Synthesis and Characterization of all-*meta*-Substituted Imidodiphosphorimidates for the Investigation of London-Dispersion Interactions in Organocatalysis

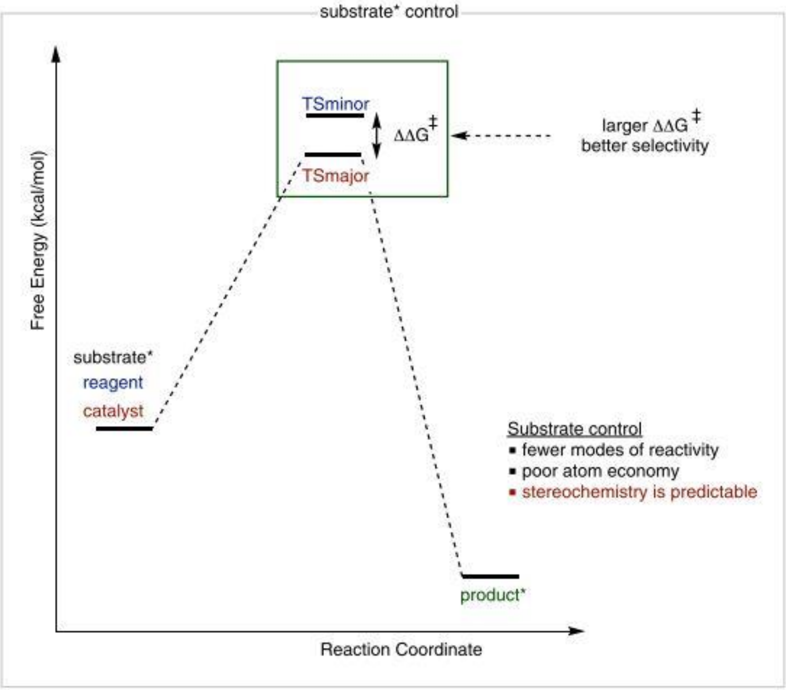
Group Seminar

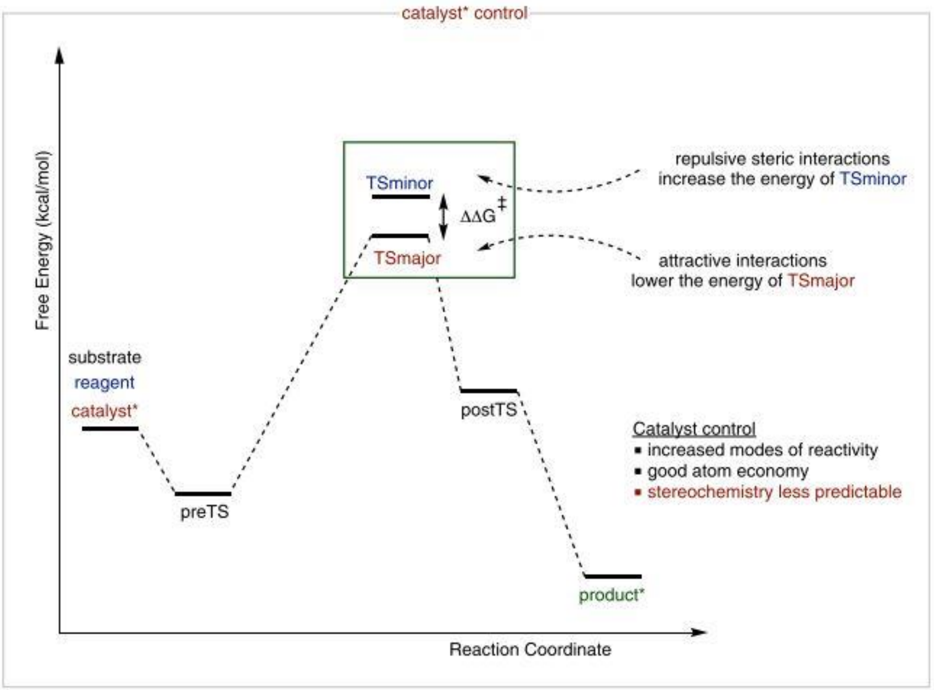
Michael Fuhrmann

06.05.2022

Institute of Organic Chemistry, Justus Liebig University Giessen

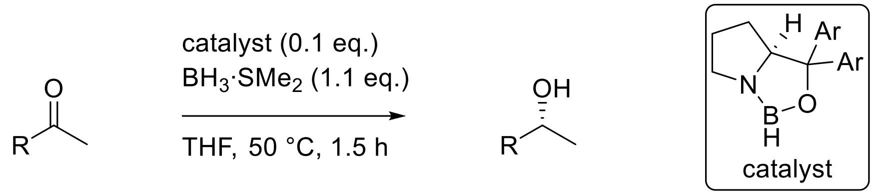
Open Questions on Chirality Transfer



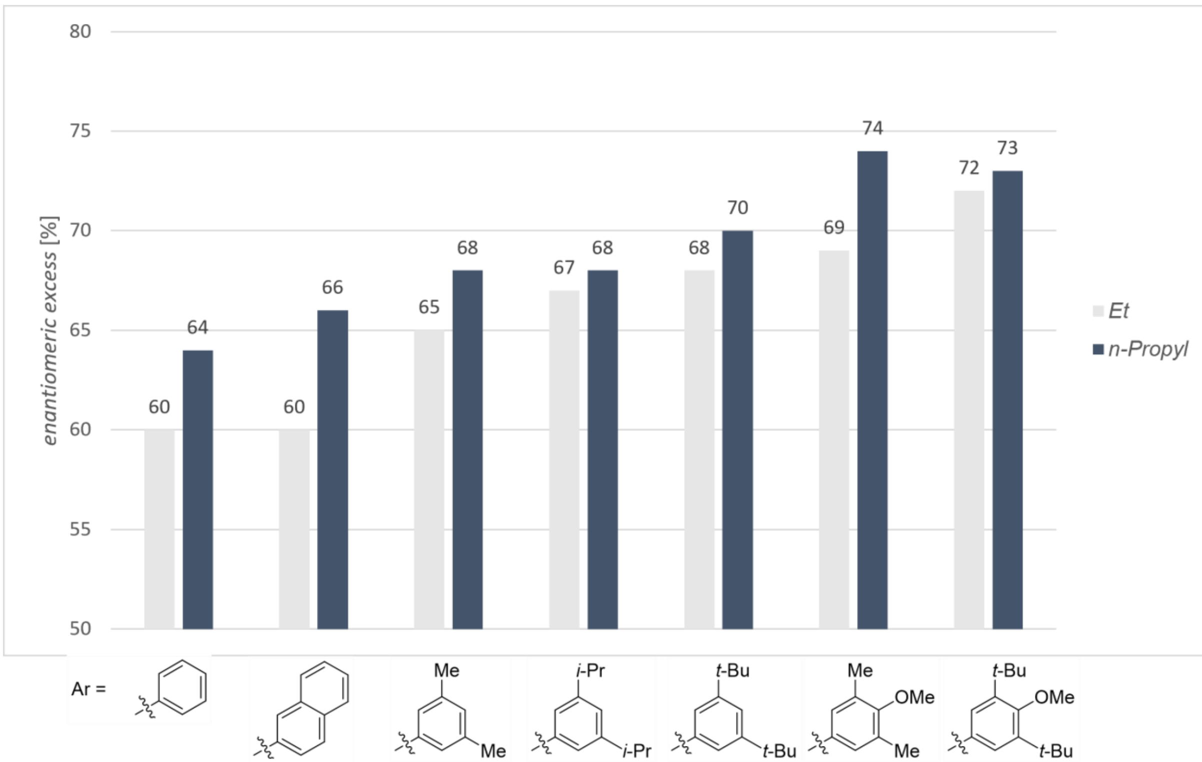


J. P. Reid, *Commun. Chem.* **2021**, *4*, 1–4.

