

Supporting Information

Pushing the Ir-catalyzed C–H polyborylation of aromatic compounds to maximum capacity by exploiting reversibility.

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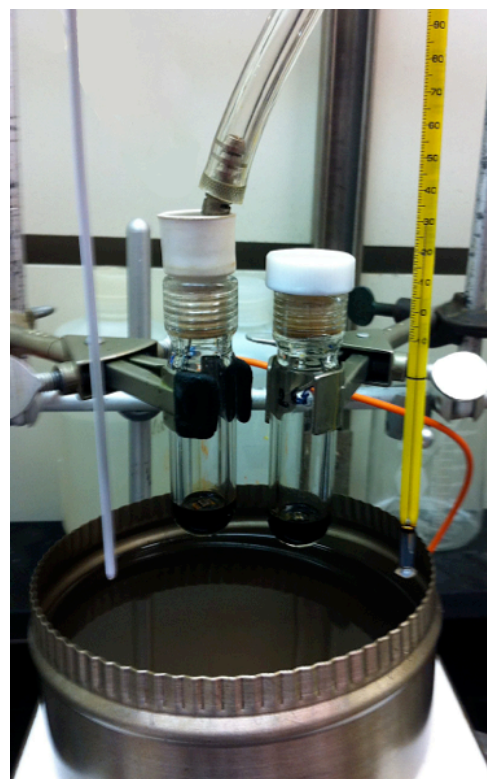
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1. Solvents, reagents, catalysts, silica gel, spectroscopy, and precautions

Corannulene was initially synthesized in-house by a modified version¹ of the Siegel procedure.² The final experiments were conducted using corannulene received, with much gratitude, as a gift from Professor Siegel. Sincerest thanks are also extended to Dr. Dustin Cefalo and Frontier Scientific, Inc. for generous gifts of *bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)diborane (B_2pin_2). All other commercially available chemicals and solvents were purchased from Strem, Acros, Fisher, Aldrich, or AlfaAesar and were used without purification, unless otherwise stated. Tetrahydrofuran (THF) was dried and purified with a Glass Contour solvent purification system. Anhydrous cyclohexane and hexanes were obtained by house vacuum distillation from CaH_2 under N_2 . Column chromatographies were performed using Sorbent Technologies standard grade silica gel (porosity = 60 Å, particle size = 32-63 μm). Medium pressure gradient chromatography was performed on a Teledyne Isco CombiFlash automated flash chromatography system with a 200-780 nm UV-vis variable wavelength detector. Proton and carbon NMR spectra were recorded on a Varian 500 MHz NMR spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane, using the solvent signal as an internal reference, in chloroform- d (δH = 7.26 ppm, δC = 77.16 ppm) or benzene- d_6 (δH = 7.16 ppm). Low resolution mass spectrometric 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 inlet capabilities. High-resolution mass spectra were obtained by the Boston College Mass Spectrometry Center using various TOF instruments. Elemental analyses were carried out by Robertson Microlit Laboratories.

SAFETY NOTE: all pressure vessel reactions were run behind a blast shield.

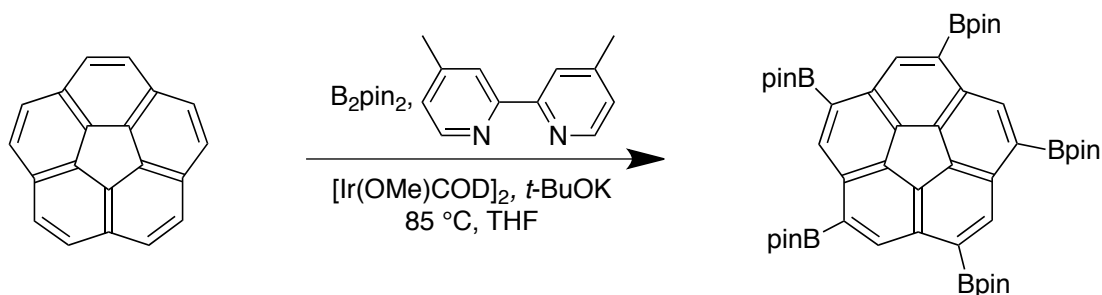
For the borylation reactions, 15 mL heavy-walled pressure vessels were used (purchased from Chemglass: product number CG-1880-01) with a Teflon bushing and Perfluoro O-ring. The set up for the reaction is shown in the photograph to the right. A pressure vessel with a septum and nitrogen line is pictured on the left, and a sealed pressure vessel is pictured on the right.



¹ Smith, N. J. Ph.D. dissertation, Boston College, Chestnut Hill, Massachusetts, 2011.

² Butterfield, A. M.; Gilomen, B.; Siegel, J. S. *Org. Proc. Res. Devel.* **2012**, *16*, 664-676.

2a. 1,3,5,7,9-Pentakis(Bpin)corannulene (1) (1.0 mmol scale)



A 15 mL flame-dried glass pressure vessel was equipped with a Teflon-coated magnetic stirring bar and a silicon rubber septum and was purged with dry nitrogen. The vessel was then charged with $[\text{Ir}(\text{OMe})\text{COD}]_2$ (132 mg, 0.20 mmol), 4,4'-dimethyl-2,2'-bipyridyl (74 mg, 0.40 mmol), B_2pin_2 (1.320 g, 5.2 mmol), and potassium *t*-butoxide (11 mg, 0.10 mmol). THF (0.9 mL)³ 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 (250 mg, 1.00 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, opened to the air, and immediately diluted with dichloromethane (~5 mL). The reaction was quenched by the drop wise addition of 10% aqueous HCl (~5 mL).⁴ 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.⁵ The filtrate was concentrated to dryness on a rotary evaporator to give a dark red-brown oily semi-solid mixture, which was kept under reduced pressure for a couple of hours.

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.⁶ The precipitate was collected by vacuum filtration with a Buchner funnel and a paper filter,^{7,8} 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_2pin_2 , but it still contained some tetraborylated corannulene, so it was redissolved and precipitated a second time (see Chart S1). 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 light yellow in color and could be a dry heavy

³ Concentration is crucial; the corannulene concentration should be no less than 0.8 M.

⁴ **Caution: Gas evolves!**

⁵ When filtering, the drying agent was washed with dichloromethane several times, but it remained orange.

⁶ A lot of white-pink precipitate accumulated in the flask

⁷ The filtration was slow.

⁸ Sometimes, 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 a second vacuum filtration with methanol washing.

powder or a fluffy⁹ solid. The yield of analytically pure product was typically 440-616 mg (50-70%): mp 322-326 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.98 (s, 5H), 1.46 (s, 60H); ¹H NMR (500 MHz, C₆D₆) δ 9.75 (s, 5H), 1.01 (s, 60H); ¹³C NMR (125 MHz, CDCl₃) δ 138.9, 137.0, 133.3, 128.6 (broad) 83.8, 25.2; HRMS (MALDI): calcd for C₅₀H₆₅O₁₀B₅: 880.5038, found 880.5057; elemental analysis calcd for C₅₀H₆₅O₁₀B₅: C, 68.23%, H, 7.44%, B, 6.14%; found C, 68.43%, H, 7.35%, B, 6.28%.

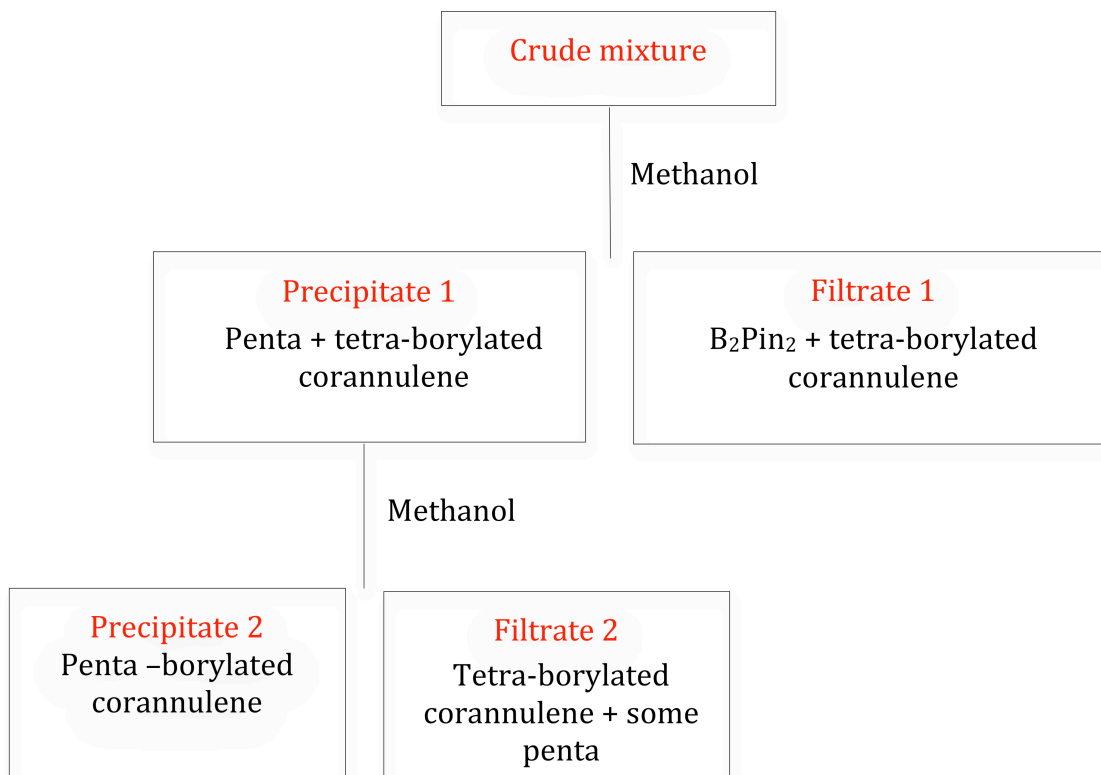
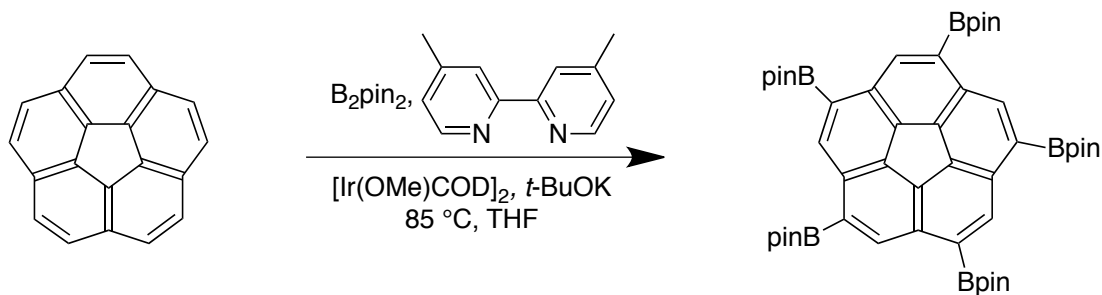


Chart S1. Summary of steps for the isolation of pure 1,3,5,7,9-pentakis(Bpin)corannulene (**1**) from the borylation reaction. Filtrate 1 and filtrate 2 are combined at the end for recycling of corannulene.

⁹ After precipitation from the rotary evaporator.

2b. 1,3,5,7,9-Pentakis(Bpin)corannulene (1) (100 mg scale)

A 15 mL flame dried pressure vessel was equipped with a Teflon-coated magnetic stirring bar and a silicon rubber septum and was purged with dry nitrogen. The vessel was then charged with $[\text{Ir}(\text{OMe})\text{COD}]_2$ (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)¹⁰ 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 immediately diluted with dichloromethane (~3 mL). The reaction was quenched by the drop wise addition of 10% HCl (~3 mL).¹¹ 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.¹² 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.

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.¹³ The precipitate was collected by vacuum filtration with a small Buchner funnel and a paper filter,¹⁴ 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.¹⁵ Spectroscopic data matched those reported in the previous procedure.

¹⁰ Concentration is crucial; important to keep the corannulene concentration at no less than 0.8M.

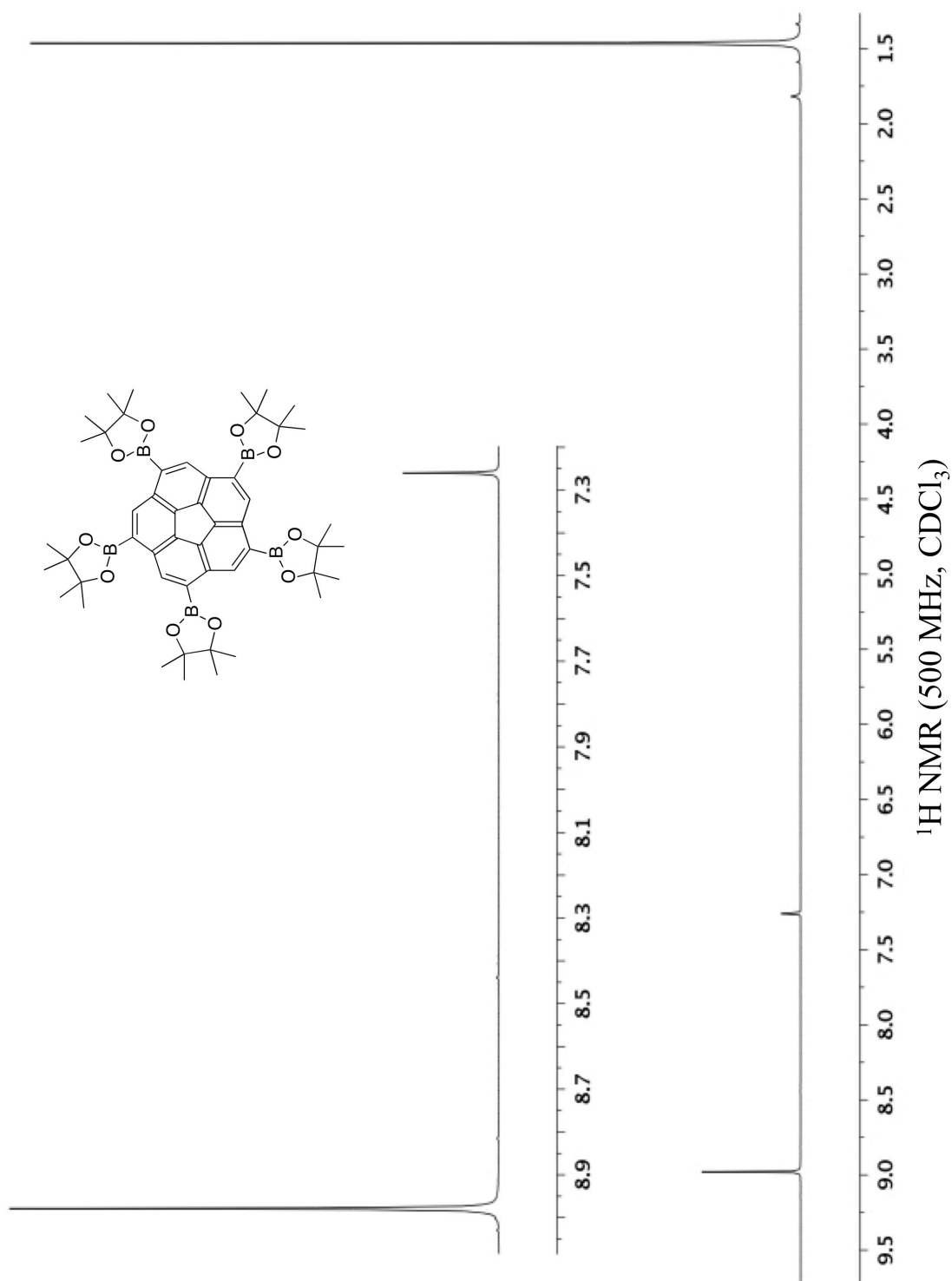
¹¹ **Caution! Gas evolves!**

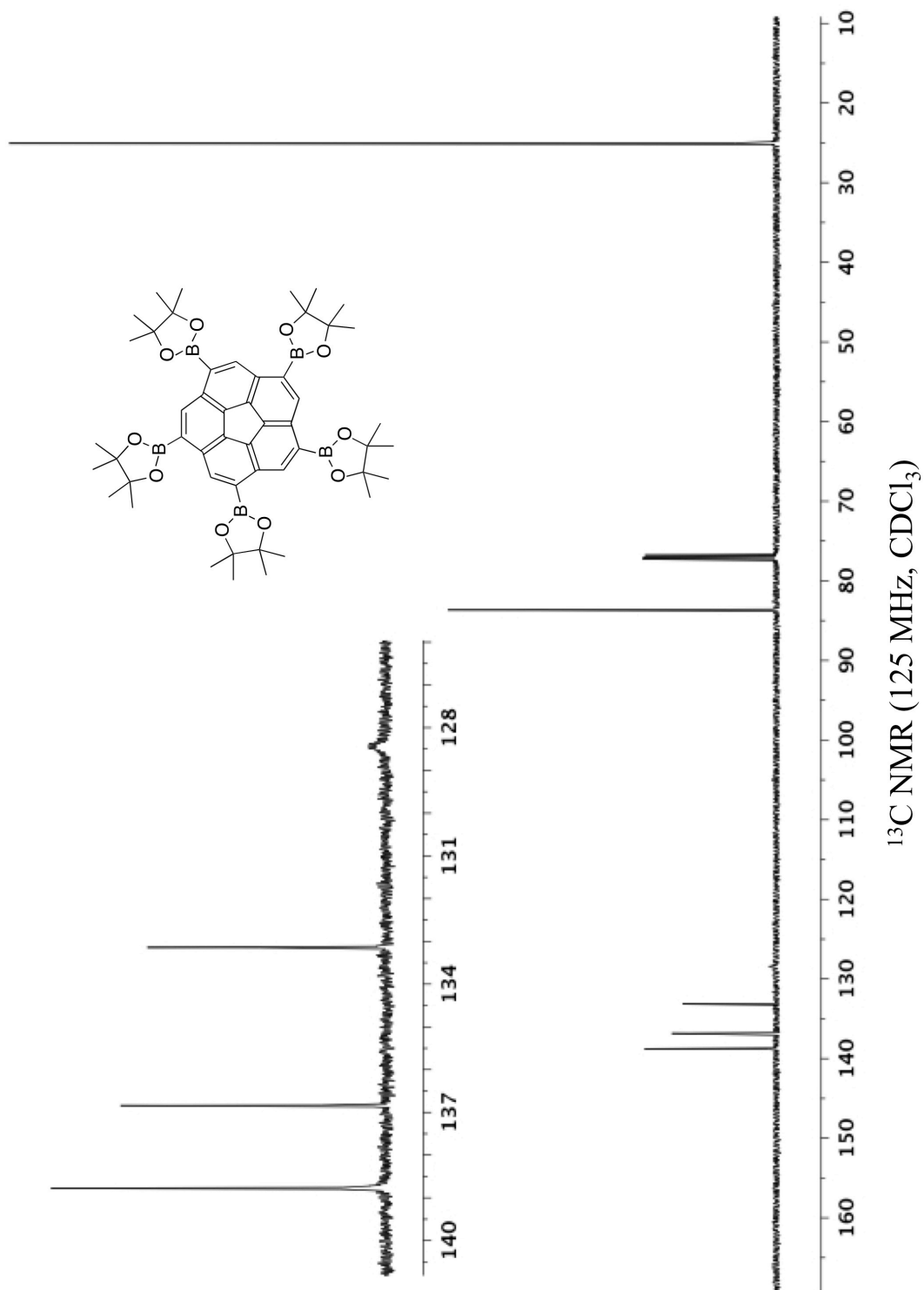
¹² When filtering, the drying agent is washed with dichloromethane several times, but it remains orange.

