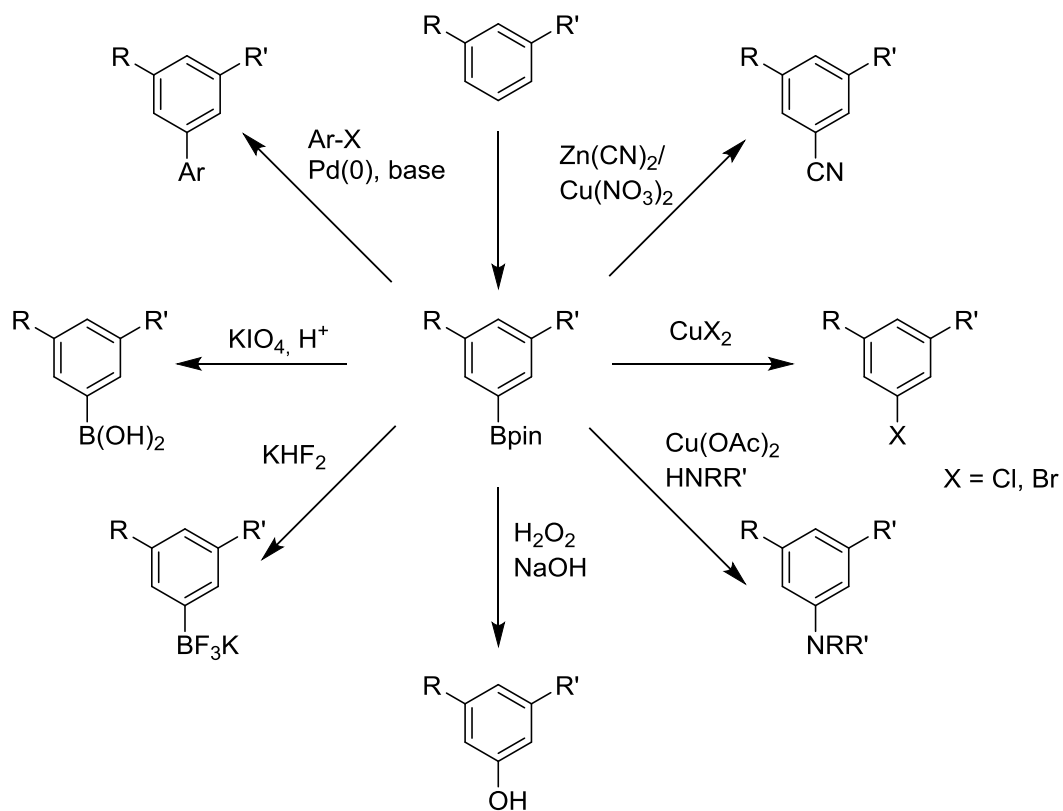
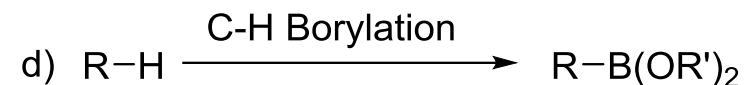
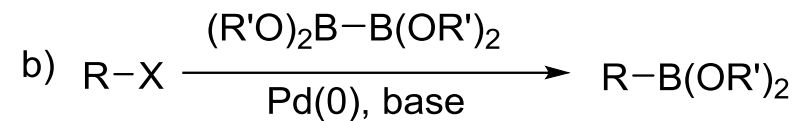


Why make Arylboronate esters?

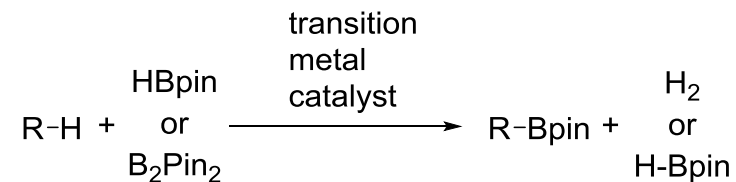
- Versatile and unique method for functionalization



How to make Arylboronate esters



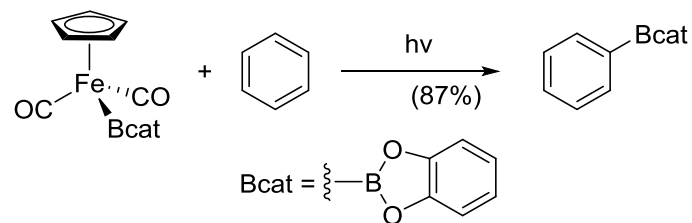
General reaction scheme



R = Alkyl, Aryl

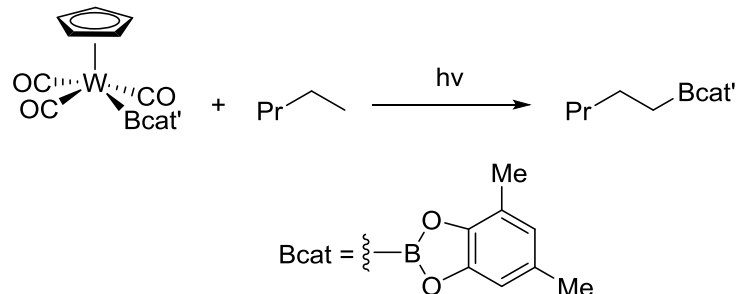
History

1995: first conversion of aryl C–H bond into C–B bond using Fe-complex



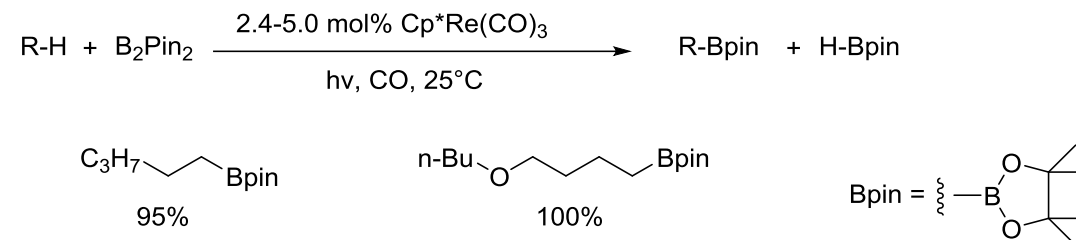
Waltz, K. M.; He, X.; Muhoro, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11357.
<https://doi.org/10.1021/ja00150a041>

