rotary evaporator until the precipitate formed again. The additional precipitate was then collected by vacuum filtration with methanol washing.

<sup>46</sup> After precipitation from the rotary evaporator.

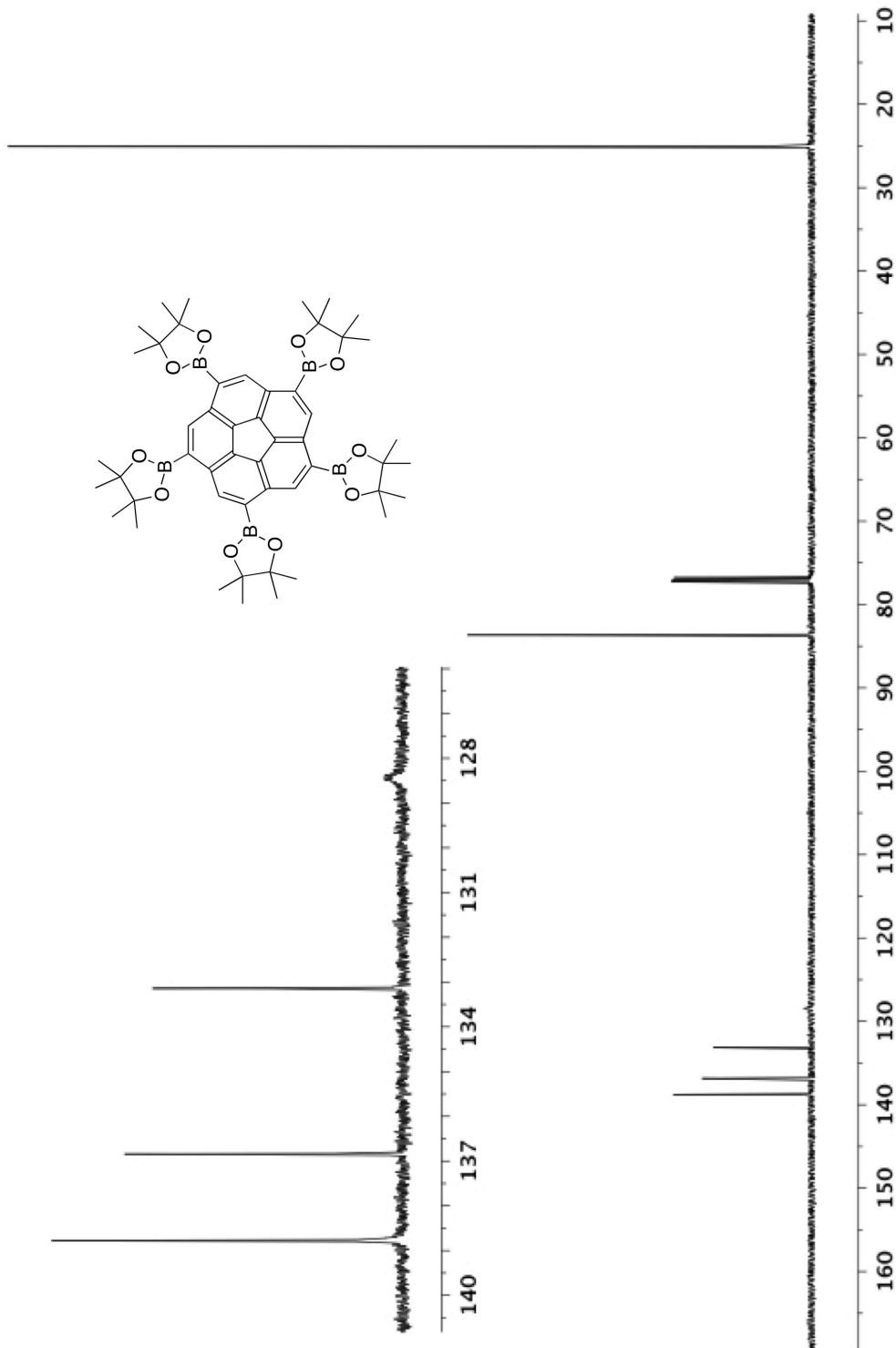


Filtrate 1 and filtrate 2 are combined at the end for recycling of corannulene

**Chart 1.** Summary of steps for the borylation reaction

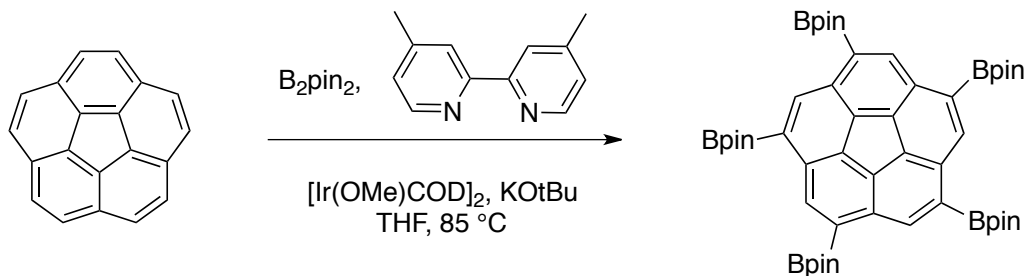






$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

### 1,3,5,7,9-Pentakis(Bpin)corannulene (5) (100 mg scale)



A 15 mL flame dried pressure vessel was equipped with a stirring bar and a septum and was purged with nitrogen. The vessel was then charged with  $[Ir(OMe)COD]_2$  (53 mg, 0.8 mmol), 4,4'-dimethyl-2,2'-bipyridyl (30 mg, 0.16 mmol),  $B_2pin_2$  (528 mg, 2.08 mmol), and potassium *t*-butoxide (5 mg, 0.04 mmol). THF (0.4 mL)<sup>47</sup> was added by syringe, and the mixture was heated at 50 °C for 10 min. A dark brown-red solution formed. The vessel was charged with corannulene (100 mg, 0.4 mmol), purged with nitrogen, and sealed, and the resulting mixture was stirred at 85 °C for 3 days. The mixture was removed from the oil bath, cooled, and diluted with dichloromethane (~3 mL). The reaction was quenched by the dropwise addition of 10% HCl (~3 mL).<sup>48</sup> The layers were separated, and the aqueous layer was thoroughly extracted with dichloromethane. The combined organic layers were washed with water (1×) and brine (1×), and dried over magnesium sulfate.<sup>49</sup> The filtrate was concentrated to dryness on a rotary evaporator to give a dark red-brown oily semi-solid mixture, which was left under vacuum for 15 minutes.

<sup>47</sup> Concentration is crucial; important to keep the corannulene concentration at no less than 0.8M.

<sup>48</sup> Caution! Gas evolves!

<sup>49</sup> When filtering, the drying agent is washed with dichloromethane several times, but it remains orange.

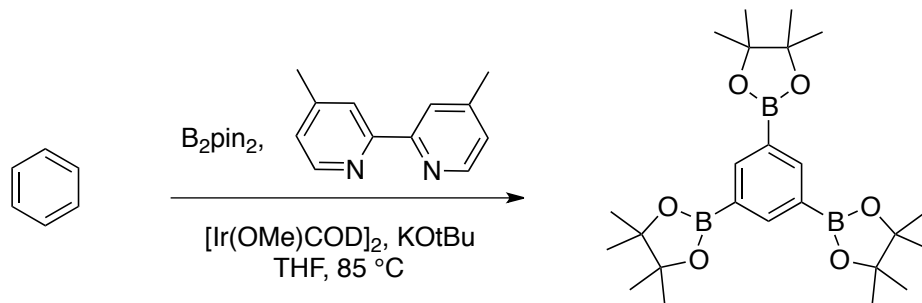