¹³ A lot of white-pink precipitate accumulated in the flask

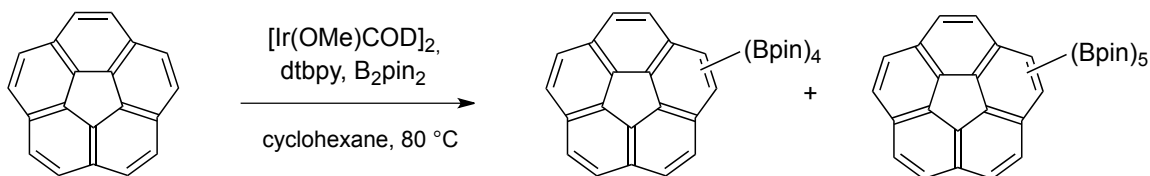
¹⁴ Sometimes, some additional penta-borylated corannulene began to precipitate from the first filtrate. In that case, the filtrate was transferred from the side arm flask to a round-bottom flask with the help of dichloromethane, and the mixture was concentrated on the rotary evaporator until the precipitate formed again. The additional precipitate was then collected by vacuum filtration with methanol washing.

¹⁵ Even better yields are sometimes obtained when CsF is used as the base.





3. Borylation of corannulene under normal conditions

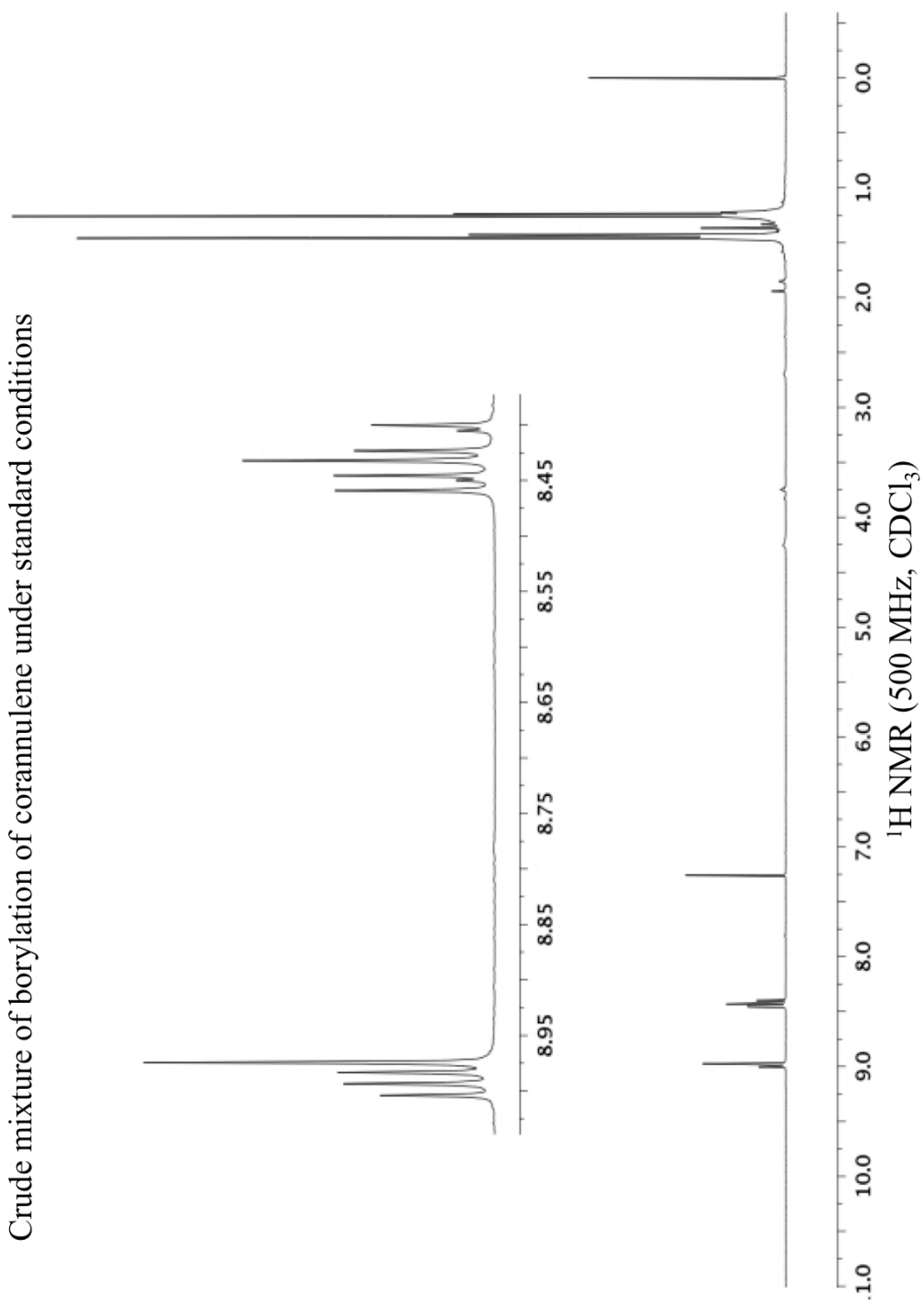


To a 15 mL flame-dried glass pressure vessel equipped with a Teflon-coated magnetic stirring bar and a silicon rubber septum were added $[\text{Ir}(\text{OMe})\text{COD}]_2$ (13 mg, 0.02 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (11 mg, 0.04 mmol), B_2pin_2 (559 mg, 2.2 mmol), and distilled cyclohexane (1.5 mL) under an atmosphere of dry nitrogen. The mixture was heated at 50°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°C for 24 h. The mixture was removed from the oil bath, cooled, and diluted with dichloromethane (~5 mL). The reaction was quenched by the drop wise addition of 10% aqueous HCl (~5 mL).¹⁶ 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.¹⁷ 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 spectroscopy and found to contain a mixture of *tetrakis*(Bpin)corannulenes and *pentakis*(Bpin)corannulene (see manuscript Figure 1 and Appendix 1).

16. **Caution: Gas evolves!**

17. When filtering, the drying agent was washed with dichloromethane several times, but it remained orange.

Crude mixture of borylation of corannulene under standard conditions



4. Dependence of the corannulene polyborylation on reaction conditions

A few experiments were run using HBpin as the borylating agent, but these were discontinued when we began having success with B₂(pin)₂. Good results were obtained using as little as 5.2 equiv of B₂(pin)₂; the yields of *pentakis*(Bpin)corannulene (**1**) began to drop, however, when 5.0 equiv or less of B₂(pin)₂ were used. We found that [IrClCOD]₂/dtbpy (1:2) catalyzes the borylation of corannulene in THF at 85 °C about as effectively as [Ir(OMe)COD]₂/dtbpy (1:2); (Ind)Ir(COD)/dmpe (1:1) in dioxane, on the other hand, is ineffective, even at 130-150 °C for 4 days. Other factors are treated separately below.

a) Solvent. A preliminary screening of solvents commonly used for direct borylations or aromatic hydrocarbons (without added base) showed that the choice of solvent has little effect on the proportion of 1,3,5,7,9-*pentakis*(Bpin)corannulene (**1**) formed under conditions of kinetic control (Table S1). THF was chosen for subsequent studies, therefore, primarily as a matter of convenience.

Table S1. Screening of solvents for the borylation of corannulene with 5.5 equiv B₂(pin)₂, 0.05 equiv [Ir(OMe)COD]₂, and 0.10 equiv dtbpy, without added base

Entry	Solvent	Temp (°C)	Time (h)	Conc. (M)	Yield of <i>pentakis</i> (Bpin) ^a
1	cyclohexane	80	24	0.26	19
2	1,4-dioxane	120	48	0.2	23
3	THF	80	18	0.2	23
4	THF	80	18	0.4	23
5	THF	120	48	0.2	23

^aYield is based on the NMR integrated ratio of *pentakis*(Bpin)-corannulene (**1**) to the mixture of tetra-borylated isomers (see Appendix 1 for details).

b) Temperature. The borylation of corannulene with 5.5-10.5 equiv B₂pin₂, 0.05 equiv [Ir(OMe)COD]₂, and 0.10 equiv dtbpy is slow to reach completion at room temperature and in refluxing THF. Running the reaction in a glass pressure vessel allows the use of higher temperatures and prevents solvent losses over time. The borylation reaches completion with 5.5 equiv B₂pin₂ at 80 °C in ≤18 h (Table S2, entry 4); higher temperatures and longer reaction times have essentially no effect on the ratio of products formed (Table S2, entry 7).

Table S2. Effects of temperature on the borylation of corannulene (0.2 M) with B₂(pin)₂, 0.05 equiv [Ir(OMe)COD]₂, and 0.10 equiv dtbpy in THF (pressure vessel), without added base

Entry	B ₂ pin ₂ (eq)	Temp (°C)	Time (h)	Yield of <i>pentakis</i> (Bpin) ^a
1	10.5	70	48	23
2	8	80	36	23
3	7	80	36	23
4	5.5	80	18	23
5	5.2	85	18	23
6	7	100	16	23
7	5.5	120	48	23

^aYield is based on the NMR integrated ratio of *pentakis*(Bpin)corannulene (**1**) to the mixture of tetra-borylated isomers (see Appendix 1 for details).

c) Ligand. The borylation of corannulene with B_2pin_2 , catalyzed by $[Ir(OMe)COD]_2$, shows a strong dependence on the choice of ligand used. Table S3 summarizes the results obtained with the ligands shown below. The best results were obtained with several alkylated bipyrindyls: 4,4',5,5'-tetramethylbipyridyl (tmbpy – Table S3, entry 2),¹⁸ 4,4'-di-*t*-butylbipyridyl (dtbpy – Table S3, entry 6), 4,4'-dimethylbipyridyl (4,4'-dmbpy – Table S3, entry 10), and 5,5'-dimethylbipyridyl (5,5'-dmbpy – Table S3, entry 11).

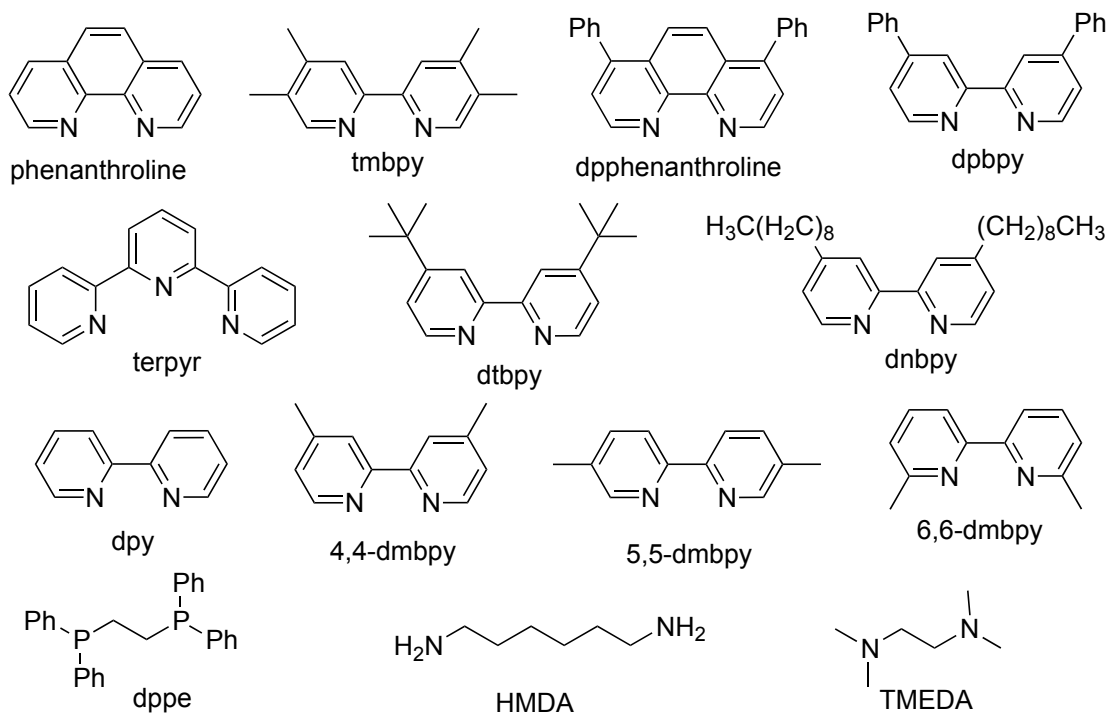


Table S3. Effects of ligand structure on the borylation of corannulene with $B_2(pin)_2$, catalyzed by $[Ir(OMe)COD]_2$, in THF (pressure vessel), without added base

Entry	Catalyst (%)	Ligand ^a	B_2pin_2 (eq)	Temp (°C)	Time (h)	Conc. (M)	Yield of <i>pentakis</i> (Bpin) ^b
1	5	phenanthroline	6	85	72	0.27	16
2	10	tmbpy	6	85	17	0.8	22
3	5	dp-phenanthroline	6	80	24	0.4	15
4	10	dpbpy	7	110	72	0.2	<1
5	10	terpyr	6	80	48	0.2	<1

¹⁸ For a synthetic procedure, see Eliseeva, M. N. M.S. thesis 2011, Boston College, Chestnut Hill Massachusetts.

6	5	dtbpy	5.5	80	18	0.2	23
7	10	dndpy	7	85	72	0.2	13
8	10	dnbpy	6	85	24	0.5	18
9	5	dpy	6	85	48	0.27	18
10	10	4,4'-dmbpy	6	85	16	0.2	23
11	10	5,5'-dmbpy	6	85	16	0.2	23
12	10	6,6'-dmbpy	6	85	72	0.2	<1
13	5	dppe	6	80	48	0.2	0 ^c
14	15	HMDA	6	80	36	0.4	0 ^c
15	15	TMEDA	6	80	36	0.4	0 ^c

^a[Ir]:[ligand] = 1:2. ^bYield is based on the NMR integrated ratio of *pentakis*(Bpin)-corannulene (**1**) to the mixture of tetra-borylated isomers (see Appendix 1 for details).

^cPartial borylation is observed, but no *pentakis*(Bpin)corannulene (**1**) is formed in the time used for this experiment.

d) Catalyst loading. Without base, the reversibility of the corannulene borylation catalyzed by $[\text{Ir}(\text{OMe})\text{COD}]_2$ in THF at 80 °C is very slow and begins to become apparent only when the reaction is run at high concentrations with high catalyst loadings (Table S4).