1997: first conversion of alkyl C–H bond into C–B bond using W-complex



Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211.
<https://doi.org/10.1126/science.277.5323.211>

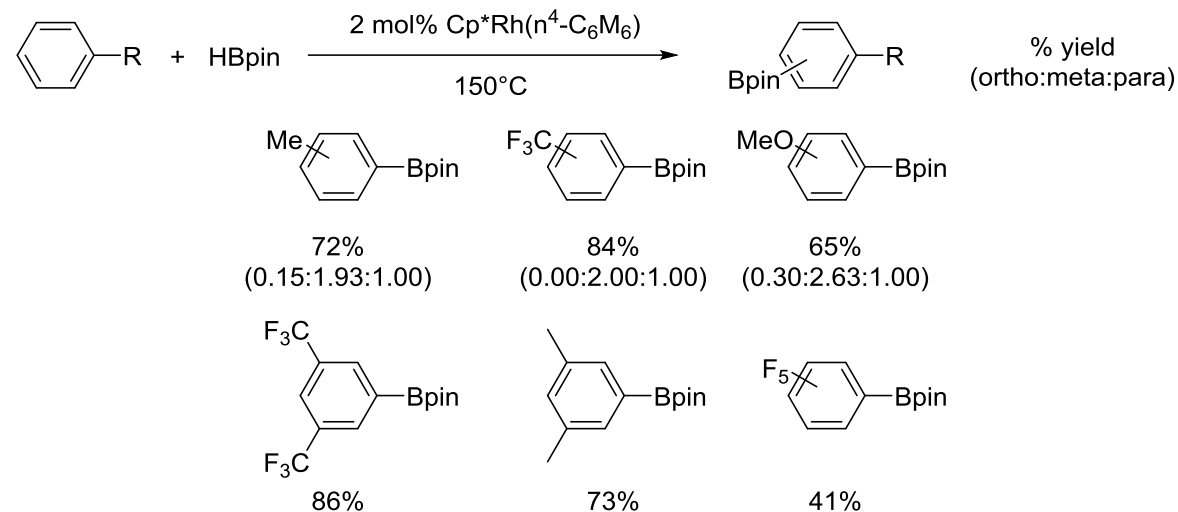
1999: Re-catalyzed borylation of alkane with B₂pin₂ as B-source



Chen, H.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3391.

[https://doi.org/10.1002/\(SICI\)1521-3773\(19991115\)38:22<3391::AID-ANIE3391>3.0.CO;2-N](https://doi.org/10.1002/(SICI)1521-3773(19991115)38:22<3391::AID-ANIE3391>3.0.CO;2-N)

2000: Rh-catalyzed borylation of arenes and alkenes with H-Bpin



Cho, J.-Y.; Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **2000**, *122*, 12868.

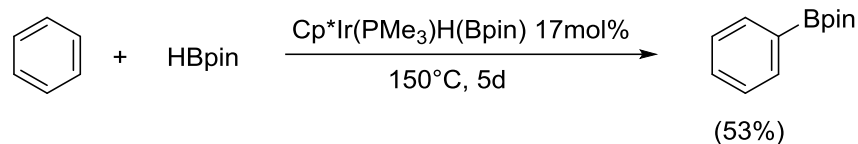
<https://doi.org/10.1021/ja0013069>

Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995.

<https://doi.org/10.1126/science.287.5460.1995>

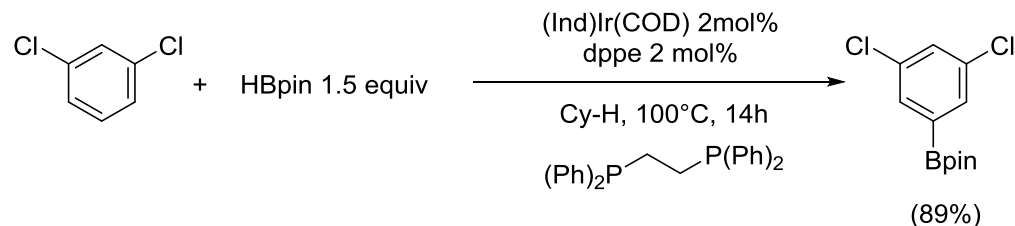
History

1999: first Ir-catalyzed borylation on arene by Smith and Meleczka



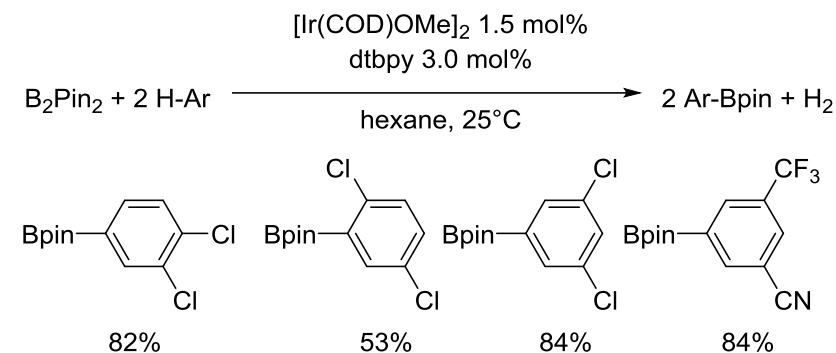
Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **1999**, *121*, 7696.
<https://doi.org/10.1021/ja991258w>