Methanol (~15-20 mL) was added to the flask, and the mixture was sonicated for 5 min, until the dark mixture separated into a dark solution and an off-white precipitate.<sup>50</sup> The precipitate was collected by vacuum filtration with a small Buchner funnel and a paper filter,<sup>51</sup> and the precipitate was washed with methanol (2 × 10 mL). Usually, the first precipitate was clean product and afforded 176-246 mg 50-70% yield. Spectroscopic data matched those reported in the general procedure.

---

<sup>50</sup> A lot of white-pink precipitate accumulated in the flask

<sup>51</sup> Sometimes, some additional penta-borylated corannulene began to precipitate from the first filtrate. In that case, the filtrate was transferred from the side arm filter flask to a round-bottom flask with the help of dichloromethane, and the mixture was concentrated on the rotary evaporator until the precipitate formed again. The additional precipitate was then collected by vacuum filtration with methanol washing.

### 1,3,5-Tris(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (14) from benzene



To a flame-dried 15 mL pressure vessel equipped with a magnetic stir bar and flushed with nitrogen were added  $[Ir(OMe)COD]_2$  (53 mg, 0.08 mmol), 4,4'-dimethyl-2,2'-bipyridyl (30 mg, 0.16 mmol),  $B_2pin_2$  (406 mg, 1.60 mmol), and potassium *t*-butoxide (5 mg, 0.04 mmol). THF (0.3 mL)<sup>52</sup> was added by syringe, and the mixture was heated at  $50\text{ }^\circ C$  for 10 min. Benzene (35  $\mu L$ , 0.40 mmol) was added, the rubber septum was replaced with a pressure vessel cap, and the reaction mixture was heated at  $85\text{ }^\circ C$  in an oil bath for 4 days. The mixture was removed from the oil bath, cooled, and diluted with dichloromethane (~2 mL). The reaction was quenched by the dropwise addition of 10% HCl (~2 mL).<sup>53</sup> The layers were separated, and the aqueous layer was thoroughly extracted with dichloromethane. The combined organic layers were washed with water (1 $\times$ ) and brine (1 $\times$ ), and dried over magnesium sulfate. The filtrate was concentrated to dryness on a rotary evaporator, and the mixture was left under vacuum overnight. Upon addition of methanol (~15 mL) a precipitate crashed out. The material was collected by vacuum filtration and washed with methanol (~10 mL). The product was recovered as a light-beige precipitate (73 mg, 40%). More 1,3,5-tri(Bpin)benzene remained in the filtrate