London Dispersion in the Corey-Bakshi-Shibata Reduction

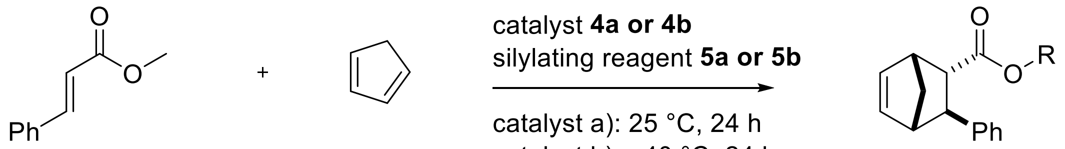


R = Et; *n*-Propyl



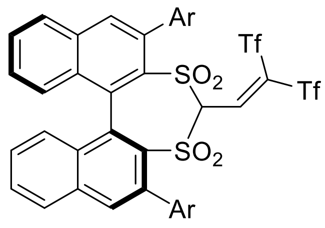
C. Eschmann, L. Song, P. R. Schreiner, *Angew. Chemie Int. Ed.* **2021**, *60*, 4823–4832.

London Dispersion in IDPi-Catalysis



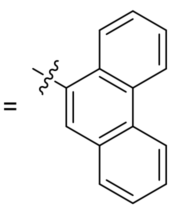
1 **2** **3**

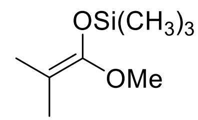
catalyst a): 2% ee (endo)
catalyst b): 94% ee (endo)



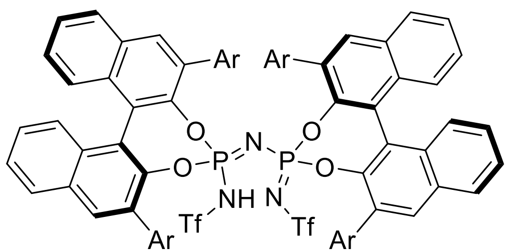
4a (*S*)-BALT
Tf = SO_2CF_3

Ar =

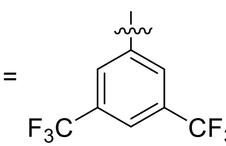


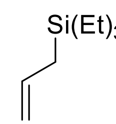


5a



Ar =





4b (*S,S*)-IDPi
Tf = SO_2CF_3

5b

T. Gatzenmeier, M. Turberg, D. Yepes, Y. Xie, F. Neese, G. Bistoni, B. List, *J. Am. Chem. Soc.* **2018**, *140*, 12671–12676; T. Gatzenmeier, M. Van Gemmeren, Y. Xie, D. Höfler, M. Leutzsch, B. List, *Science* **2016**, *351*, 949–952; D. Yepes, F. Neese, B. List, G. Bistoni, *J. Am. Chem. Soc.* **2020**, *142*, 3613–3625.