Table S4. Effects of catalyst loading on the borylation of corannulene with $\text{B}_2(\text{pin})_2$, catalyzed by $[\text{Ir}(\text{OMe})\text{COD}]_2$ in THF at 80 °C (pressure vessel), without added base; all reactions were stopped after 1 day

Entry	$[\text{Ir}(\text{OMe})\text{COD}]_2$ (%)	Ligand (%)	B_2pin_2 (eq)	Conc. (M)	Yield of <i>pentakis</i> (Bpin) ^a
tmbpy					
1	5	10	5.5	1.0	18
2	10	20	6.0	0.8	22
3	20	40	5.5	1.0	26
dtbpy					
4	10	20	6.0	1.0	21
5	20	40	5.5	1.0	21
4,4'-dmbpy					
6	10	20	6.0	0.8	23
7	20	40	5.5	1.0	32
8	30	60	5.5	1.0	48
9	40	80	5.5	0.8	50
5,5'-dmbpy					
10	5	10	6.0	1.0	22
11	10	20	6.0	1.0	24
12	20	40	5.5	1.0	26
13	30	60	5.5	1.0	31

^aYield is based on the NMR integrated ratio of *pentakis*(Bpin)corannulene (**1**) to the mixture of tetra-borylated isomers (see Appendix 1 for details).

e) Base and time. When 4,4'-dmbpy and tmbpy are used as the ligand, added base clearly promotes the formation of more *pentakis*(Bpin)corannulene (**1**) at the expense of the tetra-borylated isomers (Table S5, entries 1/2, 5/6, 8/9, 11/12). Even with a 20% catalyst loading and high concentrations of corannulene, however, the deborylation/reborylation requires several days to convert all of the tetra-borylated isomers to *pentakis*(Bpin)corannulene (**1**) (Table S5, entries 2,3,4,5 and 17,18,19). Higher catalyst loadings accelerate the process (Table S5, entries 2/9), and lower catalyst loadings are impractical (Table S5, entries 4/10). Sodium methoxide and potassium *t*-butoxide are comparably effective (Table S5, entries 3/17, 4/18, 5/19), and even cesium carbonate, potassium carbonate, and cesium fluoride work well with bipyridyl as the ligand (Table S5, entries 20-25).

When 5,5'-dmbpy and dtbpy are used as the ligand, added base has little or no effect on the product distribution (Table S5, entries 13/14, 15/16). Thus, of the four bipyridyl ligands that perform best in the absence of base (Table S3), only the two that have methyl groups at positions 4 and 4' (4,4'-dimethylbipyridyl and 4,4',5,5'-tetramethylbipyridyl) respond favorably to the presence of added base. Bipyridyls having methyl groups only at positions 5 and 5' or *t*-butyl groups at positions 4 and 4' are unresponsive. We do not know the explanation for this curious observation but speculate below on a possible cause.

Table S5. Effects of added base and time on the borylation of corannulene with B₂(pin)₂, catalyzed by [Ir(OMe)COD]₂ in THF at 80 °C (pressure vessel)

Entry	[Ir(OMe)COD] (%)	Ligand (%)	B ₂ pin ₂ (eq)	Base (%)	Time (days)	Conc. (M)	Yield of <i>pentakis</i> (Bpin) ^a
		4,4'-dmbpy		NaOMe			
1	20	40	5.5	-	1	1.0	32
2	20	40	5.5	10	1	1.0	45
3	20	40	5.5	10	2	1.0	55
4	20	40	5.2	10	3	1.0	74
5	20	40	5.2	10	4	1.0	85
6	20	40	5.5	-	4	1.0	41
7	20	40	5.5	45	1	1.0	40
8	40	80	5.5	-	1	0.8	50
9	40	80	5.5	10	1	0.8	63
10	10	20	5.5	10	4	1.0	27

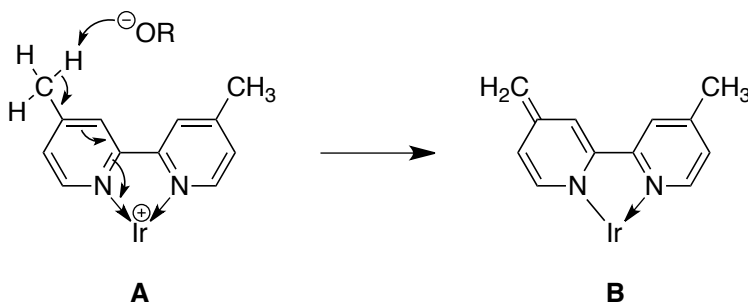
Table S5. (continued)

		tmbpy	NaOMe				
11	20	40	5.5	-	3	0.8	48
12	20	40	5.5	10	3	0.8	90
		5,5'-dmbpy	NaOMe				
13	20	40	5.5	-	3	0.8	26
14	20	40	5.5	10	3	0.8	35
		dtbpy	NaOMe				
15	20	40	5.5	-	2	0.8	23
16	20	40	5.5	10	2	0.8	24
		4,4'-dmbpy	KOtBu				
17	20	40	5.2	10	1	1.3	50
18	20	40	5.2	10	3	1.3	80
19	20	40	5.2	10	4	1.3	90
		4,4'-dmbpy	Cs ₂ CO ₃				
20	20	40	5.2	10	4	1.3	85
		4,4'-dmbpy	K ₂ CO ₃				
21	20	40	5.2	10	4	1.0	75
		4,4'-dmbpy	CsF				
22	20	40	5.2	10	1	0.8	40
23	20	40	5.2	10	2	0.8	55
24	20	40	5.2	10	3	1.0	70

25	20	40	5.2	10	4	1.0	88
bpy			KOTBu				
26	20	40	5.2	10	4	1.3	26

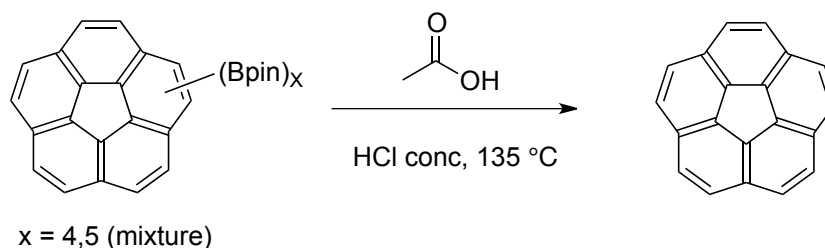
^aYield is based on the NMR integrated ratio of *pentakis*(Bpin)corannulene (**1**) to the mixture of tetra-borylated isomers (see Appendix 1 for details).

We speculate that cationic iridium may acidify the C–H bonds of methyl groups in the 4 and 4' positions of coordinated bipyridyl ligands (**A**) to enable reversible deprotonation by sodium methoxide and potassium *t*-butoxide, as shown below. The resulting neutral iridium species (**B**) may then perform better in the catalytic deborylation/reborylation.



The C–H bonds of methyl groups in the 5 and 5' positions of coordinated bipyridyl ligands would not be acidified, and *t*-butyl groups in the 4 and 4' positions of coordinated bipyridyl ligands could not be deprotonated.

5. Deborylation of poly(Bpin)corannulenes back to corannulene



The collected filtrates from a 100 mg scale borylation reaction were concentrated to dryness under reduced pressure.¹⁹ The solid (269 mg) was dissolved in 6 mL of acetic acid, and 6 mL of concentrated HCl was added. The mixture was allowed to reflux overnight (oil bath temperature ~ 135 °C). The reaction mixture was cooled to room temperature, and 10% sodium hydroxide was added slowly (~50 mL) until the pH was neutral. The mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with 10% sodium hydroxide, water and brine, then dried over magnesium sulfate, filtered and concentrated to dryness 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 32 mg of corannulene (32% of the original 100 mg of corannulene was recovered). Spectroscopic data matched those reported in the literature.^{20,21}

The yield of pure 1,3,5,7,9-*pentakis*(Bpin)corannulene (**1**) from this particular 100 mg scale reaction was 67%. Thus, 99% (67% + 32%) of the original 100 mg of corannulene ended up either as *pentakis*(Bpin)corannulene (**1**) or as recovered corannulene. The yield of *pentakis*(Bpin)corannulene (**1**) based on unrecovered corannulene is essentially quantitative.

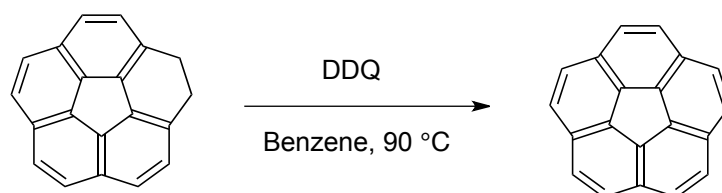
Taking into account the 67% yield of *pentakis*(Bpin)corannulene (**1**), the maximum amount of corannulene that could have been recovered from the filtrate was 33 mg. Thus, the recovery of 32 mg corresponds to a 97% yield for the deborylation step.

¹⁹ For details on the previous step, see the original borylation procedure on page S5.

²⁰ 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.

²¹ Sometimes we see a minor byproduct from the deborylation, dihydrocorannulene, formed in varying amounts. Spectroscopic data: ¹H NMR (400 MHz, CDCl₃; 298 K): δ 7.72 (d, *J* = 9.0 Hz, 2H), 7.69 (d, *J* = 9.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.38 (s, 4H). If the amount is more than a few percent, a simple oxidation with DDQ can be performed according to the procedure on the next page.

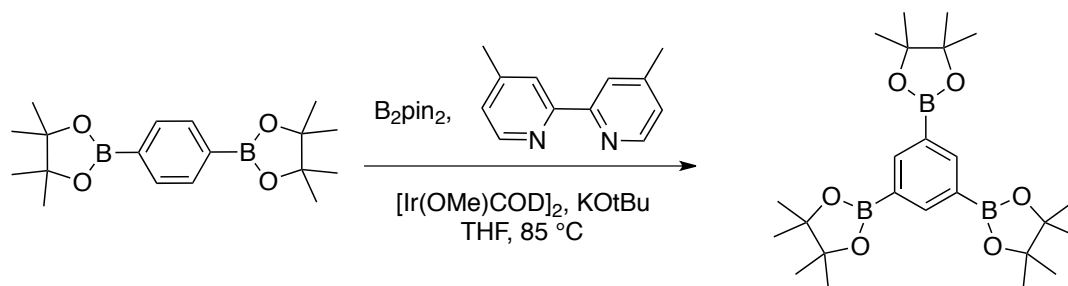
Dehydrogenation of dihydrocorannulene with DDQ



A mixture of corannulene and dihydrocorannulene that contained significant quantities of the latter (94 mg, ~0.38 mmol, 82:18 ratio)²² was dissolved in 2 mL of benzene. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (32 mg, 0.14 mmol)²³ was added, and the reaction was refluxed overnight (oil bath ~90 °C). After being cooled to room temperature, the reaction mixture was diluted with saturated sodium bicarbonate (~5 mL). The mixture was extracted with benzene. The combined organic layers were washed with saturated sodium bicarbonate and water, dried over magnesium sulfate, and concentrated to dryness under reduced pressure. The precipitate was subjected to a short silica plug eluted with hexane to provide 90 mg of pure corannulene, which corresponds to 92 % recovery.

²² The mixture was obtained after deborylation from a 250 mg scale borylation reaction, from which 61% of 1,3,5,7,9-pentakis(Bpin)corannulene (**1**) was isolated.

²³ A 2:1 ratio of DDQ to dihydrocorannulene was used ($\sim 0.38 \text{ mmol} \times 0.18 \times 2 = 0.14 \text{ mmol}$)

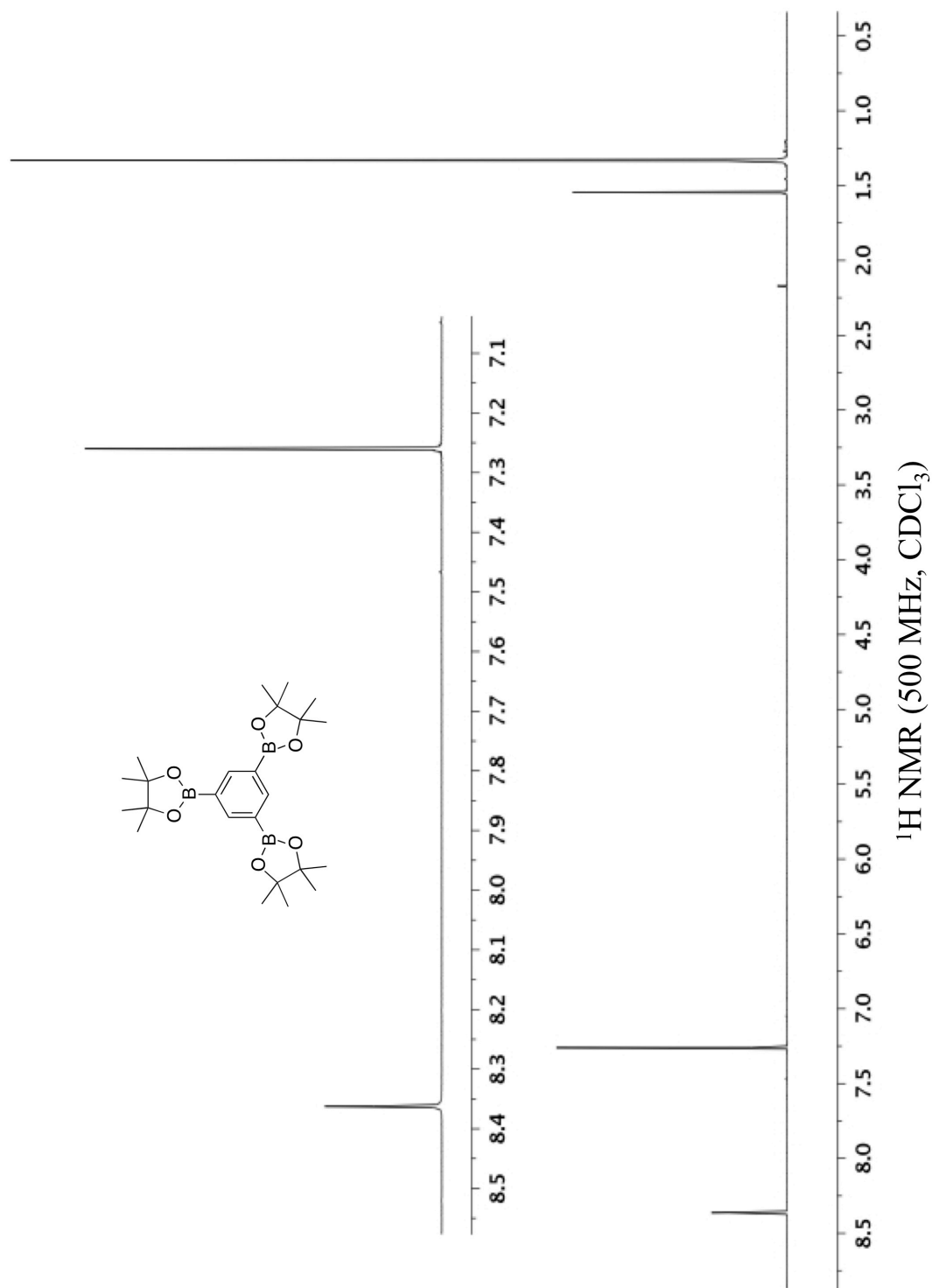
6. 1,3,5-*Tris*(Bpin)benzene (6) from 1,4-*bis*(Bpin)benzene (5) (Figure 2)

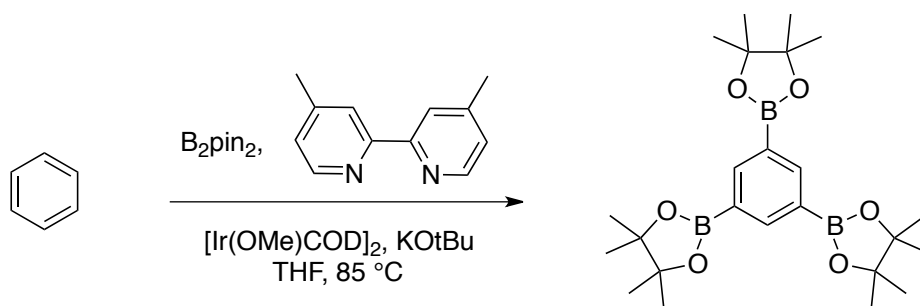
A 15 mL flame-dried 15 mL glass pressure vessel equipped with a Teflon-coated magnetic stirring bar and a silicon rubber septum was flushed with nitrogen and charged with $[\text{Ir}(\text{OMe})\text{COD}]_2$ (53 mg, 0.08 mmol), 4,4'-dimethyl-2,2'-bipyridyl (30 mg, 0.16 mmol), B_2pin_2 (335 mg, 1.32 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. A sample of 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 drop wise addition of 10% aqueous HCl (~2 mL).²⁴ 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 analysis of the crude product mixture was taken and showed predominantly the 1,3,5-*tris*(Bpin)benzene. Upon addition of methanol (~15 mL) some of the product precipitated out. The material was collected by vacuum filtration and washed with methanol (~10 mL) to yield 20 mg of pure 1,3,5-*tris*(Bpin)benzene (11%).²⁵ ^1H NMR (500 MHz, CDCl_3) δ 8.36 (s, 3H, Ar-H), 1.33 (s, 18H, CH_3), matched the literature values.²⁶

²⁴ **Caution: Gas evolves!**

²⁵ No attempt was made to isolate the remaining product or to optimize the yield.

²⁶ Liu, Y.; Niu, F.; Lian, J.; Zeng, P.; Niu, H. *Synth. Met.* **2010**, *160*, 2055-2060.