2002: improved catalytic system based on $[(\text{Ind})\text{Ir}(\text{COD})]$ and biphosphine ligand



Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E.; Smith, M. R. *Science* **2002**, *295*, 305.
<https://doi.org/10.1126/science.1067074>

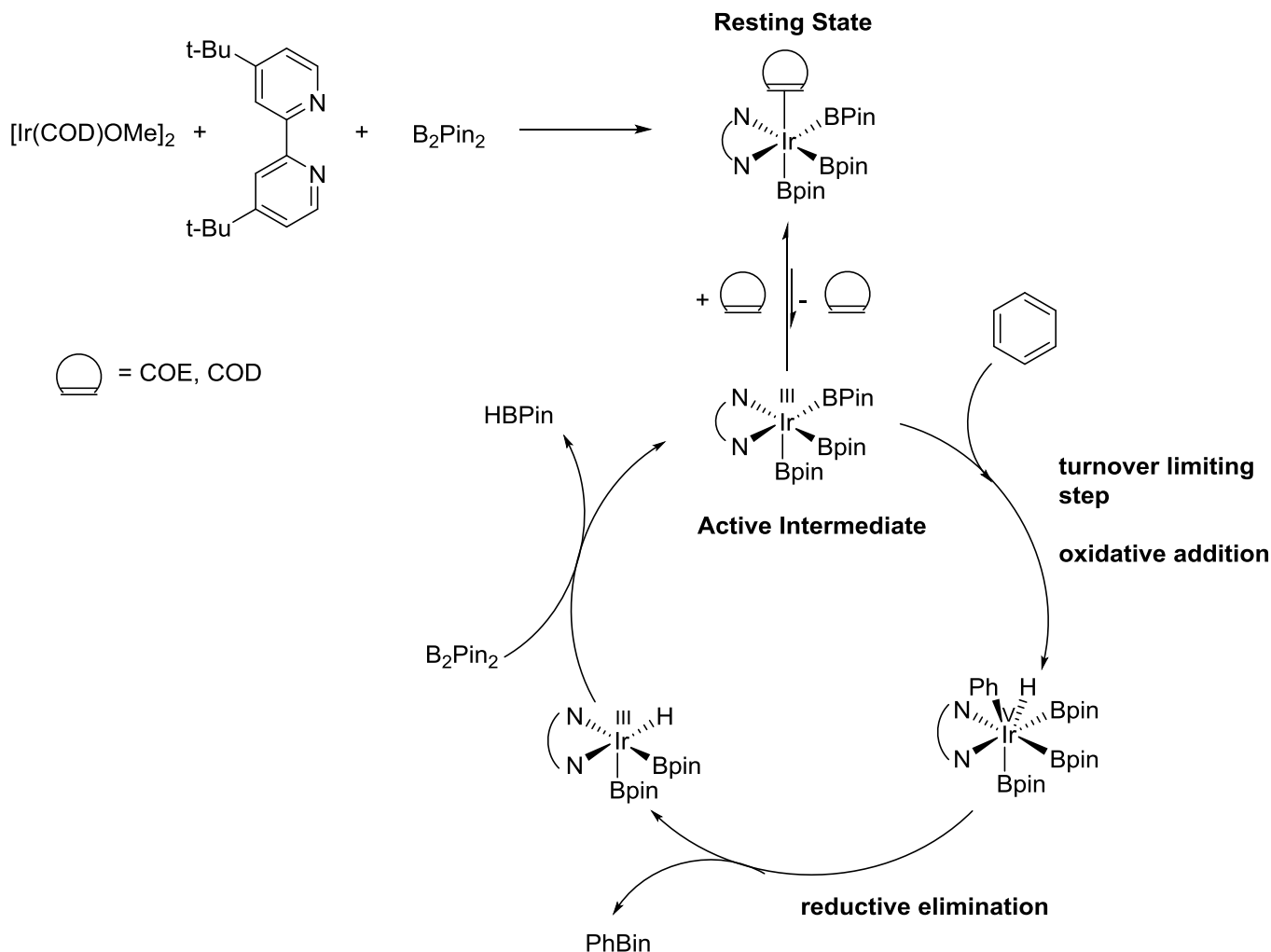
2002: borylation of arenes with $[\text{Ir}(\text{COD})\text{OMe}]_2$ and bipyridine ligand



- Mild conditions
- Regioselectivity controlled by steric properties
- High tolerance of functional groups
- Borylation on heteroarenes feasible

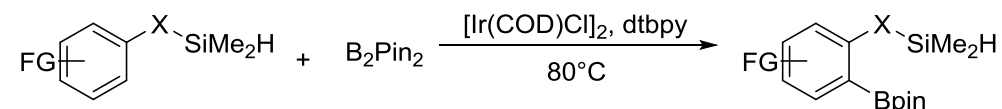
Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390.
<https://doi.org/10.1021/ja0173019>

Mechanism for the Iridium-Catalyzed Borylation of Arenes



Directed *ortho*-Borylation

a: Catalytic C-H Borylation Directed by Covalent Int.