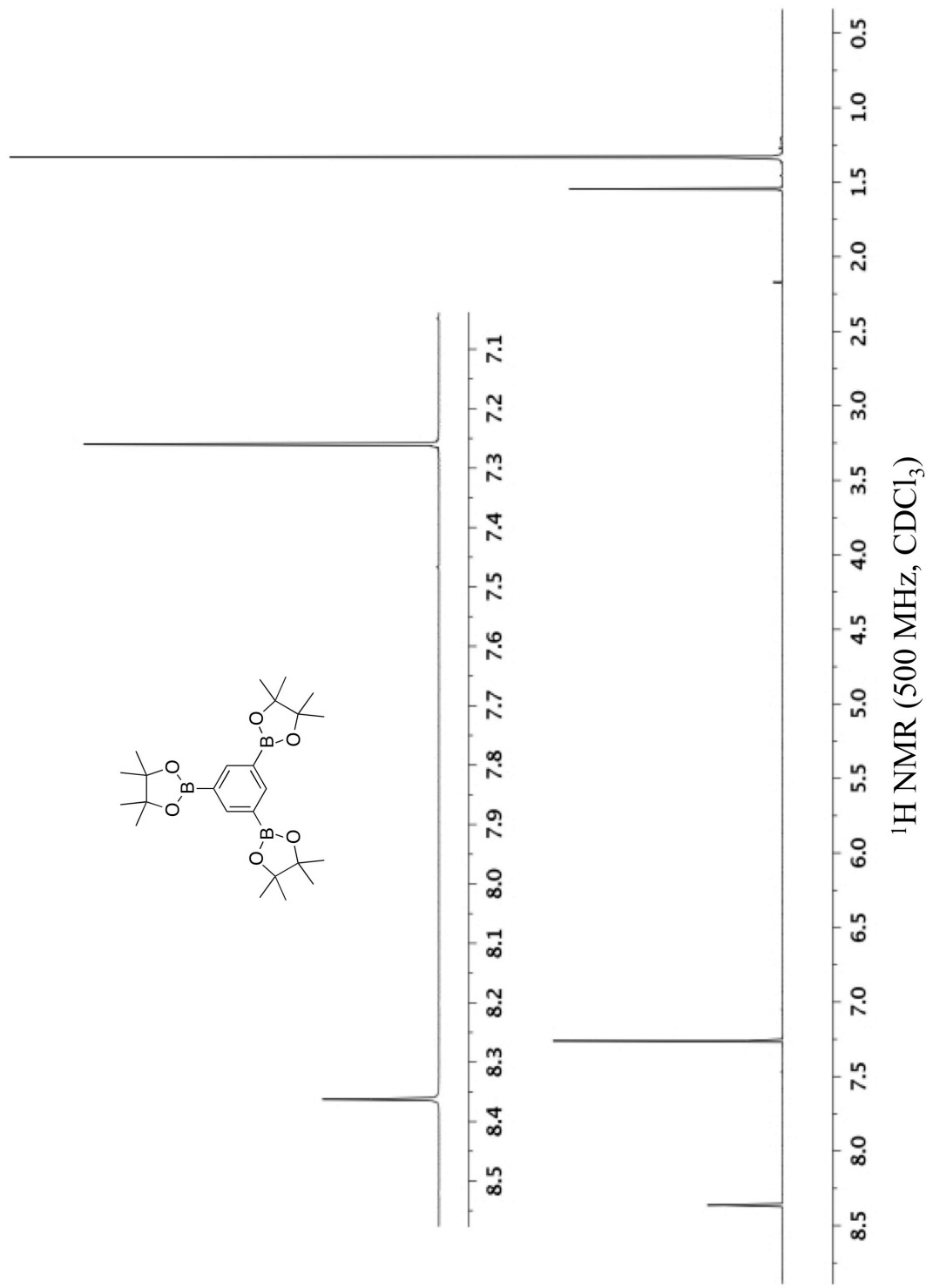
<sup>52</sup> Concentration is crucial; important to keep no less than 0.8 M

<sup>53</sup> Caution! Gas evolves!

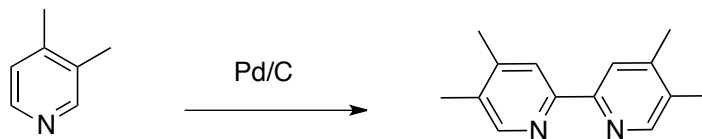
but was not isolated.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (s, 3H, Ar-H), 1.33 (s, 18H,  $\text{CH}_3$ ) matched the literature values.<sup>54</sup>

---

<sup>54</sup> Liu, Y.; Niu, F.; Lian, J.; Zeng, P.; Niu, H. *Synth. Met.* **2010**, *160*, 2055-2060.