7. 1,3,5-*Tris*(Bpin)benzene (**6**) from benzene

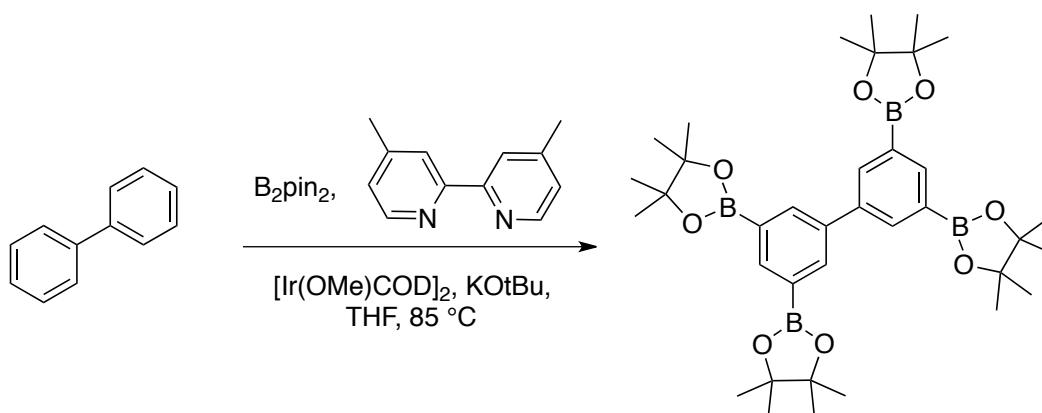
A flame-dried 15 mL glass pressure vessel equipped with a Teflon-coated magnetic stirring bar and a silicon rubber septum was flushed with nitrogen and charged with $[Ir(OMe)COD]_2$ (53 mg, 0.08 mmol), 4,4'-dimethyl-2,2'-bipyridyl (30 mg, 0.16 mmol), B_2pin_2 (406 mg, 1.60 mmol), and potassium *t*-butoxide (5 mg, 0.04 mmol). THF (0.3 mL)²⁷ was added by syringe, and the mixture was heated at 50 °C for 10 min. Benzene (35 μ L, 0.40 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 drop wise addition of 10% aqueous HCl (~2 mL).²⁸ 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 reduced pressure overnight. Upon addition of methanol (~15 mL) a solid precipitated. The material was collected by vacuum filtration and washed with methanol (~10 mL) to give 73 mg of 1,3,5-*tris*(Bpin)benzene as a light-beige precipitate (40%). More 1,3,5-*tris*(Bpin)benzene remained in the filtrate but was not isolated. 1H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 3H, Ar-H), 1.33 (s, 18H, CH_3), matched the literature values.²⁹

²⁷ Concentration is crucial; the benzene concentration should be no less than 0.8 M.

²⁸ **Caution: Gas evolves!**

²⁹ Liu, Y.; Niu, F.; Lian, J.; Zeng, P.; Niu, H. *Synth. Met.* **2010**, *160*, 2055-2060.

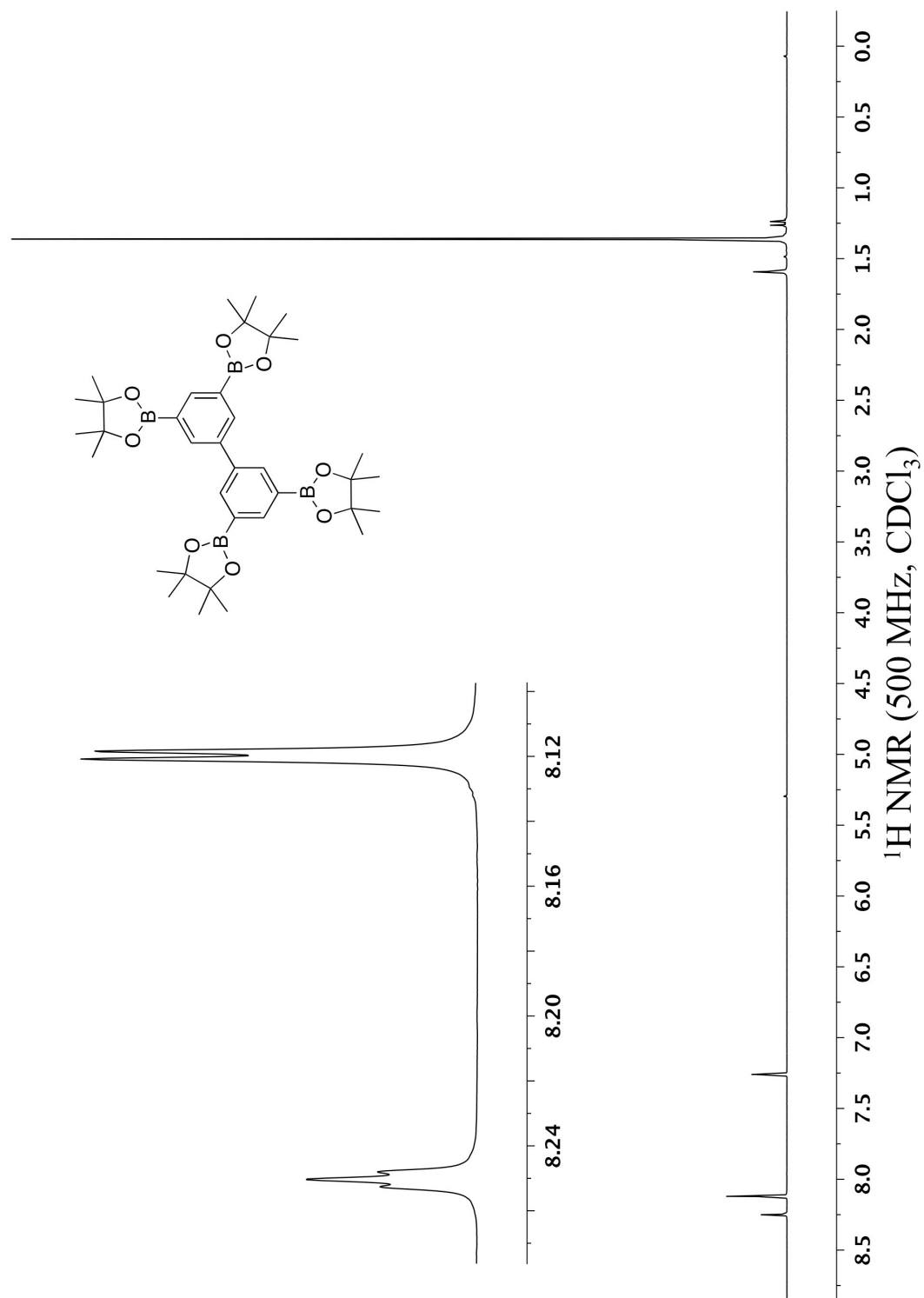
8. 3,5,3',5'-Tetrakis(Bpin)biphenyl from biphenyl

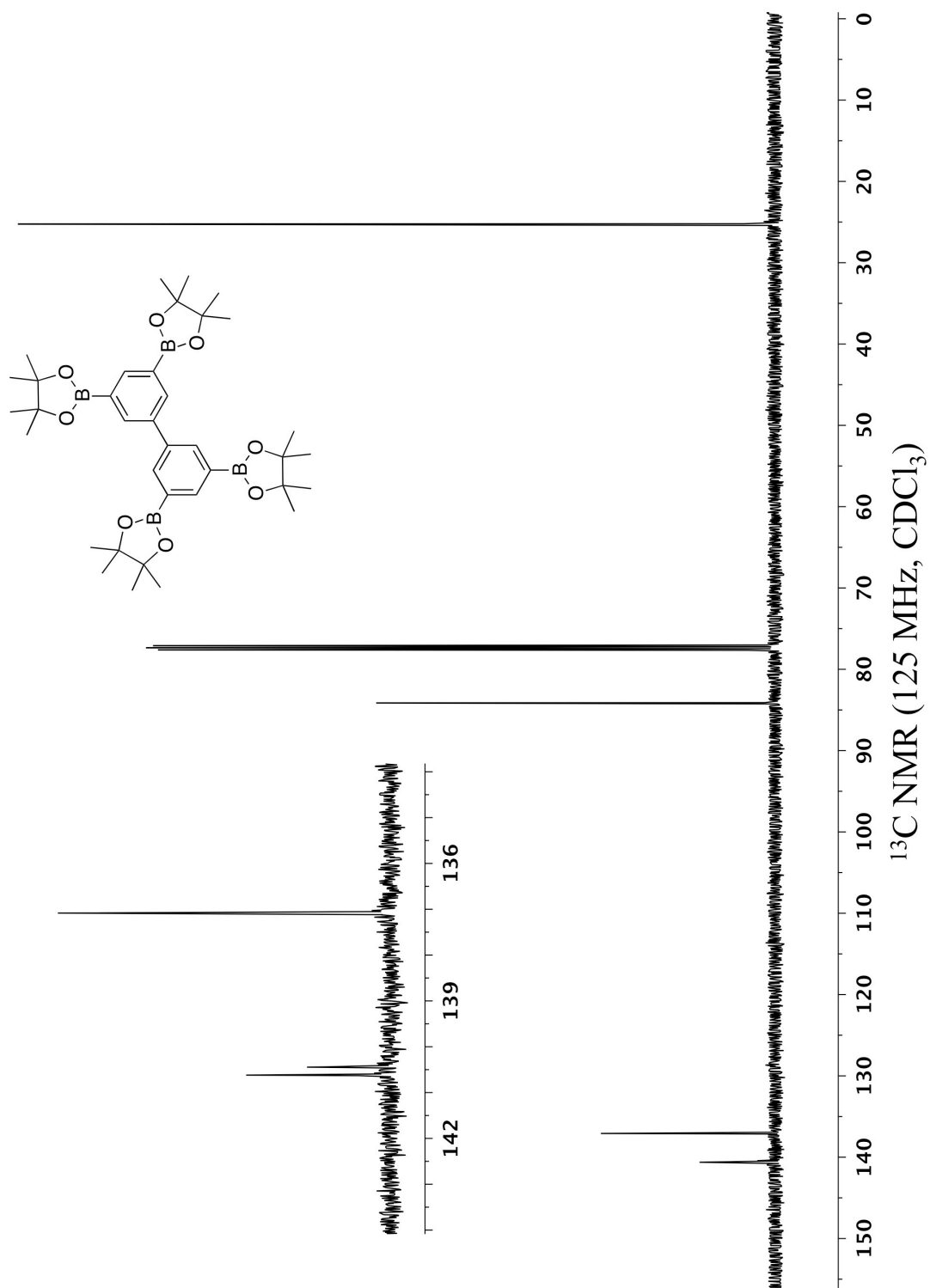


A flame-dried 15 mL glass pressure vessel equipped with a Teflon-coated magnetic stirring bar and a silicon rubber septum was purged with nitrogen. The vessel was then charged with $[Ir(OMe)COD]_2$ (53 mg, 0.08 mmol), 4,4'-dimethyl-2,2'-bipyridyl (30 mg, 0.16 mmol), B_2pin_2 (609 mg, 2.40 mmol), and potassium *t*-butoxide (5 mg, 0.04 mmol). THF (0.4 mL)³⁰ was added by syringe, and the mixture was heated at 50 °C for 10 min. Biphenyl (62 mg, 0.40 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, opened to the air, and diluted with dichloromethane (~2 mL). The reaction was quenched by the drop wise addition of 10% aqueous HCl (~2 mL).³¹ 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, and the mixture was left under reduced pressure overnight. Upon addition of methanol (~15 mL) a solid precipitated. The material was collected by vacuum filtration and washed with methanol (~10 mL) to give 230 mg of 3,5,3',5'-tetrakis(Bpin)biphenyl as a light-beige precipitate (87%): mp 352-354 °C; 1H NMR (500 MHz, $CDCl_3$) δ 8.25 (t, J = 1.0 Hz, 2H), 8.12 (d, J = 1.0 Hz, 4H) 1.36 (s, 48H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.62, 140.44, 137.08, 84.14, 25.25; HRMS DART (m/z) $[M]^+$: calcd for $C_{36}H_{54}B_4O_8$: 658.4191, found 658.4166.

³⁰ Concentration is crucial; the biphenyl concentration should be no less than 0.8 M.

³¹ **Caution: Gas evolves!**





9. Comparison of biphenyl borylation under normal conditions and new conditions.

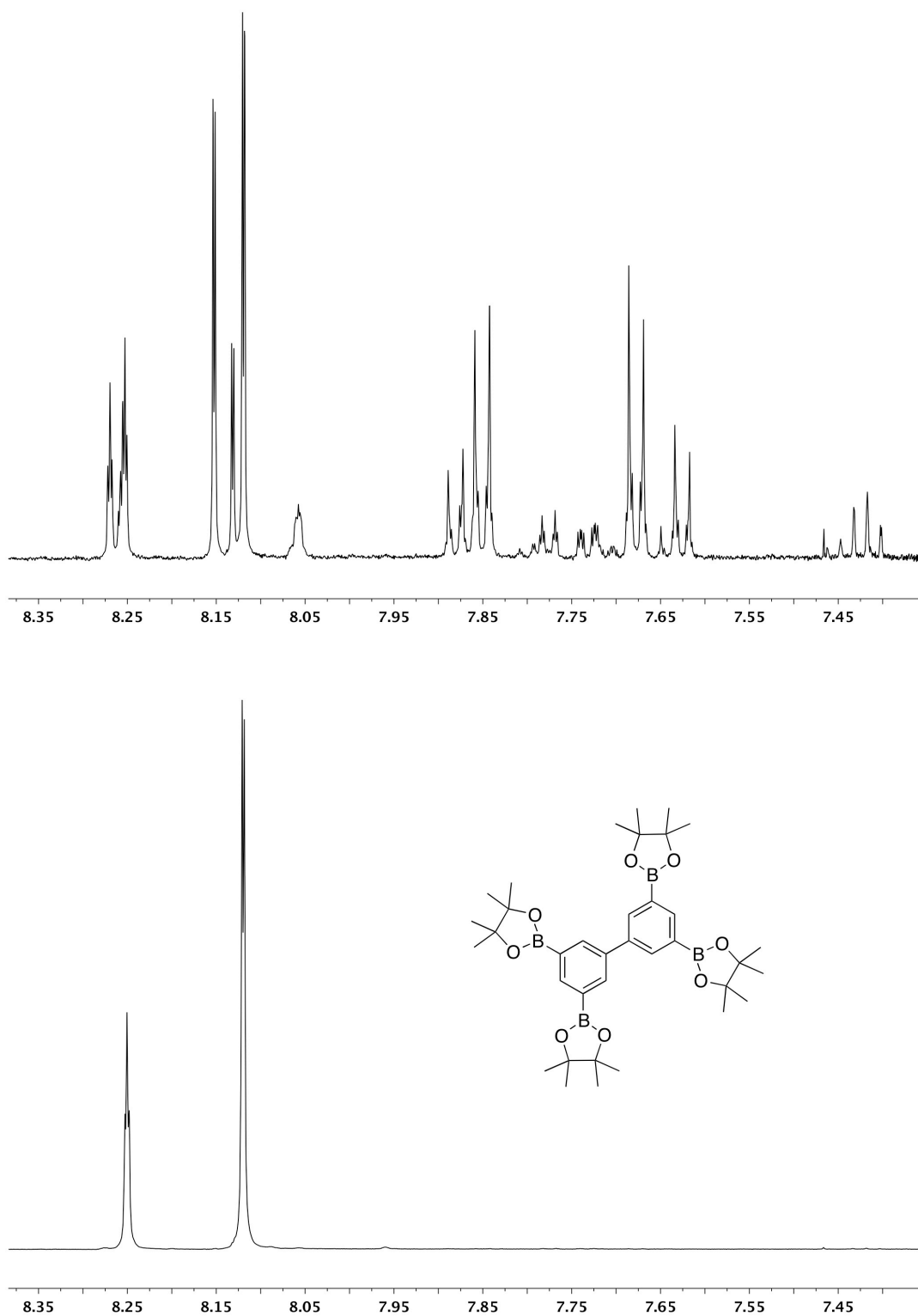


Figure S1. ^1H NMR (500 MHz, CDCl_3) of unchromatographed product from borylation of biphenyl under normal conditions (top) and new conditions (bottom).