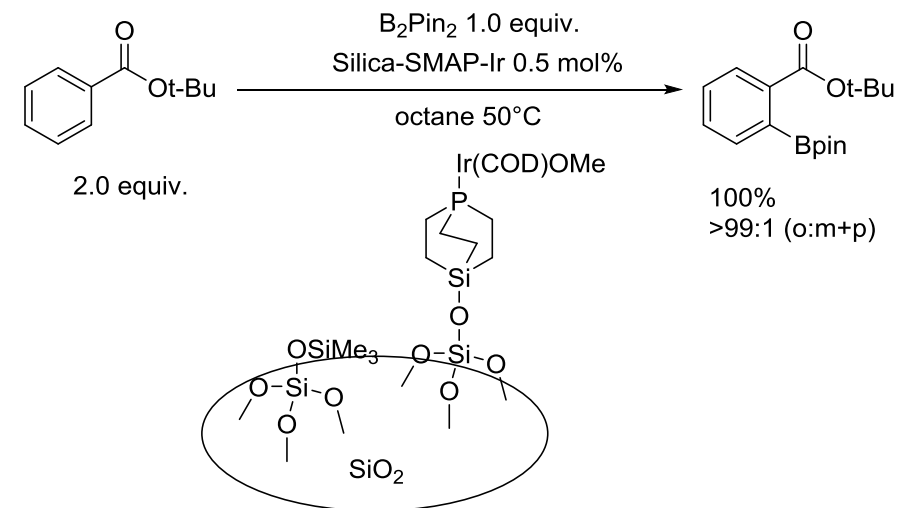


X = CH₂, O, NR

Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 7534.

<https://doi.org/10.1021/ja8015878>

b: Catalytic C-H Borylation Directed by Dative Int.



Kawamorita, S.; Ohmiya, H.; Hara, K.; Fukuoka, A.; Sawamura, M. *J. Am. Chem. Soc.* **2009**, *131*, 5058.

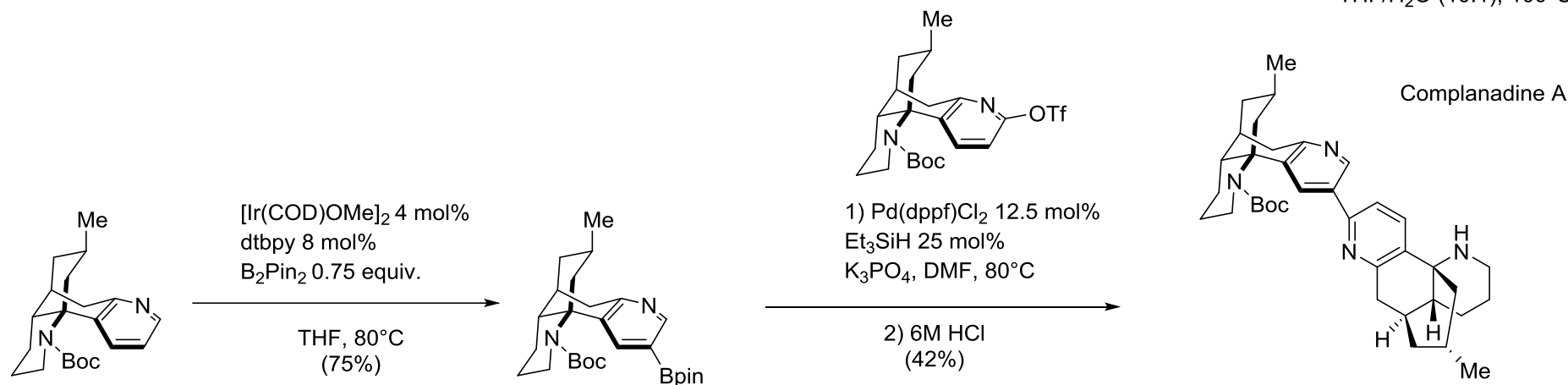
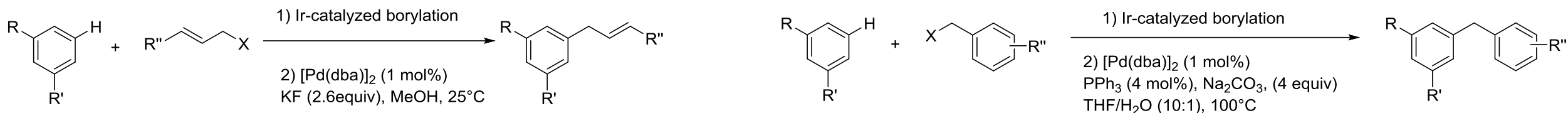
<https://doi.org/10.1021/ja9008419>

Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyaoura, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 14263.