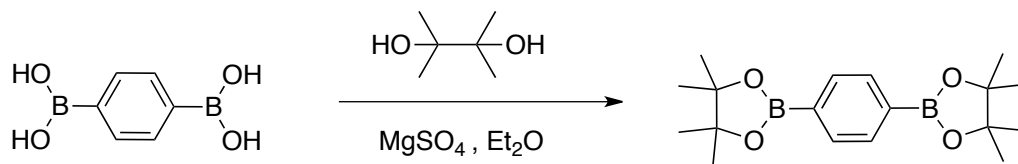
### 4,4',5,5'-Tetramethyl-2,2'-bipyridine<sup>55</sup>



3,4-Lutidine (5 mL) was mixed with 0.4 g of Pd on carbon (5%). The mixture was allowed to reflux (oil bath at 175 °C, b.p. of lutidine is 163-164 °C) under nitrogen for 4 days. A solid material was obtained upon cooling. Dichloromethane (30 mL) was added, and the mixture was filtered through a celite plug to remove the catalyst and carbon. The filtrate was collected, and the solvent and unreacted lutidine were removed under reduced pressure. The product was recrystallized from ethyl acetate. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.37 (s, 2H, Ar-H), 8.13 (s, 2H, Ar-H), 2.35 (s, 6H, CH<sub>3</sub>), 2.29 (s, 6H, CH<sub>3</sub>), matched the literature values.<sup>55</sup>

<sup>55</sup> Shen, Y.; Maliwal, B. P.; Lakowicz, J. R. *J. Fluoresc.* **2003**, *13*, 163-168.

**1,4-Bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (13)**<sup>56, 57</sup>



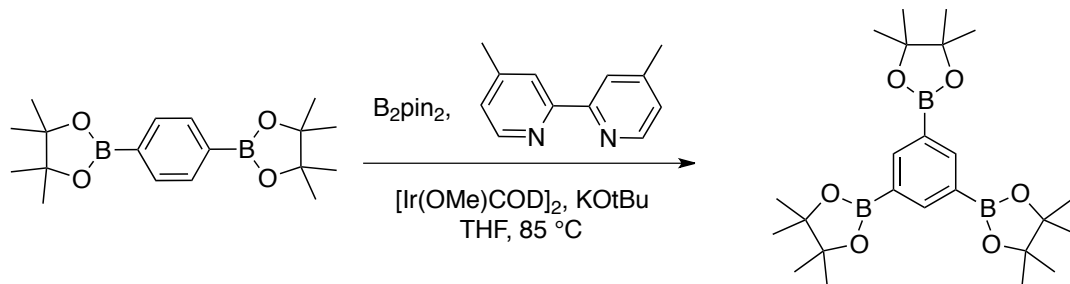
An ether solution (2 mL) of 1,4-phenylenediboronic acid (200 mg, 1.2 mmol), pinacol (314 mg, 2.64 mmol), and MgSO<sub>4</sub> (400 mg, 3.3 mmol) was stirred for 2 days at room temperature, and the ether completely evaporated over that time. The residue was extracted with ethyl acetate (twice), and the combined organic layers were dried over magnesium sulfate. The solution was filtered, and the solvent was removed in vacuo. The residue was rinsed with n-hexanes to yield a white crystalline solid (337 mg, 85%). The product was used in the next step without further purification. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.80 (s, 4H, Ar-H), 1.34 (s, 24H, CH<sub>3</sub>) matched the literature values.<sup>56</sup>

<sup>56</sup> Roche, A. J.; Canturk, B. *J. Fluorine Chem.* **2005**, 126, 483-490.

<sup>57</sup> Sato, H.; Tashiro, K.; Shinmori, H.; Osuka, A.; Aida, T. *Chem. Commun.* **2005**, 2324-2326.