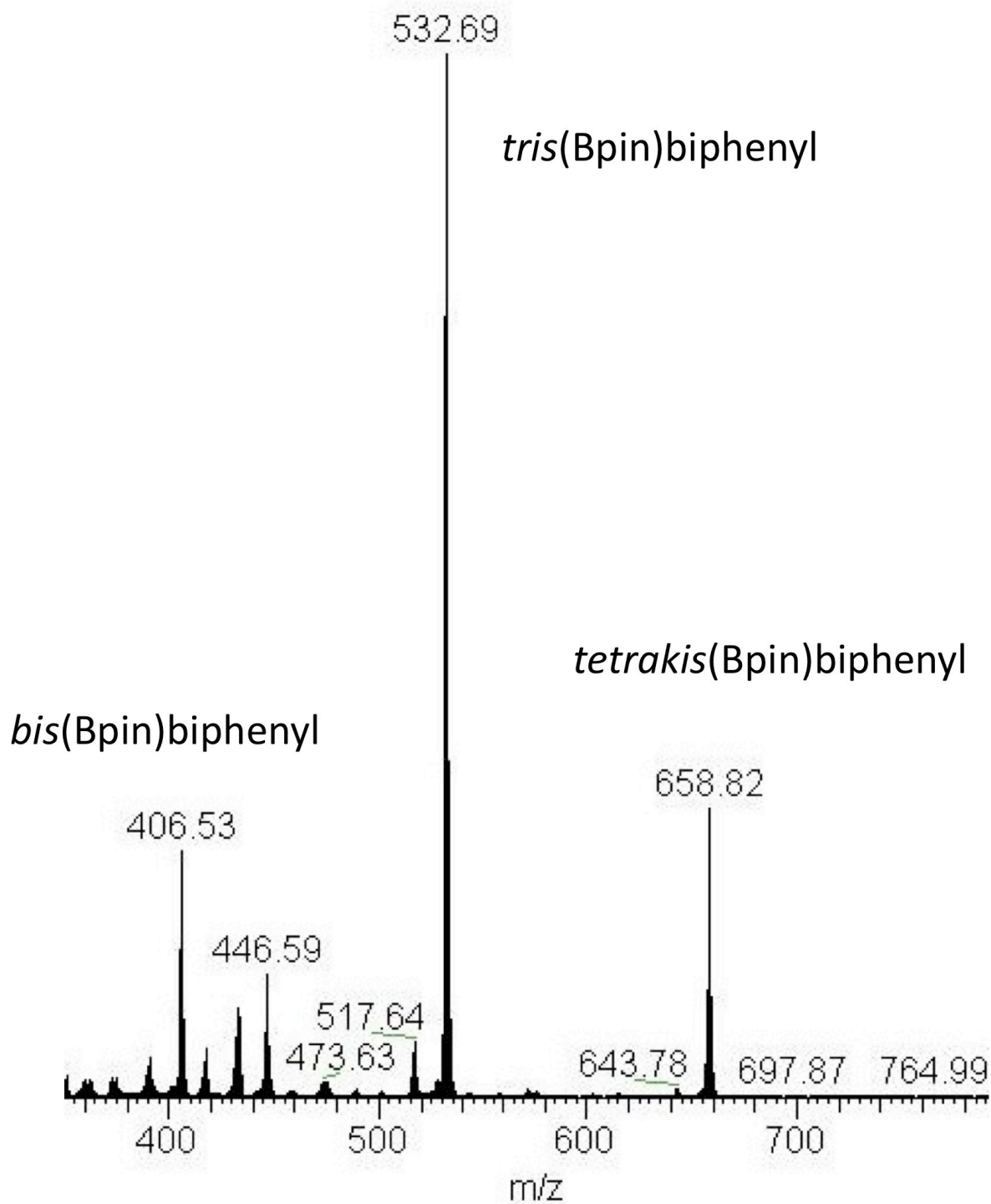
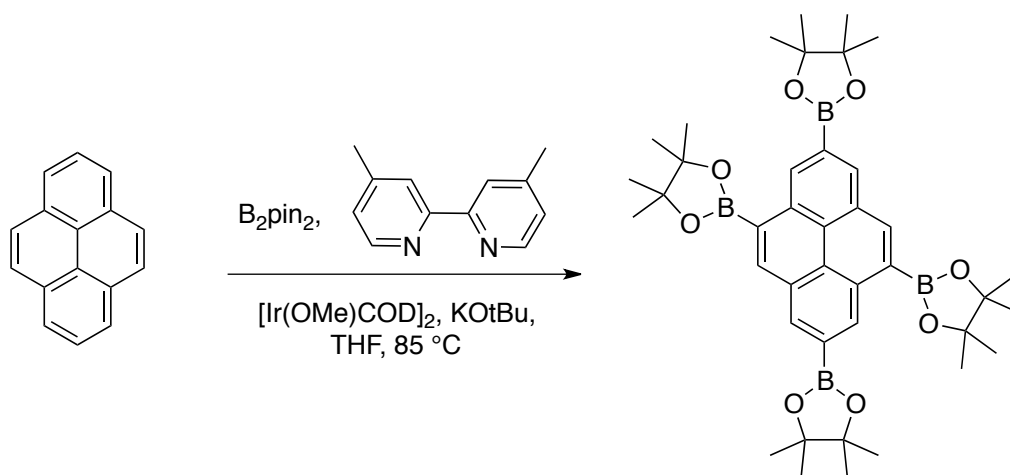


Figure S2. EI (70 eV) mass spectrum of unchromatographed product from borylation of biphenyl under normal conditions.

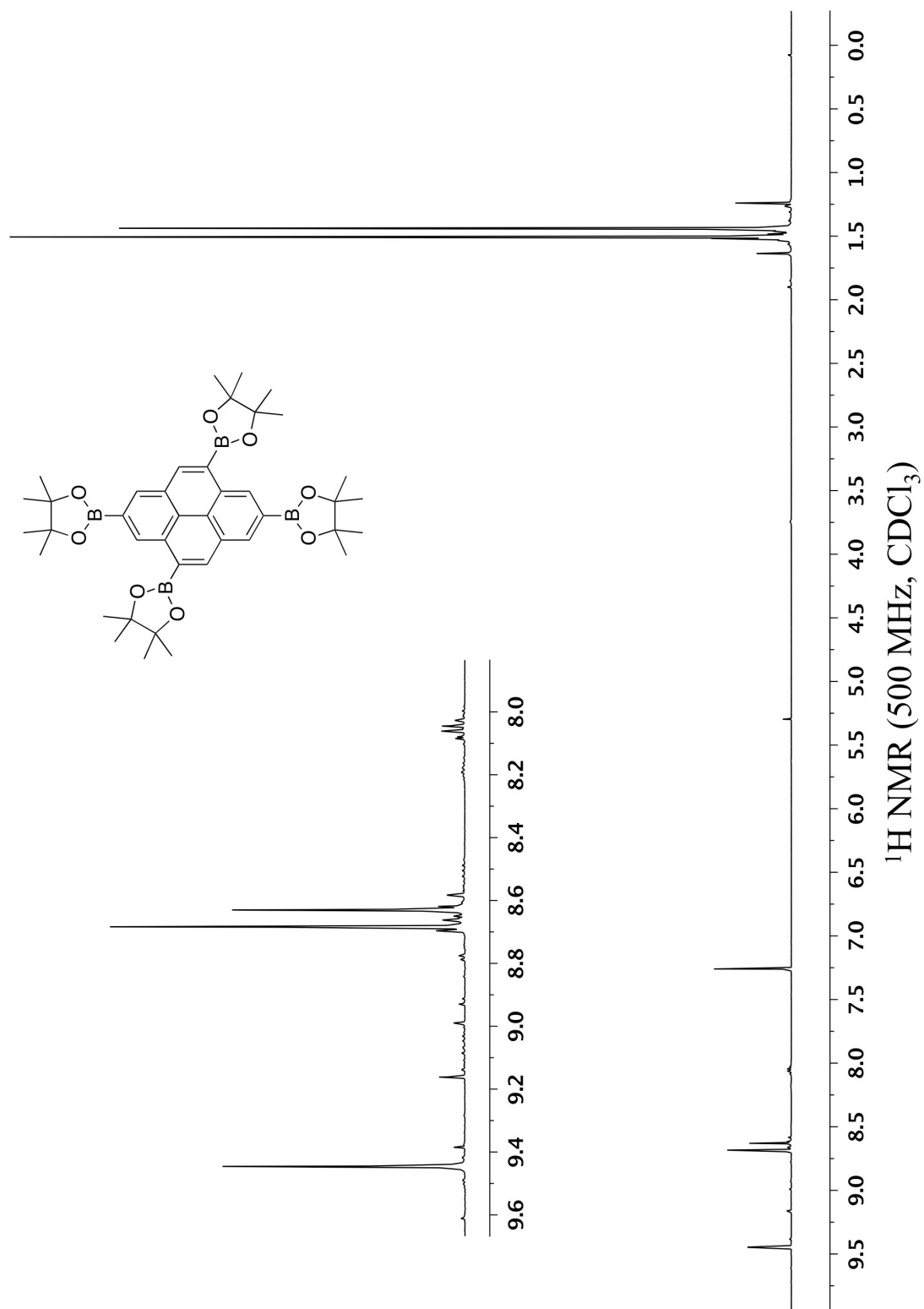
10. 2,4,7,9-Tetrakis(Bpin)pyrene (8) from pyrene.

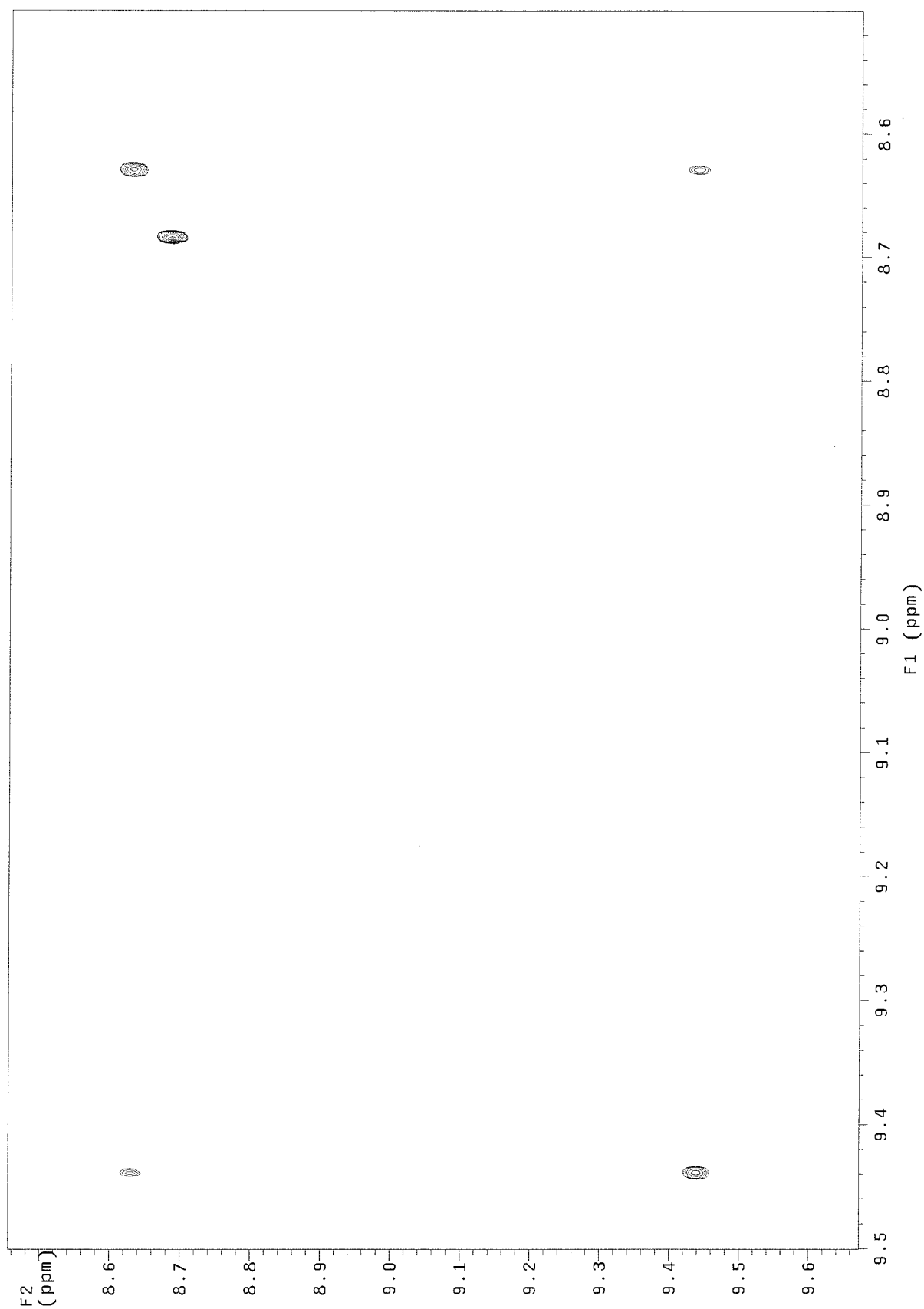


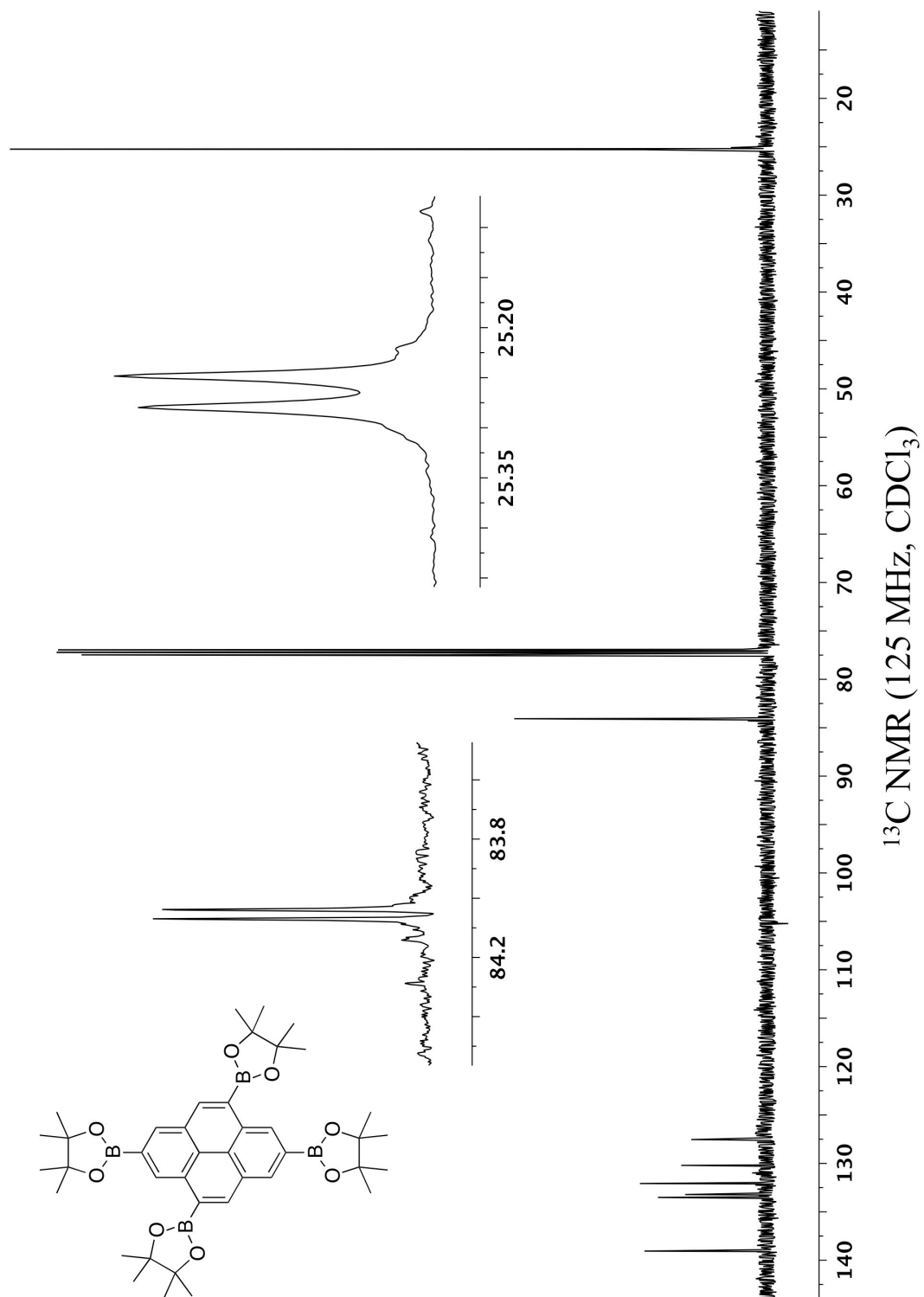
A flame-dried 15 mL glass pressure vessel equipped with a Teflon-coated magnetic stirring bar and a silicon rubber septum was flushed with nitrogen and charged with $[Ir(OMe)COD]_2$ (53 mg, 0.08 mmol), 4,4'-dimethyl-2,2'-bipyridyl (30 mg, 0.16 mmol), B_2pin_2 (609 mg, 2.40 mmol), and potassium *t*-butoxide (5 mg, 0.04 mmol). THF (0.4 mL)³² was added by syringe, and the mixture was heated at $50\text{ }^\circ\text{C}$ for 10 min. Pyrene (81 mg, 0.40 mmol) was added, the rubber septum was replaced with a pressure vessel cap, and the reaction mixture was heated at $85\text{ }^\circ\text{C}$ in an oil bath for 4 days. The mixture was removed from the oil bath, cooled, opened to the air, and diluted with dichloromethane (~2 mL). The reaction was quenched by the drop wise addition of 10% aqueous HCl (~2 mL).³³ 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, and the mixture was left under reduced pressure overnight. Upon addition of methanol (~15 mL) a solid precipitated. The material was collected by vacuum filtration and washed with methanol (~10 mL) to give 168 mg (59%) of 2,4,7,9-tetrakis(Bpin)pyrene as a white precipitate, contaminated with minor amounts of *tris*(Bpin)pyrenes. The spin-spin splitting of the signals for H(1) and H(3) ($J = 1.0\text{ Hz}$, validated by COSY) confirms the assignment of this compound as the 2,4,7,9-isomer, because none of the signals in the 2,4,7,10-isomer should show any spin-spin splitting. In the ^{13}C NMR spectrum, as usual, no signals are seen for the carbon atoms bearing Bpin substituents; the observation of only six strong signals in the region for “aromatic” carbon atoms and signals for only two Bpin groups further supports the assignment of the product as 2,4,7,9-tetrakis(Bpin)pyrene and not the 2,4,7,10-isomer or a mixture of isomers: ^1H NMR (500 MHz, CDCl_3) δ (9.45 (d, $J = 1.0\text{ Hz}$, 2H), 8.68 (s, 2H) 8.63 (d, $J = 1.0\text{ Hz}$, 2H), 1.51 (s, 24H), 1.44 (s, 24H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.86, 133.52, 133.23, 132.09, 130.21, 127.55, 84.08, 84.04, 25.28, 25.25; HRMS DART (m/z) $[M+H]^+$ calcd for $\text{C}_{40}\text{H}_{55}\text{B}_4\text{O}_8$: 707.4269, found 707.4259.