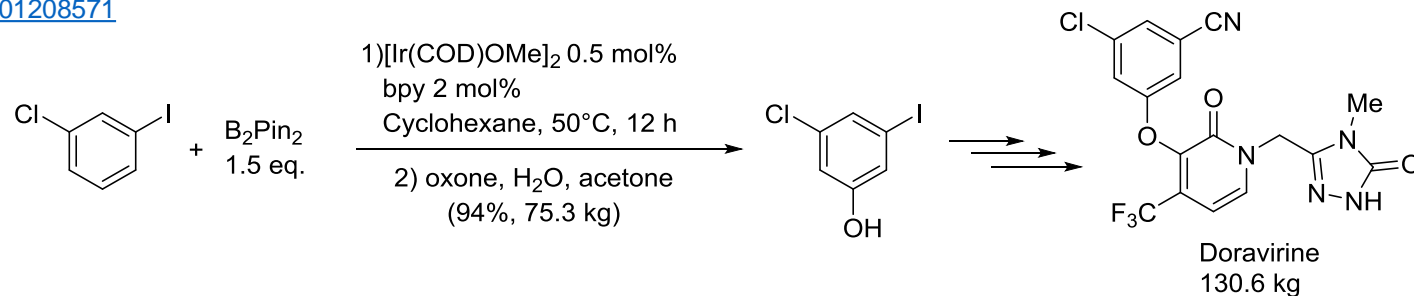
<https://doi.org/10.1021/ja053433g>

Examples: synthesis based on C–H borylation and Suzuki cross-coupling

General reaction scheme

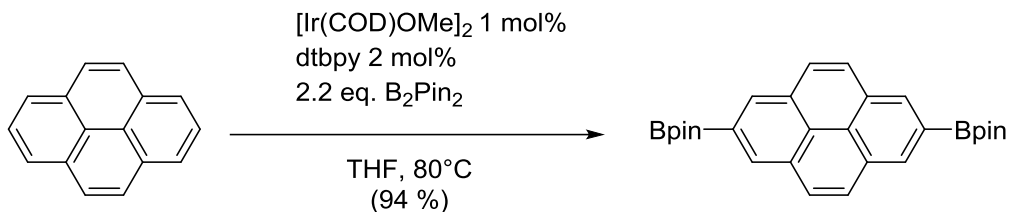


Fischer, D. F.; Sarpong, R. *J. Am. Chem. Soc.* **2010**, *132*, 5926
<https://doi.org/10.1002/anie.201208571>

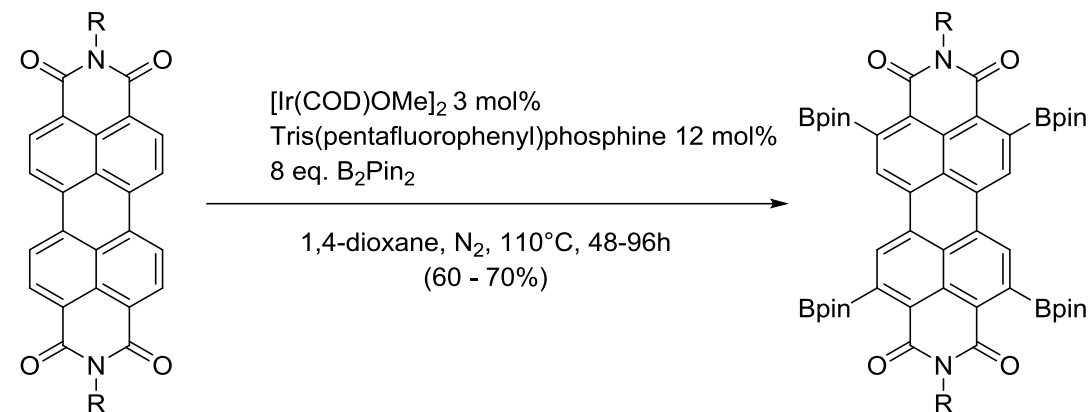


Campeau, L.-C.; Chen, Q.; Gauvreau, D.; Girardin, M.; Belyk, K.; Maligres, P.; Zhou, G.; Gu, C.; Zhang, W.; Tan, L.; O'Shea, P. D. *Org. Process Res. Dev.* **2016**, *20*, 1476.
<https://doi.org/10.1021/acs.oprd.6b00163>

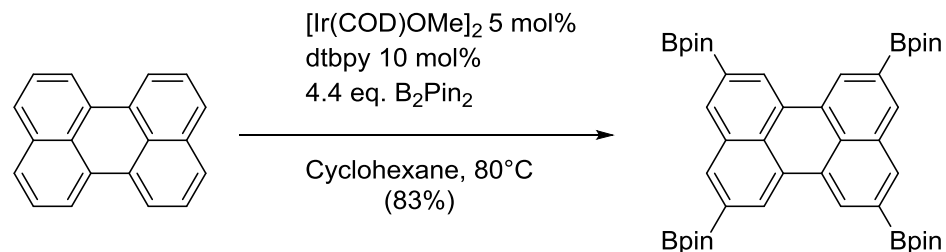
Example: C–H borylation on polycyclic aromatic systems



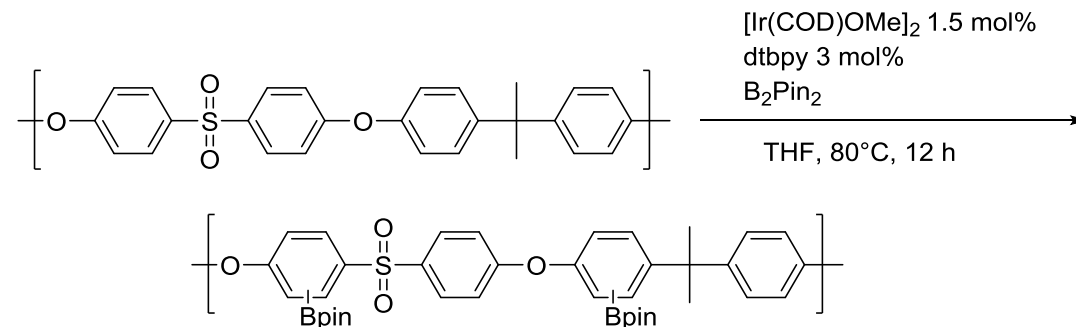
Howard, A. K. J.; Marder, T. B. *Chem. Eur. J.* **2012**, *18*, 5022.
<https://doi.org/10.1002/chem.201103774>