### 1,3,5-*Tris*(Bpin)benzene (14) from 1,4-*bis*(Bpin)benzene (13)



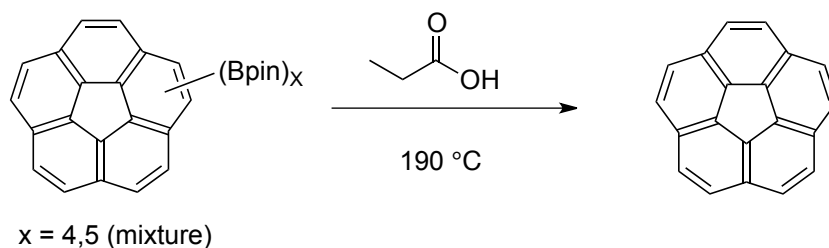
To a flame-dried 15 mL pressure vessel equipped with a magnetic stir bar and flushed with nitrogen were added [Ir(OMe)COD]<sub>2</sub> (53 mg, 0.08 mmol), 4,4'-dimethyl-2,2'-bipyridyl (30 mg, 0.16 mmol), B<sub>2</sub>pin<sub>2</sub> (335 mg, 1.32 mmol), and potassium *t*-butoxide (5 mg, 0.04 mmol). THF (0.3 mL) was added by syringe, and the mixture was heated at 50 °C for 15 min. 1,4-*Bis*(Bpin)benzene (132 mg, 0.4 mmol) was added, the rubber septum was replaced with a pressure vessel cap, and the reaction mixture was heated at 85 °C in an oil bath for 4 days. The mixture was removed from the oil bath, cooled, and diluted with dichloromethane (~2 mL). The reaction was quenched by the dropwise addition of 10% HCl (~2 mL). The layers were separated, and the aqueous layer was thoroughly extracted with dichloromethane. The combined organic layers were washed with water (1×) and brine (1×), and dried over magnesium sulfate. The filtrate was concentrated to dryness on a rotary evaporator. NMR of the crude mixture was taken and showed predominantly the product. Upon addition of methanol (~15 mL) a precipitate crashed out. The material was collected by vacuum filtration and washed with

methanol (~10 mL) to yield 20 mg of product (11%).<sup>58</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.36 (s, 3H, Ar-H), 1.33 (s, 18H, CH<sub>3</sub>), matched the literature values.<sup>54</sup>

---

<sup>58</sup> Not optimized yield.

### Corannulene recovery from a mixture of borylated corannulene



The collected filtrates from a borylation reaction that started with 500 mg of corannulene (for conditions see Table 1 entry 14) were concentrated to dryness under reduced pressure.<sup>59</sup> The solid (3.05 g) was dissolved in 50 mL of propionic acid, transferred to a 150 mL pressure vessel, equipped with a stirring bar and heated at 190 °C for 24 h.<sup>60</sup> The reaction mixture was cooled to room temperature, and 10% sodium hydroxide solution was added slowly (~100 mL) until the pH was neutral. The mixture was extracted with hexane (3×50 mL). The organic layer was washed with 10% sodium hydroxide, water and brine, and dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude material was adsorbed onto silica gel and flushed through a short silica gel plug with hexanes as eluent to provide recovered corannulene in 77% yield (385 mg).<sup>61</sup> Spectroscopic data matched those reported in the literature.<sup>62</sup> The pure *pentakis*(Bpin) corannulene obtained by precipitation with methanol weighed 158 mg, which corresponds to a 9% yield based on the original 500 mg of corannulene used and 39% based on corannulene consumed/unrecovered.

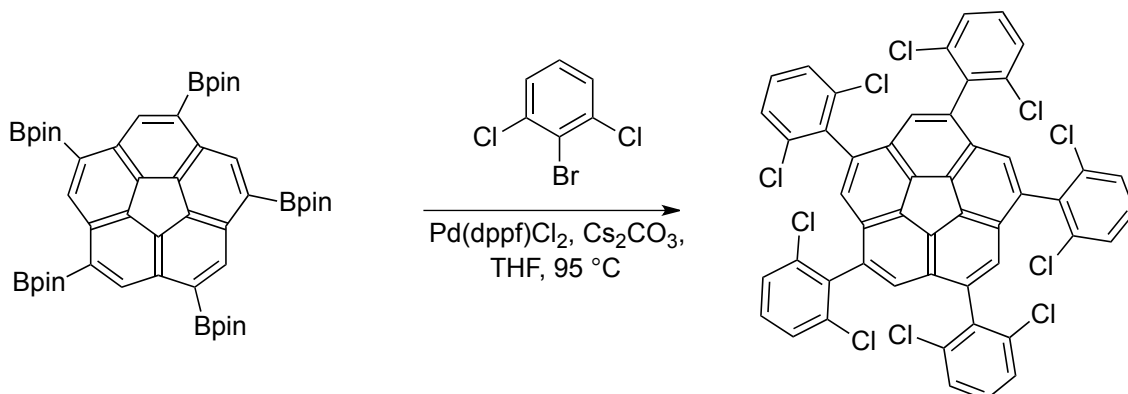
<sup>59</sup> For details on the previous step see the original borylation procedure (page 47)

<sup>60</sup> The reaction was monitored by <sup>1</sup>H NMR. If some monoborylated corannulene was left, the vessel was capped again, and the reaction was heated for another 8 h to achieve completion.

<sup>61</sup> The yield is based on the 500 mg of starting corannulene.

<sup>62</sup> Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730-1745. Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804-7813.