³² Concentration is crucial; the pyrene concentration should be no less than 0.8 M.

³³ **Caution: Gas evolves!**







11. Comparison of pyrene borylation under normal conditions and new conditions.

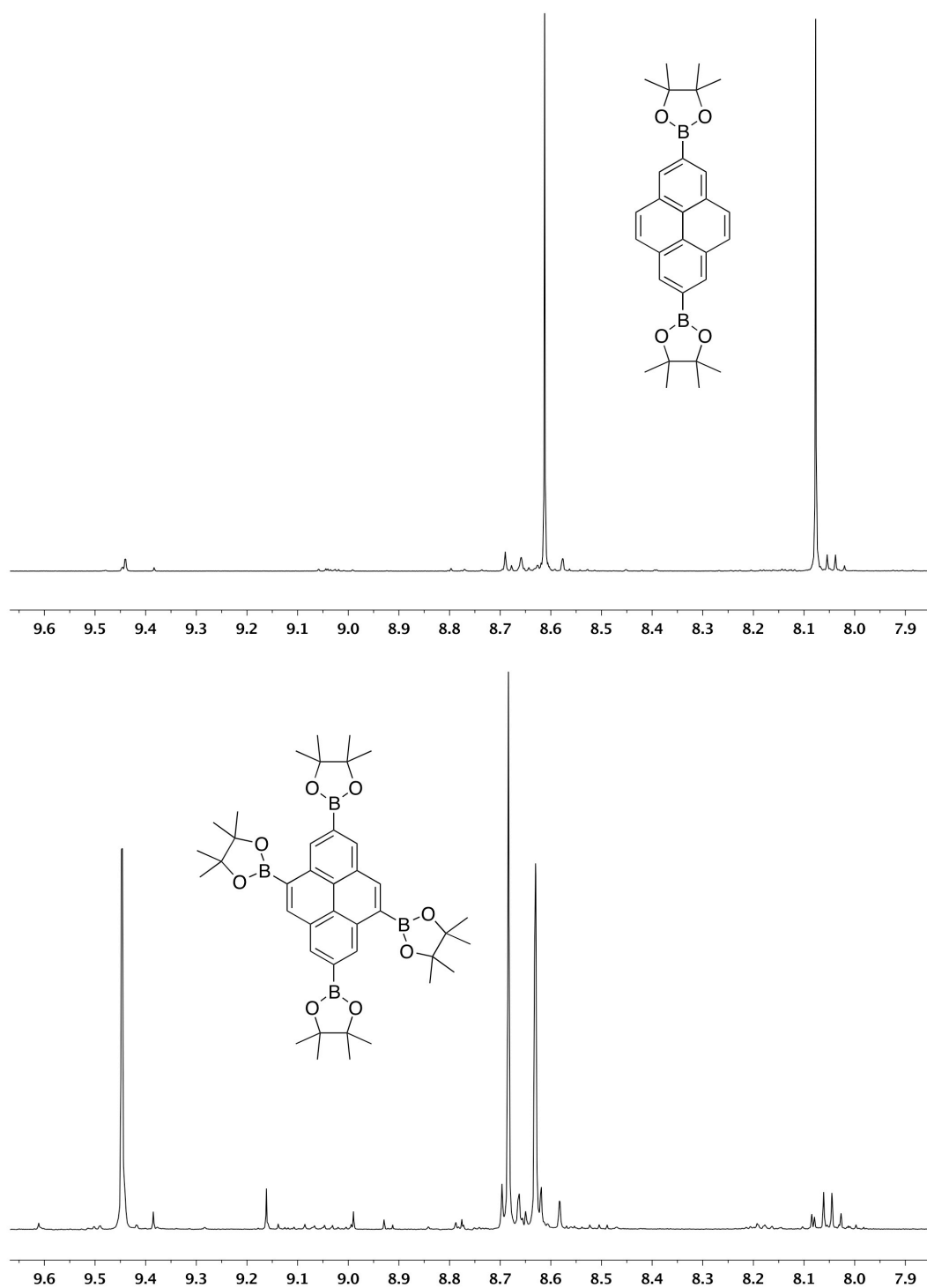
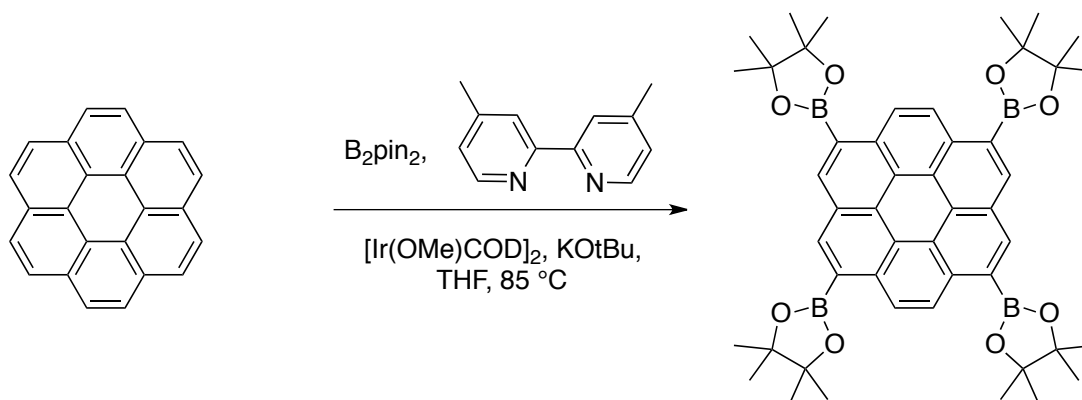


Figure S3. ^1H NMR (500 MHz, CDCl_3) of unchromatographed product from borylation of pyrene under normal conditions (modified to include 4.4 equiv B_2pin_2 for 2 days) (top) and new conditions (bottom).

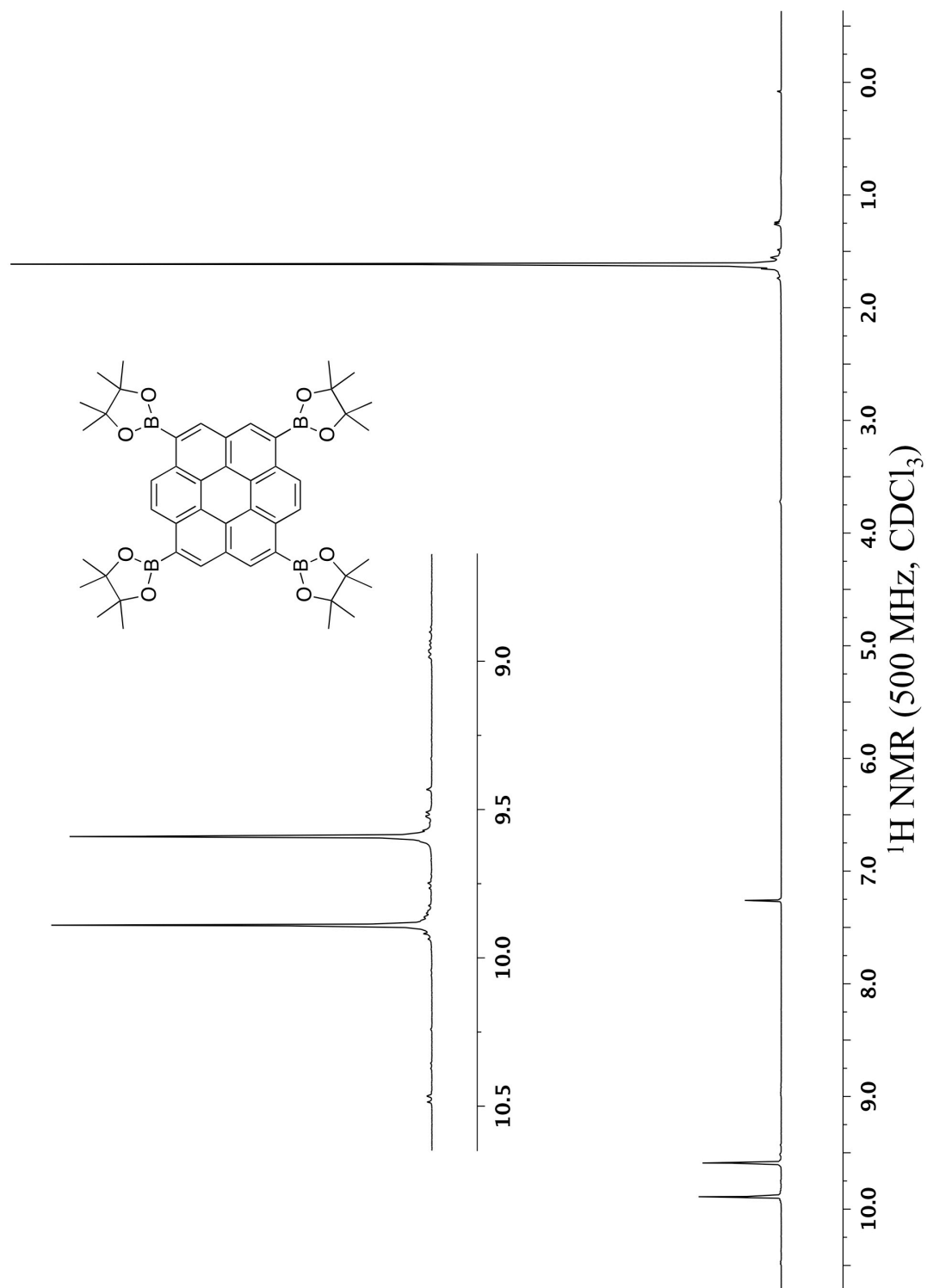
12. 1,4,7,10-Tetrakis(Bpin)coronene (**12**) from coronene.

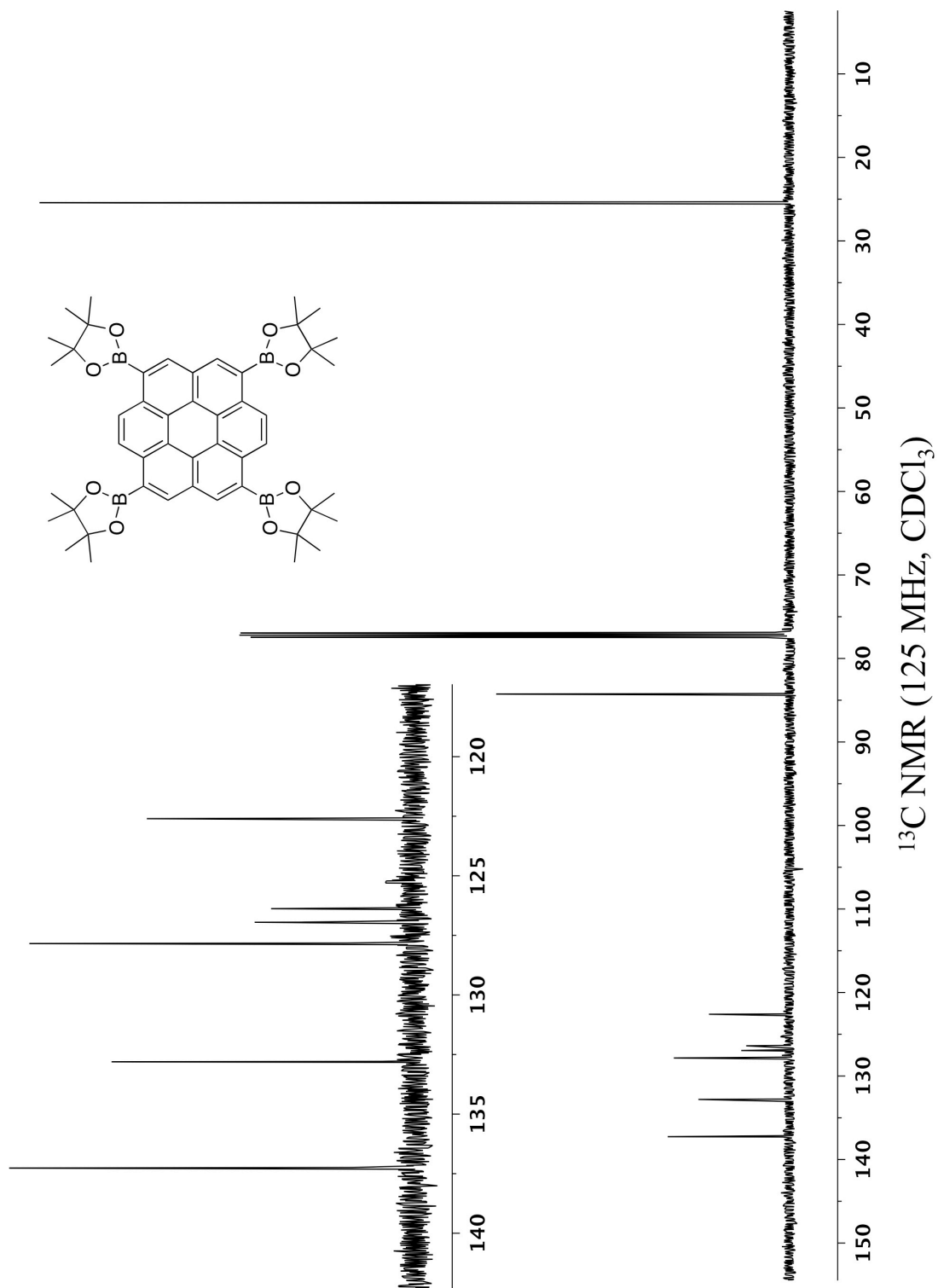
A flame-dried 15 mL glass pressure vessel equipped with a Teflon-coated magnetic stirring bar and a silicon rubber septum was flushed with nitrogen and charged with $[\text{Ir}(\text{OMe})\text{COD}]_2$ (53 mg, 0.08 mmol), 4,4'-dimethyl-2,2'-bipyridyl (30 mg, 0.16 mmol), B_2pin_2 (711 mg, 2.8 mmol), and potassium *t*-butoxide (5 mg, 0.04 mmol). THF (0.4 mL)³⁴ was added by syringe, and the mixture was heated at 50 °C for 10 min. Coronene (120 mg, 0.40 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 5 days. The mixture was removed from the oil bath, cooled, opened to the air, and diluted with dichloromethane (~2 mL). The reaction was quenched by the drop wise addition of 10% aqueous HCl (~2 mL).³⁵ 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. Upon addition of methanol (~15 mL) a solid precipitated. The material was collected by vacuum filtration and washed with methanol (~10 mL) to give 32 mg (10%) of pure 1,4,7,10-tetrakis(Bpin)coronene as a yellow precipitate, mp > 400 °C. The filtrate was adsorbed onto silica gel and subjected to medium pressure gradient chromatography. An additional 95 mg of product, still contaminated with pentakis(Bpin)coronene (~1:1), was isolated by elution with hexanes:ethyl acetate 95:5 to 90:10: ^1H NMR (500 MHz, CDCl_3) δ 9.89 (s, 4H), 9.59 (s, 4H), 1.61 (s, 48H); ^{13}C NMR (125 MHz, CDCl_3) δ 137.30, 132.84, 127.88, 126.98, 126.41, 122.63, 84.29, 25.44; HRMS DART (m/z) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{48}\text{H}_{57}\text{B}_4\text{O}_8$: 805.4426, found 805.4447.