Teraoka, T.; Hiroto, S.; Shinokubo, *Org. Lett.* **2011**, *13*, 2532.
<https://doi.org/10.1021/ol2004534>

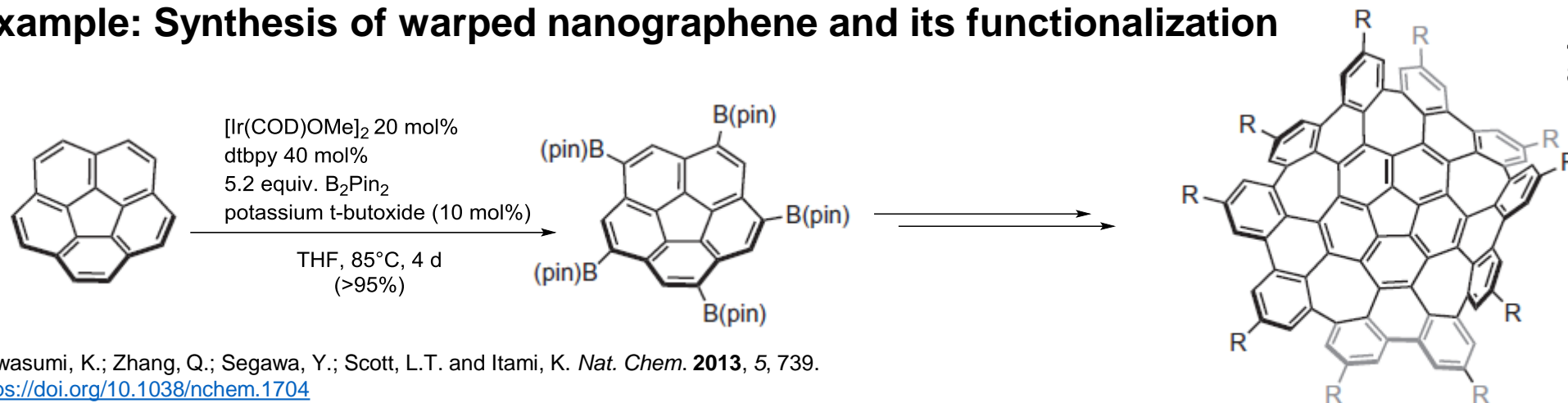


Conventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B.; Perutz, R. N. *Chem. Commun.*, **2005**, *41*, 2172.
<https://doi.org/10.1039/B501778E>



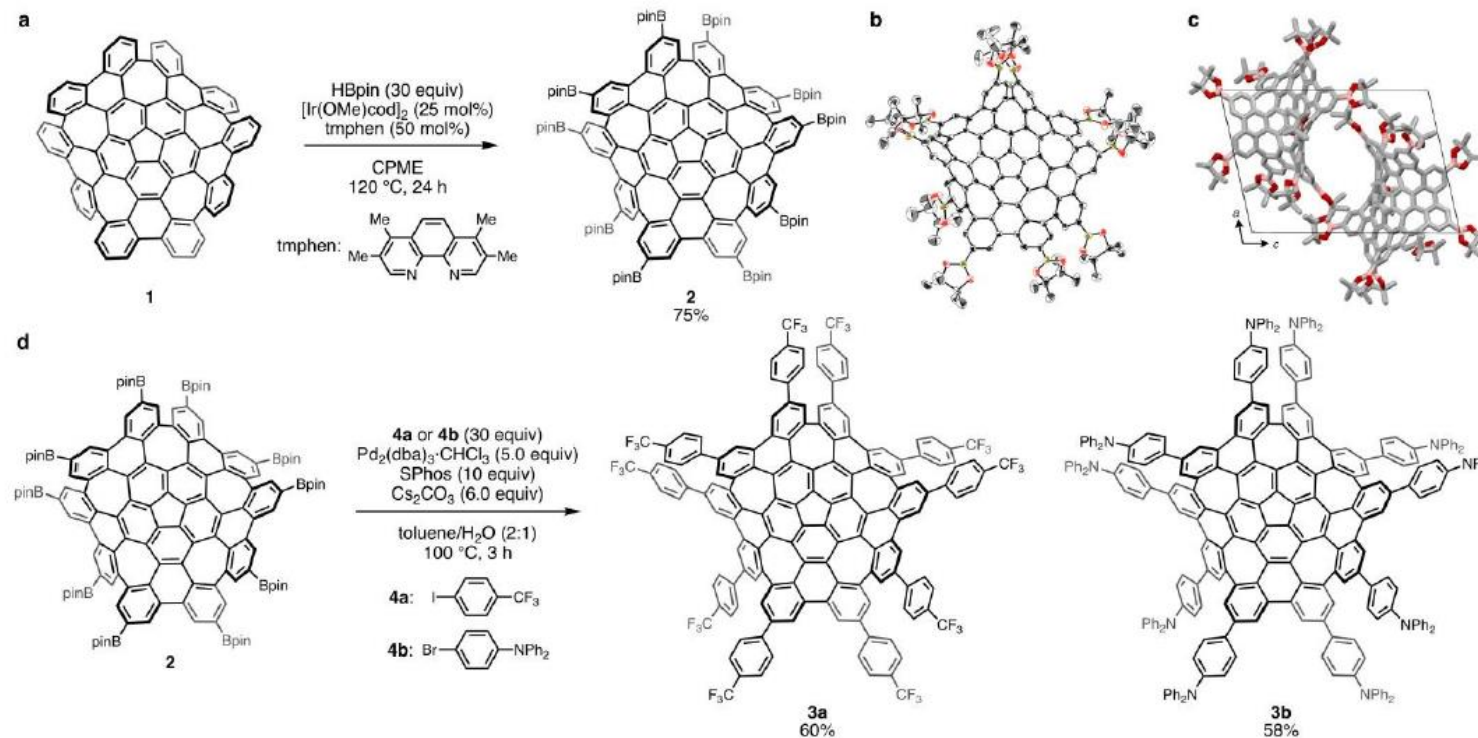
Jo, T. S.; Kim, S. H.; Shin, J.; Bae, C.; *J. Am. Chem. Soc.* **2009**, *131*, 1656.
<https://doi.org/10.1021/ja808374e>