### 1,3,5,7,9-Pentakis(2,6-dichlorophenyl)corannulene (50 mg scale)



To a flame-dried 15 mL pressure vessel<sup>63</sup> equipped with a magnetic stir bar and septum were added 1-bromo-2,6-dichlorobenzene (128 mg, 0.57 mmol), dichloro[1,1'-bis(diphenylphosphino)ferrocene]-palladium(II) (6 mg, 0.008 mmol), THF (5.0 mL), 1,3,5,7,9-pentakis(pinacolboronyl)corannulene (50 mg, 0.057 mmol), and cesium carbonate (0.279 g, 0.85 mmol). The solution was degassed<sup>64</sup> for 5 min. The reaction vessel was capped, and the reaction mixture was allowed to stir at 90 °C for 16 h.<sup>65</sup> After cooling to room temperature the crude reaction mixture was diluted with dichloromethane, washed with 10% HCl (×2), water (×1) and brine. The organic layer was then dried over magnesium sulfate, filtered and concentrated to dryness. The excess 1-bromo-2,6-dichlorobenzene was removed by heating the mixture in a Kugelrohr at 175 °C under vacuum for 1h. Preparative silica gel thin layer chromatography using 10:3 cyclohexane:dichloromethane then gave 45 mg (82% yield) of light yellow material. The

<sup>63</sup> Size of the vessel is important, not to use larger vessel!

<sup>64</sup> By purging with nitrogen.

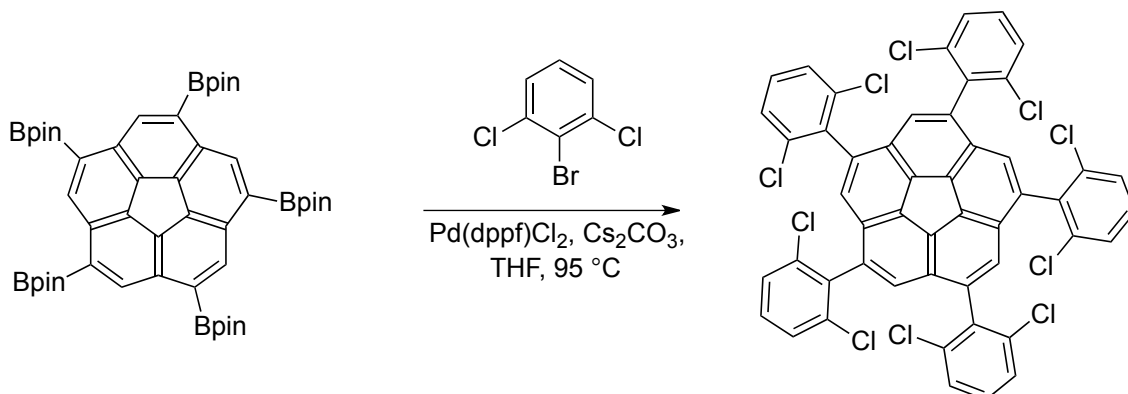
<sup>65</sup> The reaction was monitored by <sup>1</sup>H NMR, and it sometimes took longer to complete. If the reaction was not done, it was capped again and heated for another day. The reaction was kept under nitrogen while the NMR was taken.

spectral properties of this compound are consistent with those previously reported:<sup>66</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.44 (*J*=8 MHz, 10H), 7.28 (dd, *J*=8 MHz, *J*=8 MHz, 5 H), 7.26 (s, 5H).