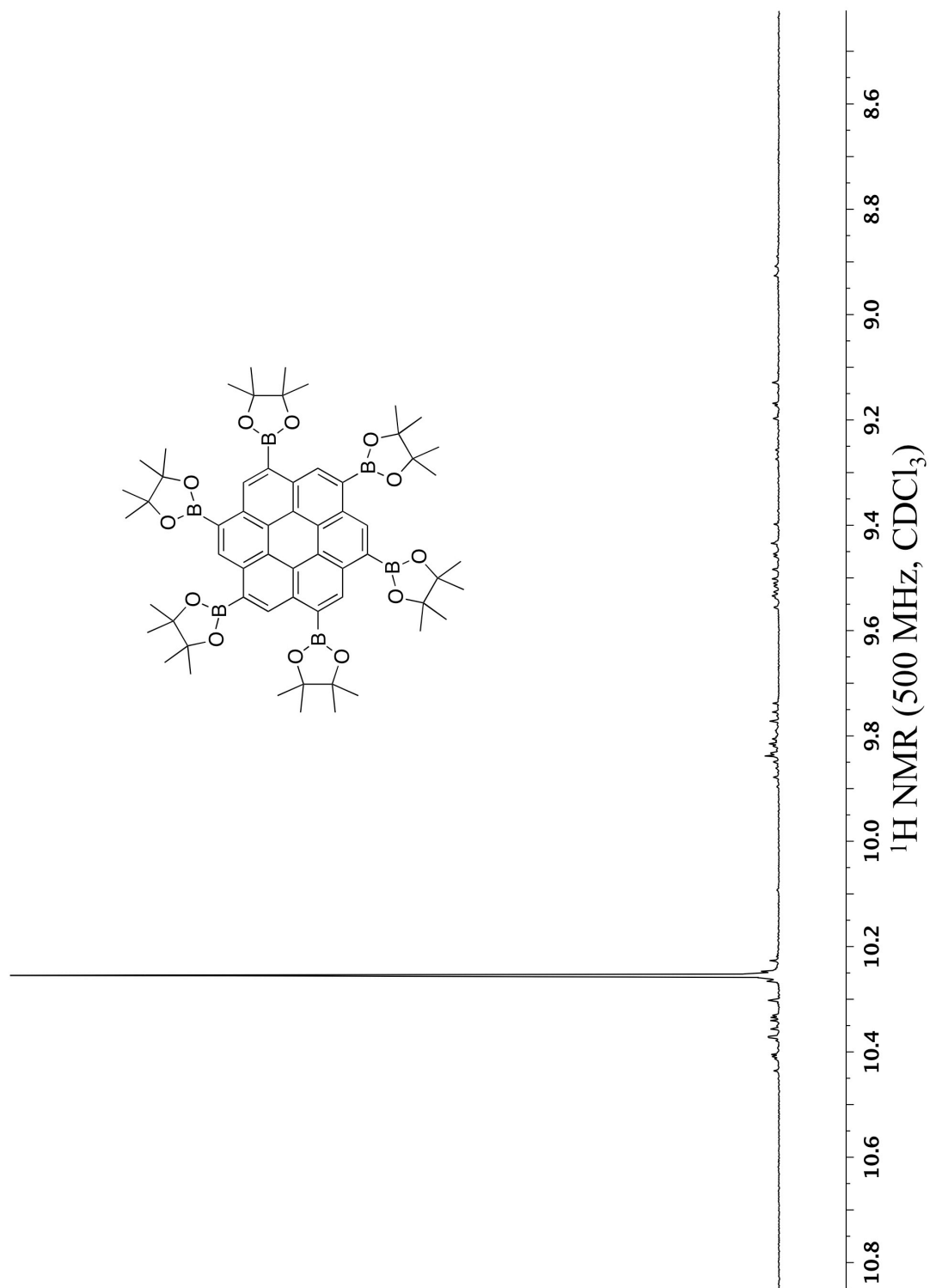
Rechromatographing the later fractions using 90:10 hexanes:ethyl acetate gave a fraction enriched in the symmetrical 1,3,5,7,9,11-hexakis(Bpin)coronene (**13**). Removal of the solvent and trituration with methanol gave a small sample of material that was sufficiently pure for characterization: ^1H NMR (500 MHz, CDCl_3) δ 10.26 (s, 6H), 1.64 (s, 72H); ^{13}C NMR (125 MHz, CDCl_3) δ 136.90, 131.48, 124.26, 84.14, 25.41; HRMS DART (m/z) $[\text{M}-\text{H}]^+$: calcd for $\text{C}_{60}\text{H}_{77}\text{B}_6\text{O}_{12}$: 1055.5973, found 1055.5940.

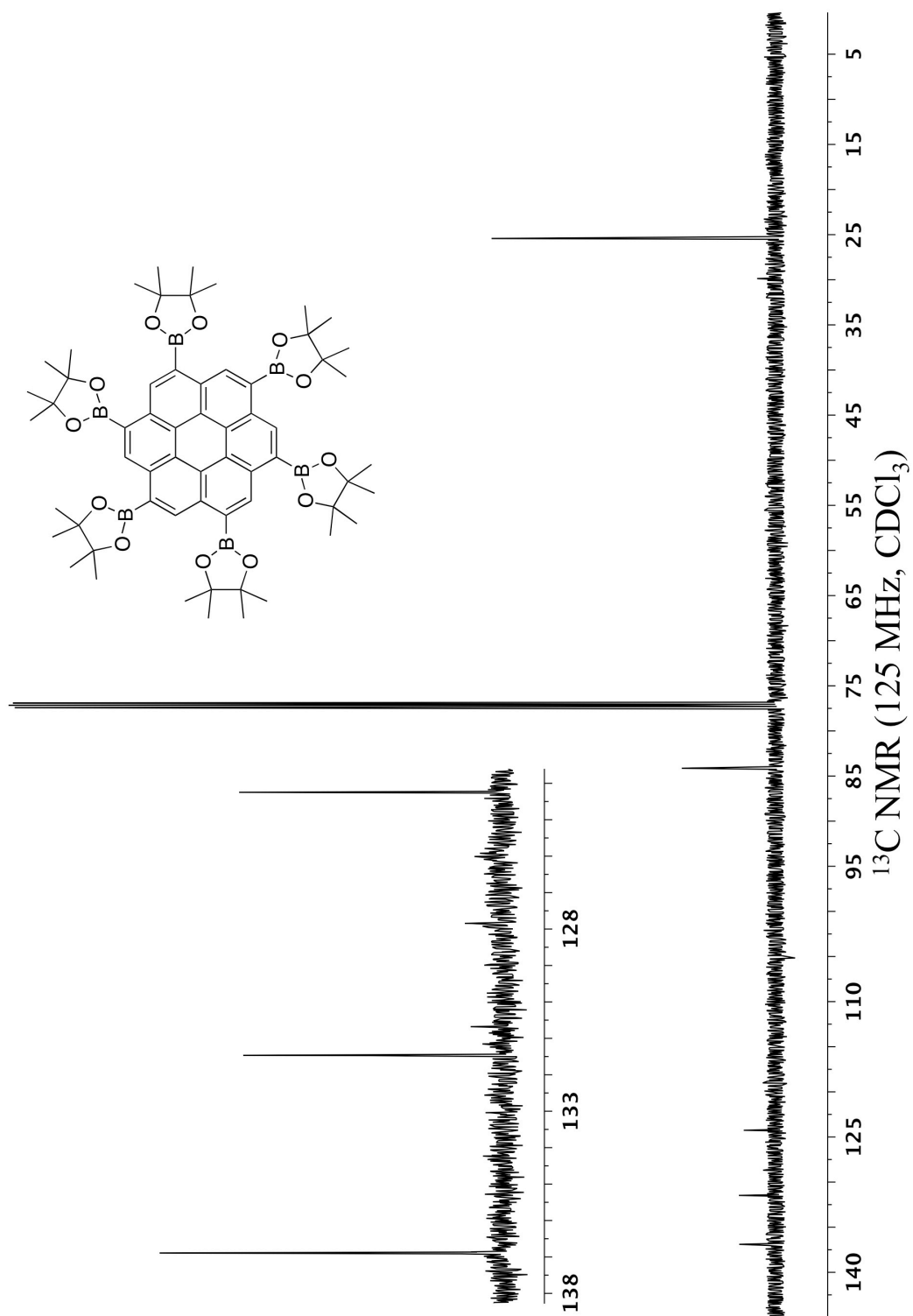
³⁴ Concentration is crucial; the coronene concentration should be no less than 0.8 M.

³⁵ **Caution: Gas evolves!**









13. Comparison of coronene borylation under normal conditions and new conditions.

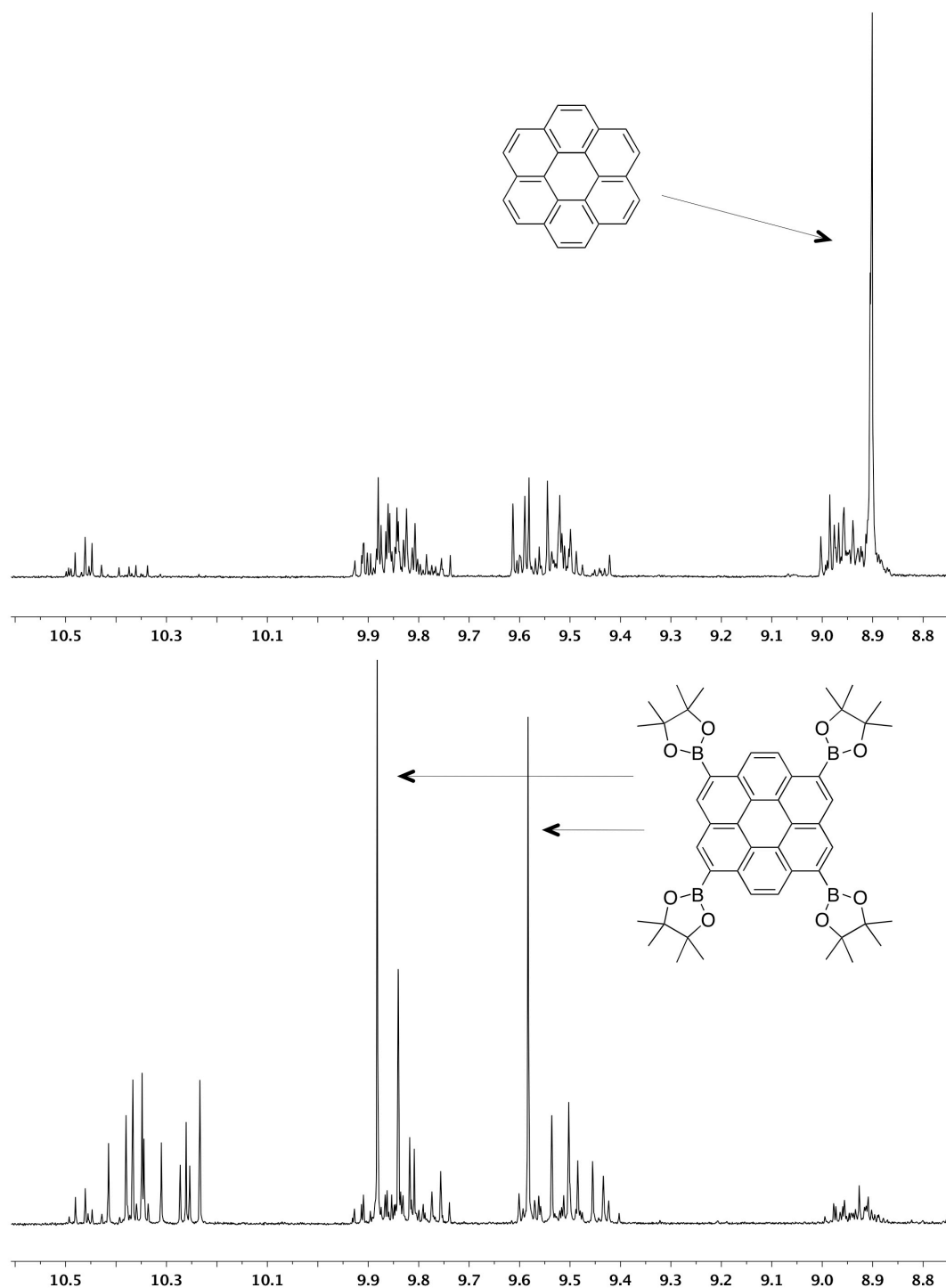
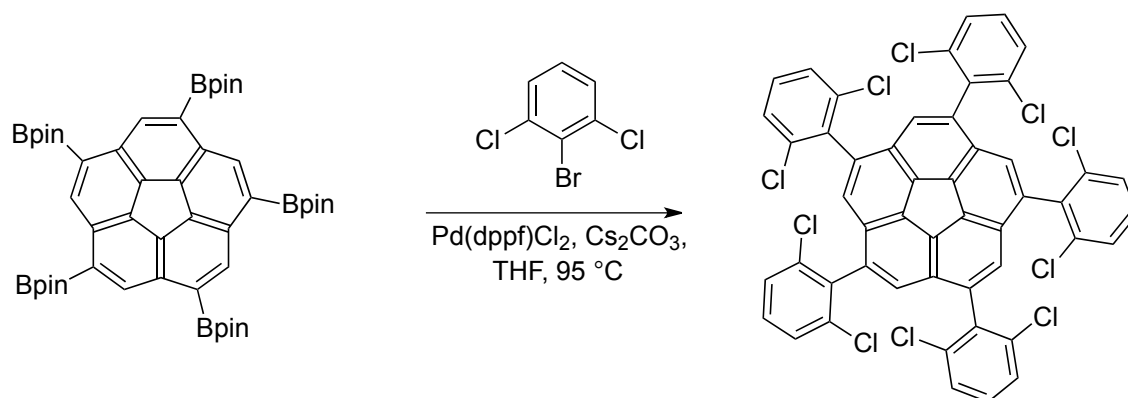


Figure S4. ^1H NMR (500 MHz, CDCl_3) of unchromatographed product from borylation of coronene under normal conditions (modified to include 6.6 equiv B_2pin_2 for 18 h) (top) and new conditions (bottom).

14. 1,3,5,7,9-Pentakis(2,6-dichlorophenyl)corannulene (**14**) from **1**

To a flame-dried 75 mL pressure vessel³⁶ 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) (45 mg, 0.062 mmol), THF (25 mL), 1,3,5,7,9-pentakis-(pinacolboryl)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 95 °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 under reduced pressure at 175 °C (Kugelrohr oven) over a period of 2h. Further purification by silica gel chromatography using 1:4 dichloromethane:cyclohexane as the eluent gave 140-190 mg (50-70% average yield from multiple experiments) of 1,3,5,7,9-Pentakis(2,6-dichlorophenyl)corannulene (**14**) as a light yellow product. The spectral properties of this compound are consistent with those previously reported.³⁷

³⁶ The size of the vessel is important.

³⁷ Scott, L. T.; Jackson, E. A.; Zhang, Q.; Steinberg, B. D.; Bancu, M.; Li, B. *J. Am. Chem. Soc.* **2012**, *134*, 107-110.

15. XYZ coordinates and energies from B3LYP/6-31G* calculations on the isomeric tetrakis(Bpin)pyrenes 8, 10, and 11.

2,4,7,9-tetrakis(Bpin)pyrene (8)

Standard Nuclear Orientation (Angstroms)				
I	Atom	X	Y	Z

1	C	-0.661568	-0.267765	0.015583
2	C	-3.259386	-1.395260	-0.002109
3	C	-0.835030	-1.685268	0.009886
4	C	-1.806891	0.592590	0.016589
5	C	-3.079462	-0.001911	0.009217
6	C	-2.129282	-2.221983	-0.001316
7	H	-3.954206	0.637331	0.012926
8	H	-2.251704	-3.302723	-0.011290
9	C	0.661568	0.267765	0.015583
10	C	3.259386	1.395260	-0.002109
11	C	0.835030	1.685268	0.009886
12	C	1.806891	-0.592590	0.016589
13	C	3.079462	0.001911	0.009217
14	C	2.129282	2.221983	-0.001316
15	H	3.954206	-0.637331	0.012926
16	H	2.251704	3.302723	-0.011290
17	C	1.610734	-2.036714	0.018219
18	C	0.327263	-2.522996	0.012452
19	H	0.168883	-3.598787	0.009791
20	C	-1.610734	2.036714	0.018219
21	C	-0.327263	2.522996	0.012452
22	H	-0.168883	3.598787	0.009791
23	B	4.688356	2.003384	-0.019181
24	B	-4.688356	-2.003384	-0.019181
25	B	2.755946	-3.093994	0.023616
26	O	4.936962	3.356659	0.012372
27	O	5.837800	1.249101	-0.071047
28	O	4.099141	-2.839600	0.188449
29	O	2.495712	-4.438882	-0.133946
30	O	-4.936962	-3.356659	0.012372
31	O	-5.837800	-1.249101	-0.071047
32	C	6.355994	3.547993	-0.243191
33	C	6.961428	2.143790	0.154165
34	C	4.828214	-4.069997	-0.076251
35	C	3.717982	-5.169979	0.150595
36	C	-6.355994	-3.547993	-0.243191
37	C	-6.961428	-2.143790	0.154165
38	C	6.496646	3.867952	-1.737548
39	H	7.535978	4.080679	-2.009170
40	H	5.891584	4.749729	-1.970445

41	H	6.136217	3.040732	-2.356930
42	C	6.843749	4.728492	0.594095
43	H	6.620285	4.590060	1.654269
44	H	6.345394	5.645049	0.262115
45	H	7.924744	4.869413	0.479143
46	C	7.321729	2.032362	1.642197
47	H	6.493032	2.358966	2.278088
48	H	8.207242	2.626686	1.892269
49	H	7.533162	0.984622	1.877213
50	C	8.132703	1.671741	-0.705626
51	H	8.451731	0.677673	-0.375493
52	H	8.988520	2.349932	-0.610481
53	H	7.857100	1.603031	-1.760214
54	C	5.317919	-3.987705	-1.528348
55	H	5.919731	-4.860722	-1.802401
56	H	5.935778	-3.091796	-1.644363
57	H	4.478682	-3.911049	-2.226829
58	C	6.019365	-4.132935	0.876975
59	H	5.705645	-4.067157	1.921012
60	H	6.689829	-3.291895	0.673227
61	H	6.586739	-5.060678	0.738714
62	C	3.787458	-6.370586	-0.790516
63	H	2.944731	-7.039359	-0.587872
64	H	4.713312	-6.937806	-0.639589
65	H	3.730446	-6.066151	-1.837882
66	C	3.621574	-5.645266	1.606955
67	H	3.546070	-4.798623	2.296730
68	H	4.487299	-6.251493	1.894210
69	H	2.720150	-6.255313	1.722306
70	C	-8.132703	-1.671741	-0.705626
71	H	-8.451731	-0.677673	-0.375493
72	H	-8.988520	-2.349932	-0.610481
73	H	-7.857100	-1.603031	-1.760214
74	C	-7.321729	-2.032362	1.642197
75	H	-6.493032	-2.358966	2.278088
76	H	-8.207242	-2.626686	1.892269
77	H	-7.533162	-0.984622	1.877213
78	C	-6.843749	-4.728492	0.594095
79	H	-6.620285	-4.590060	1.654269
80	H	-6.345394	-5.645049	0.262115
81	H	-7.924744	-4.869413	0.479143
82	C	-6.496646	-3.867952	-1.737548
83	H	-7.535978	-4.080679	-2.009170
84	H	-5.891584	-4.749729	-1.970445
85	H	-6.136217	-3.040732	-2.356930
86	B	-2.755946	3.093994	0.023616
87	O	-2.495712	4.438882	-0.133946
88	O	-4.099141	2.839600	0.188449