Example: Synthesis of warped nanographene and its functionalization



Kawasumi, K.; Zhang, Q.; Segawa, Y.; Scott, L.T. and Itami, K. *Nat. Chem.* **2013**, *5*, 739.

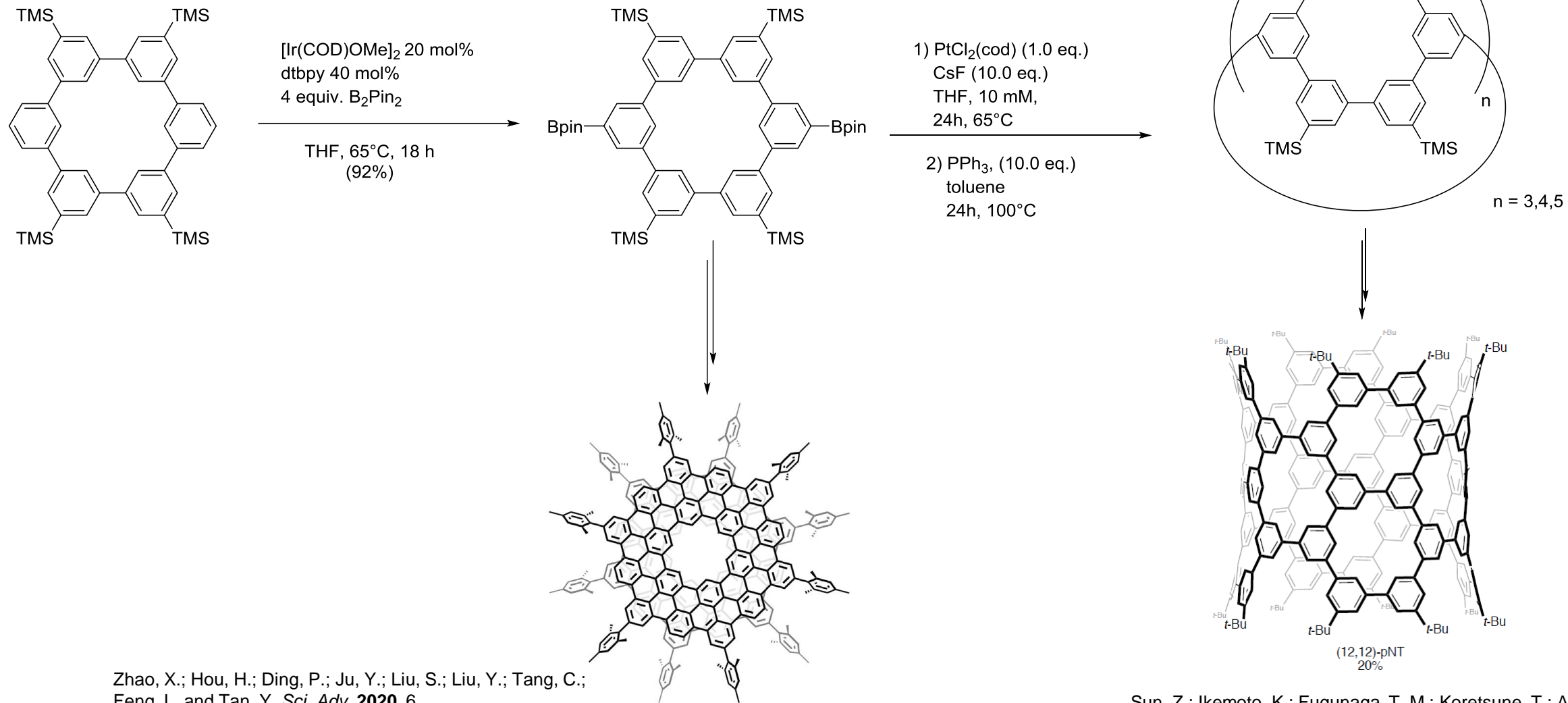
<https://doi.org/10.1038/nchem.1704>



Kato, K.; Lin, S.; Kuwayama, M.; Nagase, M.; Segawa, Y.; Scott, L.T.; Itami, K. *Chem. Sci.* **2019**, *10*, 9038.