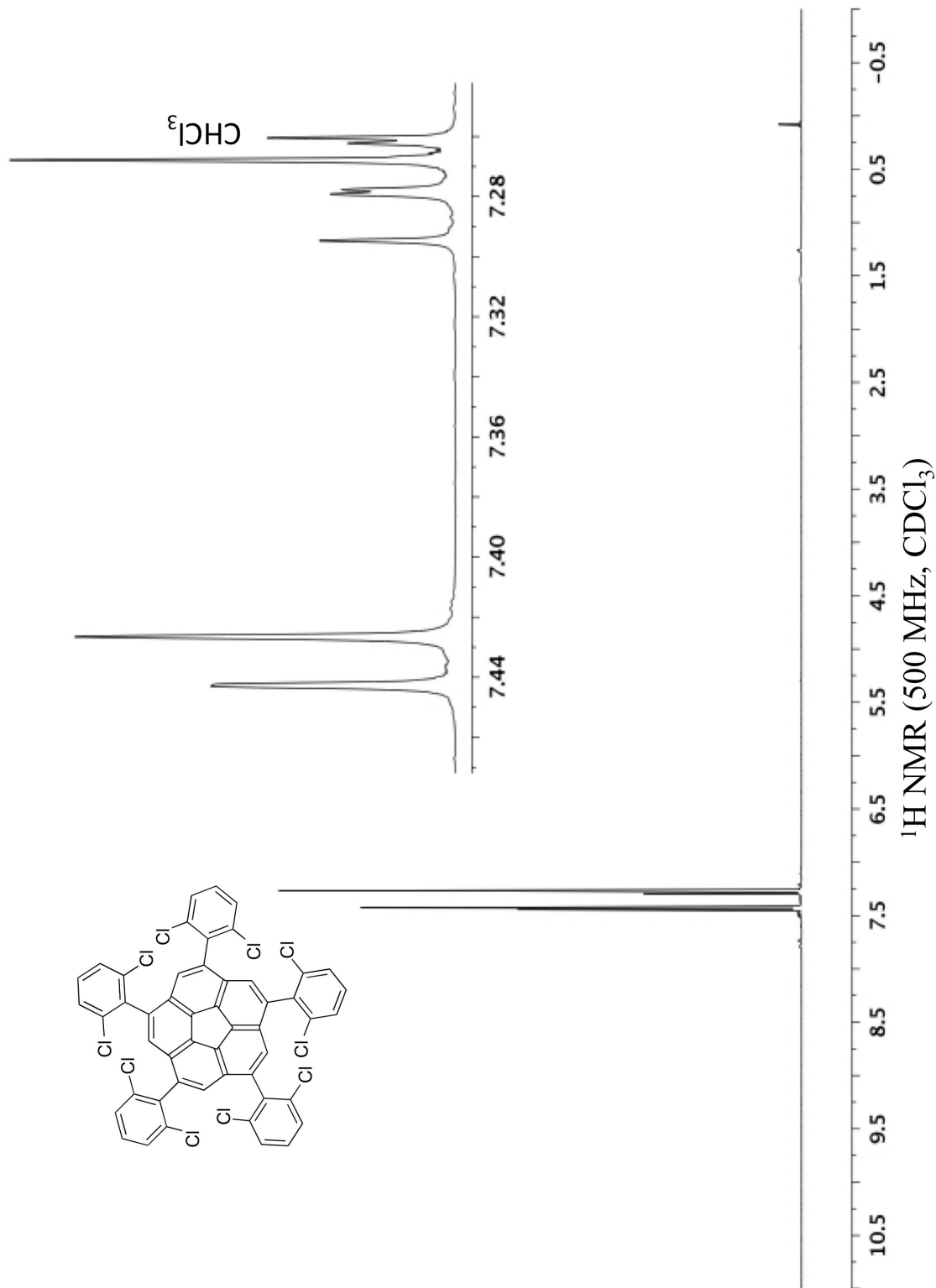
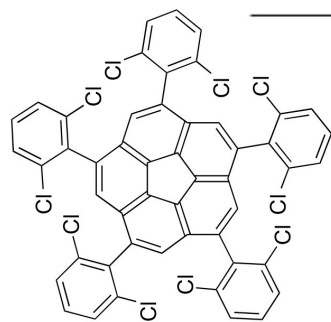
---

<sup>66</sup> Jackson, E. A. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2008. Steinberg, B. D. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2009.

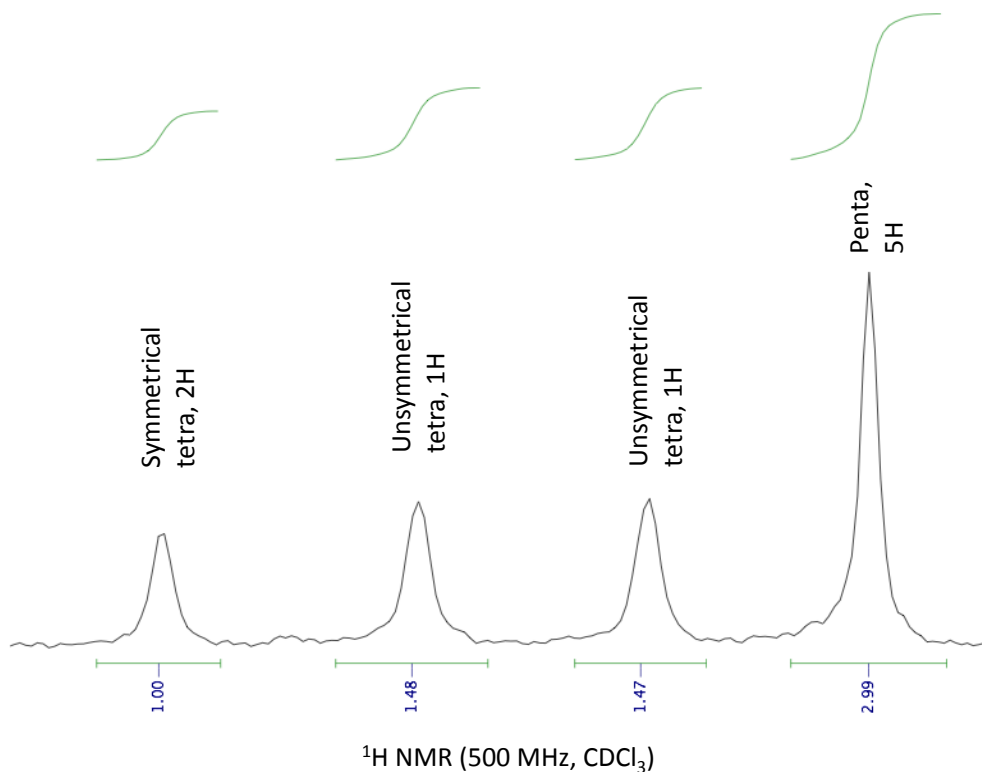
### 1,3,5,7,9-Pentakis(2,6-dichlorophenyl)corannulene (250 mg scale)