89	C	-3.717982	5.169979	0.150595
90	C	-4.828214	4.069997	-0.076251
91	C	-3.787458	6.370586	-0.790516
92	H	-2.944731	7.039359	-0.587872
93	H	-4.713312	6.937806	-0.639589
94	H	-3.730446	6.066151	-1.837882
95	C	-3.621574	5.645266	1.606955
96	H	-3.546070	4.798623	2.296730
97	H	-4.487299	6.251493	1.894210
98	H	-2.720150	6.255313	1.722306
99	C	-6.019365	4.132935	0.876975
100	H	-5.705645	4.067157	1.921012
101	H	-6.689829	3.291895	0.673227
102	H	-6.586739	5.060678	0.738714
103	C	-5.317919	3.987705	-1.528348
104	H	-5.919731	4.860722	-1.802401
105	H	-5.935778	3.091796	-1.644363
106	H	-4.478682	3.911049	-2.226829

E = -2258.539128 hartree

2,4,7,10- tetrakis(Bpin)pyrene (10)

Standard Nuclear Orientation (Angstroms)				
I	Atom	X	Y	Z
1	C	-1.454043	-0.001486	0.016784
2	C	-4.296525	-0.005328	0.031761
3	C	-2.173053	-1.233442	0.027902
4	C	-2.176517	1.228403	0.020054
5	C	-3.578893	1.200650	0.021219
6	C	-3.575426	-1.209371	0.040476
7	H	-4.121373	2.143427	0.015217
8	H	-4.115353	-2.153554	0.053185
9	C	-0.027101	0.000759	0.005827
10	C	2.794680	0.004060	0.012076
11	C	0.682413	1.248195	0.010234
12	C	0.685278	-1.244736	-0.006273
13	C	2.087659	-1.206356	-0.008994
14	C	2.085039	1.213258	0.021966
15	H	2.639962	-2.138145	-0.026014
16	H	2.636066	2.145946	0.034712
17	C	-0.058971	-2.498961	0.000049
18	C	-1.430453	-2.457888	0.023751
19	H	-1.991355	-3.389214	0.037941

20	C	-1.437335	2.454697	0.022790
21	H	-2.001133	3.384361	0.030321
22	C	-0.065713	2.500108	0.014389
23	B	4.347228	0.004336	0.033283
24	B	-5.849404	-0.007787	0.027197
25	B	0.585978	-3.919321	-0.017528
26	O	5.106418	1.130110	0.261218
27	O	5.113758	-1.122101	-0.166734
28	O	1.897963	-4.215469	-0.306813
29	O	-0.157586	-5.049850	0.249755
30	O	-6.607810	-1.139284	0.217040
31	O	-6.609593	1.120725	-0.173086
32	C	6.491897	0.788978	-0.013562
33	C	6.488229	-0.781428	0.159423
34	C	2.119344	-5.623094	-0.013808
35	C	0.654992	-6.209993	-0.072892
36	C	-7.988599	-0.796289	-0.089118
37	C	-7.993854	0.771395	0.109329
38	C	6.778911	1.243535	-1.451480
39	H	7.828241	1.091385	-1.726454
40	H	6.552883	2.311316	-1.534656
41	H	6.149232	0.709291	-2.170047
42	C	7.381390	1.552823	0.965167
43	H	7.117629	1.339634	2.003406
44	H	7.262345	2.628952	0.802517
45	H	8.437621	1.302231	0.812233
46	C	6.721570	-1.236853	1.606653
47	H	6.064879	-0.704737	2.301866
48	H	7.759508	-1.083477	1.921180
49	H	6.494602	-2.305121	1.679906
50	C	7.413447	-1.545782	-0.785254
51	H	7.289073	-2.621912	-0.625817
52	H	8.463206	-1.294563	-0.593613
53	H	7.188128	-1.334005	-1.832760
54	C	3.091674	-6.180489	-1.051518
55	H	3.260348	-7.252111	-0.893920
56	H	4.054843	-5.668286	-0.960170
57	H	2.726906	-6.030278	-2.069886
58	C	2.752375	-5.683747	1.382894
59	H	2.079557	-5.279531	2.145533
60	H	3.662620	-5.076087	1.381011
61	H	3.022723	-6.707399	1.662459
62	C	0.237505	-6.667997	-1.477442
63	H	-0.835947	-6.881526	-1.476607
64	H	0.770311	-7.575637	-1.779966
65	H	0.425799	-5.888627	-2.222523
66	C	0.353425	-7.306485	0.947332
67	H	0.509278	-6.958312	1.970931

68	H	0.984208	-8.186576	0.776432
69	H	-0.692301	-7.616414	0.852854
70	C	-8.893103	1.548546	-0.849389
71	H	-8.777510	2.622222	-0.668182
72	H	-9.946887	1.290654	-0.692659
73	H	-8.636859	1.354896	-1.893234
74	C	-8.267999	1.203038	1.556282
75	H	-7.630281	0.660203	2.261047
76	H	-9.314094	1.042110	1.838059
77	H	-8.046097	2.270349	1.654092
78	C	-8.900951	-1.577586	0.853729
79	H	-8.665698	-1.379924	1.901643
80	H	-8.775199	-2.650790	0.677329
81	H	-9.953185	-1.326624	0.676341
82	C	-8.235162	-1.228789	-1.540929
83	H	-9.276906	-1.073384	-1.841294
84	H	-8.005767	-2.294885	-1.635295
85	H	-7.588133	-0.682009	-2.233971
86	B	0.570937	3.924168	-0.012249
87	O	1.907172	4.220367	-0.153499
88	O	-0.205469	5.059757	0.090546
89	C	2.031944	5.653673	-0.371386
90	C	0.683208	6.199825	0.236114
91	C	3.306407	6.134165	0.320457
92	H	3.311321	5.882715	1.383358
93	H	3.423001	7.219379	0.215337
94	H	4.174129	5.653584	-0.142792
95	C	0.771902	6.503934	1.737819
96	H	1.196993	5.660747	2.291296
97	H	-0.236133	6.685283	2.123545
98	H	1.381815	7.391987	1.934849
99	C	2.149431	5.854961	-1.888398
100	H	2.322810	6.905140	-2.146347
101	H	1.247981	5.513286	-2.406632
102	H	2.993884	5.265522	-2.258636
103	C	0.065093	7.386354	-0.502258
104	H	-0.889228	7.647944	-0.034065
105	H	-0.128191	7.152773	-1.551751
106	H	0.718533	8.265215	-0.452892

E = -2258.538277 hartree

1,3,6,8-tetrakis(Bpin)pyrene (11)

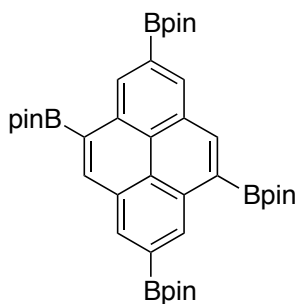
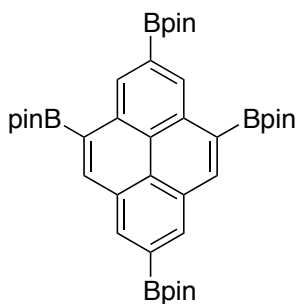
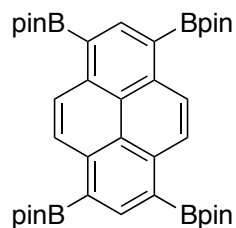
Standard Nuclear Orientation (Angstroms)				
I	Atom	X	Y	Z

1	C	0.718569	0.000000	0.000000
2	C	3.519001	0.000000	0.000000
3	C	1.438426	1.239097	0.002502
4	C	1.438426	-1.239097	-0.002502
5	C	2.860293	-1.236678	-0.004186
6	C	2.860293	1.236678	0.004186
7	H	4.604356	0.000000	0.000000
8	C	-0.718569	0.000000	0.000000
9	C	-3.519001	0.000000	0.000000
10	C	-1.438426	-1.239097	0.002502
11	C	-1.438426	1.239097	-0.002502
12	C	-2.860293	1.236678	-0.004186
13	C	-2.860293	-1.236678	0.004186
14	H	-4.604356	0.000000	0.000000
15	C	-0.680836	2.457545	-0.002108
16	H	-1.218341	3.398081	-0.004384
17	C	0.680836	2.457545	0.002108
18	H	1.218341	3.398081	0.004384
19	C	0.680836	-2.457545	-0.002108
20	H	1.218341	-3.398081	-0.004384
21	C	-0.680836	-2.457545	0.002108
22	H	-1.218341	-3.398081	0.004384
23	B	-3.775706	-2.497047	0.018350
24	B	-3.775706	2.497047	-0.018350
25	B	3.775706	2.497047	0.018350
26	B	3.775706	-2.497047	-0.018350
27	O	-3.376570	-3.816557	-0.019300
28	O	-5.148573	-2.374183	0.073115
29	O	-5.148573	2.374183	-0.073115
30	O	-3.376570	3.816557	0.019300
31	O	3.376570	3.816557	-0.019300
32	O	5.148573	2.374183	0.073115
33	O	5.148573	-2.374183	-0.073115
34	O	3.376570	-3.816557	0.019300
35	C	-4.543818	-4.647444	0.234660
36	C	-5.729958	-3.684024	-0.155319
37	C	-5.729958	3.684024	0.155319
38	C	-4.543818	4.647444	-0.234660
39	C	4.543818	4.647444	0.234660
40	C	5.729958	3.684024	-0.155319
41	C	5.729958	-3.684024	0.155319
42	C	4.543818	-4.647444	-0.234660
43	C	-4.513871	5.003895	-1.727206

44	H	-5.329419	5.682733	-1.997830
45	H	-4.584413	4.108028	-2.351534
46	H	-3.564362	5.497961	-1.955604
47	C	-4.423967	5.915242	0.609466
48	H	-4.304076	5.684129	1.670314
49	H	-5.308913	6.550145	0.486299
50	H	-3.548547	6.488803	0.288128
51	C	-6.983660	3.811273	-0.708958
52	H	-7.726123	3.075368	-0.383518
53	H	-6.768588	3.626464	-1.763879
54	H	-7.430129	4.807866	-0.611798
55	C	-6.107487	3.746137	1.642072
56	H	-5.222901	3.657339	2.280517
57	H	-6.775198	2.909983	1.872060
58	H	-6.623986	4.679224	1.891837
59	C	4.513871	5.003895	1.727206
60	H	4.584413	4.108028	2.351534
61	H	3.564362	5.497961	1.955604
62	H	5.329419	5.682733	1.997830
63	C	4.423967	5.915242	-0.609466
64	H	3.548547	6.488803	-0.288128
65	H	4.304076	5.684129	-1.670314
66	H	5.308913	6.550145	-0.486299
67	C	6.107487	3.746137	-1.642072
68	H	6.623986	4.679224	-1.891837
69	H	5.222901	3.657339	-2.280517
70	H	6.775198	2.909983	-1.872060
71	C	6.983660	3.811273	0.708958
72	H	6.768588	3.626464	1.763879
73	H	7.430129	4.807866	0.611798
74	H	7.726123	3.075368	0.383518
75	C	-4.513871	-5.003895	1.727206
76	H	-4.584413	-4.108028	2.351534
77	H	-3.564362	-5.497961	1.955604
78	H	-5.329419	-5.682733	1.997830
79	C	-4.423967	-5.915242	-0.609466
80	H	-3.548547	-6.488803	-0.288128
81	H	-4.304076	-5.684129	-1.670314
82	H	-5.308913	-6.550145	-0.486299
83	C	-6.983660	-3.811273	0.708958
84	H	-6.768588	-3.626464	1.763879
85	H	-7.430129	-4.807866	0.611798
86	H	-7.726123	-3.075368	0.383518
87	C	-6.107487	-3.746137	-1.642072
88	H	-6.623986	-4.679224	-1.891837
89	H	-5.222901	-3.657339	-2.280517
90	H	-6.775198	-2.909983	-1.872060
91	C	4.513871	-5.003895	-1.727206

92	H	5.329419	-5.682733	-1.997830
93	H	4.584413	-4.108028	-2.351534
94	H	3.564362	-5.497961	-1.955604
95	C	6.983660	-3.811273	-0.708958
96	H	7.726123	-3.075368	-0.383518
97	H	6.768588	-3.626464	-1.763879
98	H	7.430129	-4.807866	-0.611798
99	C	6.107487	-3.746137	1.642072
100	H	5.222901	-3.657339	2.280517
101	H	6.775198	-2.909983	1.872060
102	H	6.623986	-4.679224	1.891837
103	C	4.423967	-5.915242	0.609466
104	H	4.304076	-5.684129	1.670314
105	H	5.308913	-6.550145	0.486299
106	H	3.548547	-6.488803	0.288128

E = -2258.535631 hartree

**8****10****11**

E_{rel} (kcal/mol) 0.0

+0.5

+1.7

The actual difference in energy between **8** and **10** must be somewhat greater than 1.0 kcal/mol for the equilibrium to favor **8** as strongly as we see experimentally, but the identification of **8** as the most stable isomer is correctly predicted by the calculations.

Appendix 1. NMR analysis of corannulene borylation product mixtures

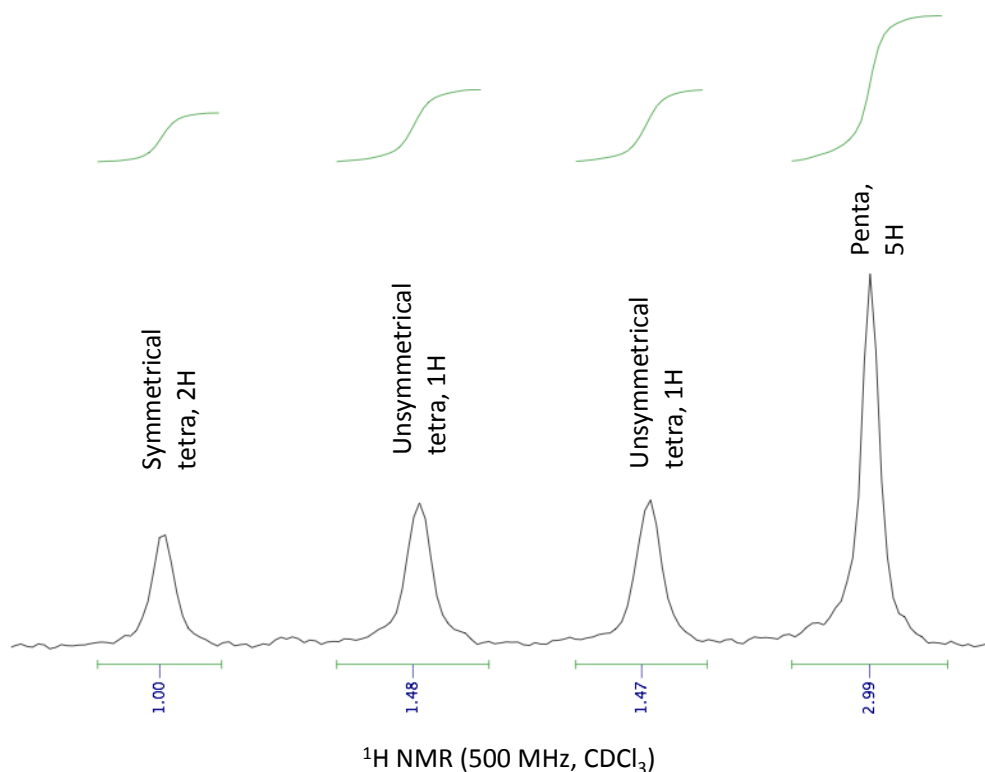


Figure S5. ^1H NMR peaks in the 9.00 ppm region and integration values for the components of the corannulene borylation mixture.

Knowing how many protons each peak represents and to which compound each belongs, one can calculate the molar ratios among the 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:

$$0.50 + 1.47 + 0.60 = 2.57$$

The normalized ratio of each compound:

$$\frac{0.50}{2.57} : \frac{1.47}{2.57} : \frac{0.60}{2.57} = 0.20 : 0.57 : 0.23 = 20\% : 57\% : 23\%$$

Thus, the ^1H NMR peak intensities establish the composition of this mixture as

20% of the symmetrical *tetrakis*(Bpin)corannulene,
57% of the unsymmetrical *tetrakis*(Bpin)corannulene, and
23% of the *pentakis*(Bpin)corannulene, in this case.