<https://doi.org/10.1039/C9SC03061A>

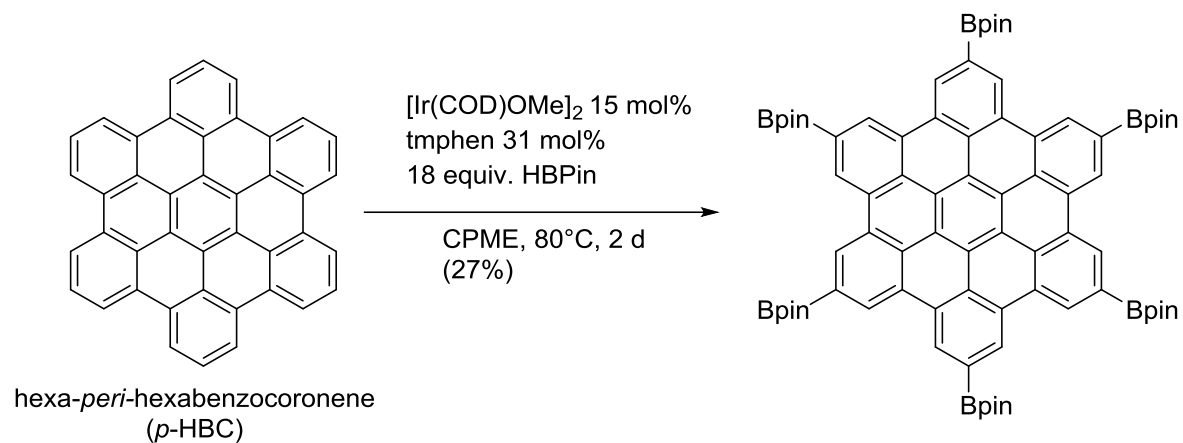
Example: Synthesis of phenine nanotubes and bilayer graphene



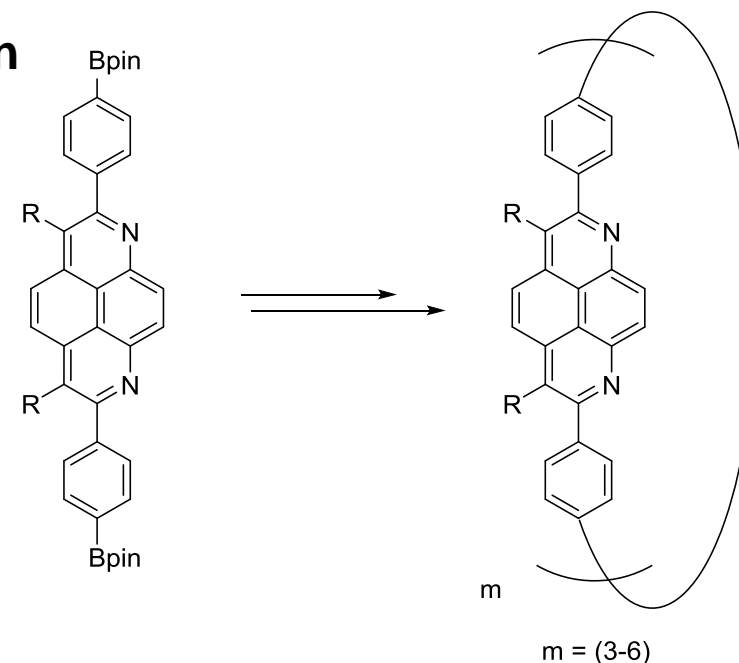
Zhao, X.; Hou, H.; Ding, P.; Ju, Y.; Liu, S.; Liu, Y.; Tang, C.; Feng, L. and Tan, Y. *Sci. Adv.* **2020**, 6, <https://doi.org/10.1126/sciadv.aay8541>

Sun, Z.; Ikemoto, K.; Fugunaga, T. M.; Koretsune, T.; Arita, R.; Sato, S.; Isobe, H. *Science* **2019**, 363, 151. <https://doi.org/10.1126/science.aau5441>

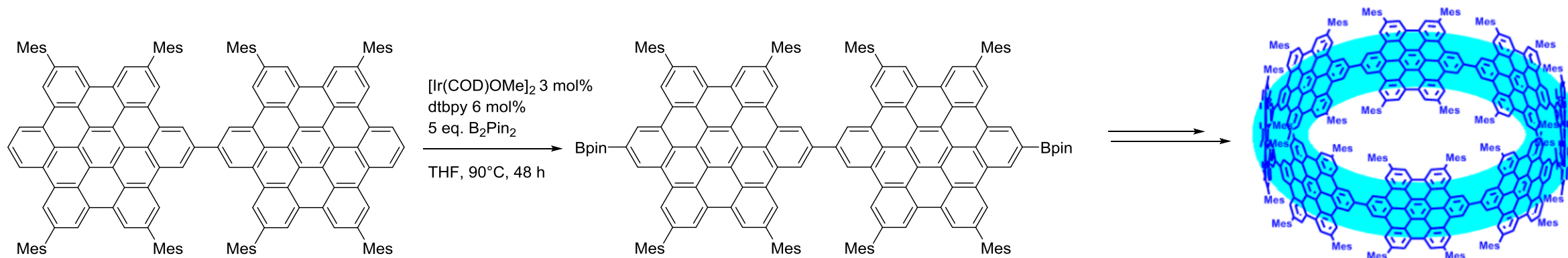
Examples: $[n]$ Cyclo-*para*-phenylene synthesis and functionalization



Nagase, M.; Kato, K.; Yagi, A.; Segawa, Y.; Itami, K.; *Beilstein J. Org. Chem.* **2020**, 16, 391–397.
<https://www.beilstein-journals.org/bjoc/articles/16/37>



Ikemoto, K.; Fujita, M.; Too, P. C.; Tnay, P. C.; Sato, S.; Chiiba, S.; Isobe, H. *Chem. Lett.* **2016**, 45, 658–660
<https://doi.org/10.1246/cl.160258>



Jia, H.; Zhuang, G.; Huang, Q.; Wang, J.; Wu, Y.; Cui, S.; Yang, S.; Du, P. *Chemistry* **2020**, 26(10):2159-2163.
<https://doi.org/10.1002/anie.201909401>