To a flame-dried 75 mL pressure vessel<sup>63</sup> equipped with a magnetic stir bar and septum were added 1-bromo-2,6-dichlorobenzene (641 mg, 2.84 mmol), dichloro[1,1'-bis(diphenylphosphino)ferrocene]-palladium(II) (31 mg, 0.042 mmol), THF (25 mL), 1,3,5,7,9-pentakis(pinacolboronyl)corannulene) (250 mg, 0.28 mmol), and cesium carbonate (1.141 g, 3.5 mmol). The solution was degassed for 10 min. The reaction vessel was capped, and the reaction mixture was allowed to stir at 90 °C for 2 d. After cooling to room temperature the crude reaction mixture was diluted with dichloromethane, washed with 10% HCl (×2), water (×1) and brine. The excess 1-bromo-2,6-dichlorobenzene was removed by heating the mixture in a Kugelrohr at 175 °C under vacuum for 2h. Further purification by silica gel chromatography using 1:4 dichloromethane:cyclohexane gave 208 mg (76% yield) of light yellow product. The spectral properties of this compound are consistent with those previously reported.<sup>66</sup>



## Appendix 1. NMR analysis of corannulene borylation product mixtures



**Picture 1.** Peaks in the 9.00 ppm region and integration values for the components of the corannulene borylation mixture

We know, how many protons every peak represents and to what compound they belong. Therefore we can calculate the molar ratio between compounds in the mixture as follows:

The integrated area per proton for each compound

$$\frac{1}{2} : \frac{1.48 + 1.47}{2} : \frac{2.99}{5} = 0.50 : 1.47 : 0.60$$



The sum of the ratios

$$0.50 + 1.47 + 0.60 = 2.57$$

Normalized ratio of each compound

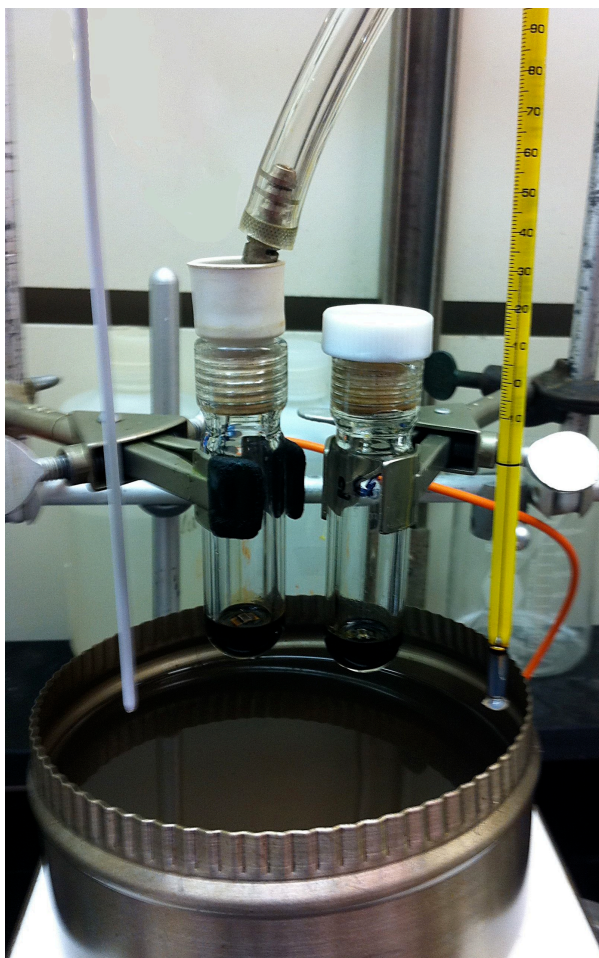
$$\frac{0.50}{2.57} : \frac{1.47}{2.57} : \frac{0.60}{2.57} = 0.20 : 0.57 : 0.23$$

This was how we performed the calculations. Based on them, we obtained 20% of the symmetrical tetra-product, 57% of the unsymmetrical tetra and 23 % of the penta-product in this case.

## Appendix 2. Details for the borylation reaction set up

For the borylation reaction, 15 mL heavy wall pressure vessels were used (purchased from Chemglass: product number CG-1880-01) with a Teflon bushing and Perfluoro o-ring.

Picture 2 shows the set up for the reaction. Pressure vessel with a septum and nitrogen line (on the left) and a sealed pressure vessel (on the right).



**Picture 2.** Representation of the borylation reaction set up