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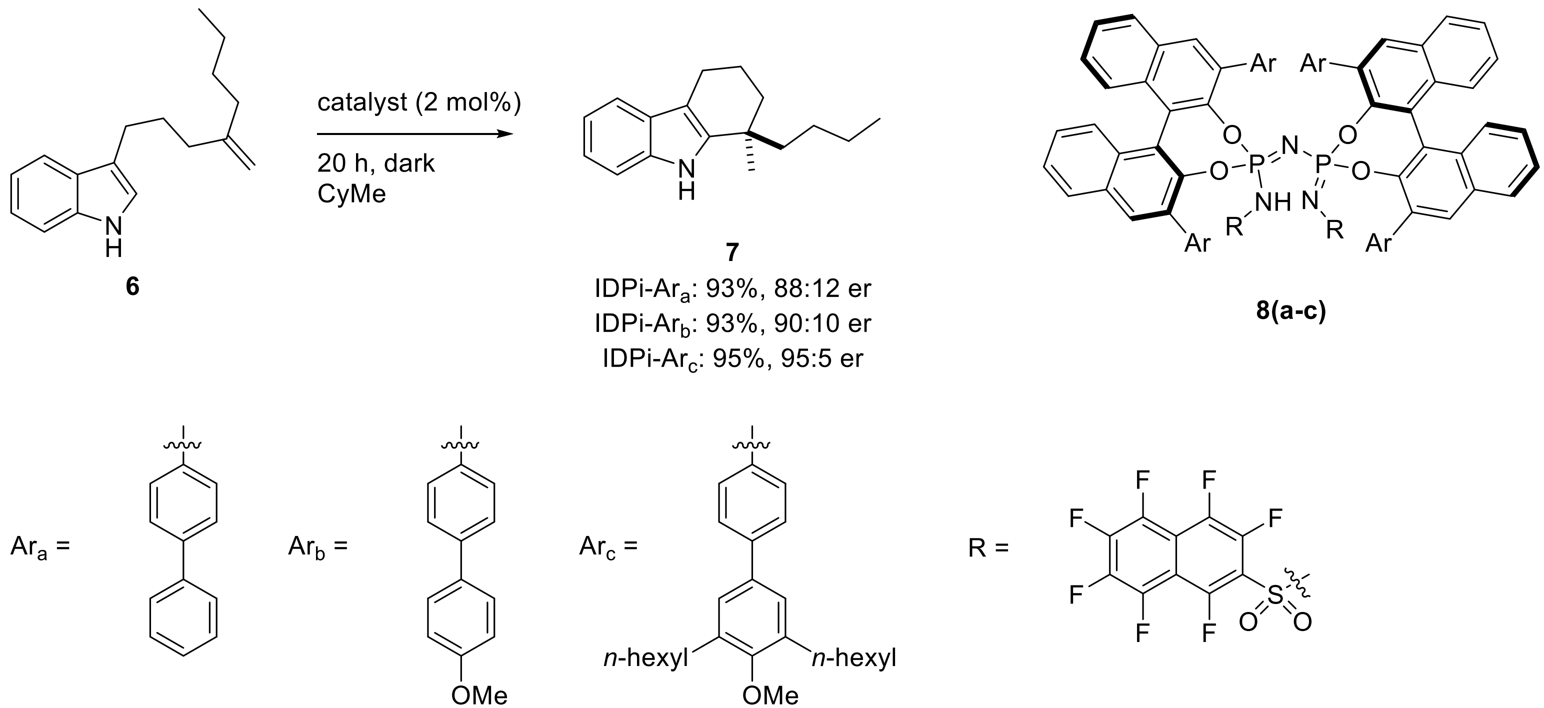
Communication

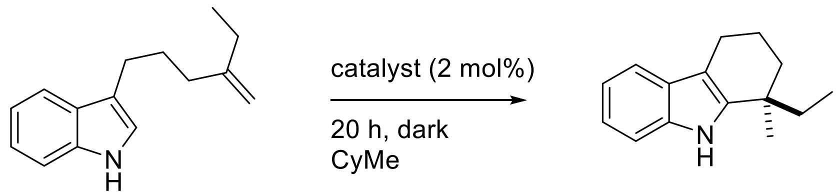
Strong and Confined Acids Catalyze Asymmetric Intramolecular Hydroarylations of Unactivated Olefins with Indoles

Pinglu Zhang, Nobuya Tsuji, Jie Ouyang, and Benjamin List*



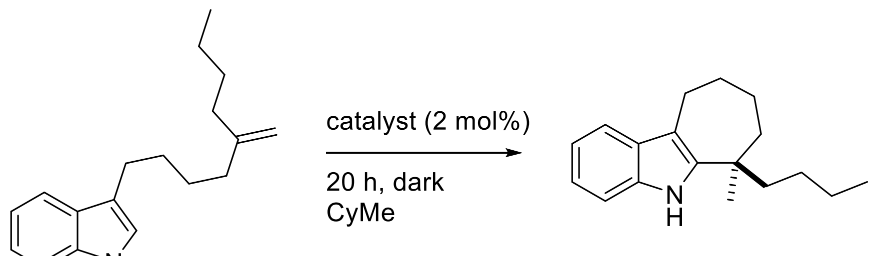
P. Zhang, N. Tsuji, J. Quyang, B. List, *J. Am. Chem. Soc*. **2021**, *143*, 675−680.

Substrate Scope



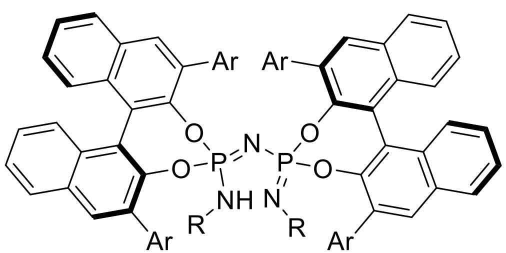
9

10
95%, 84:16 er

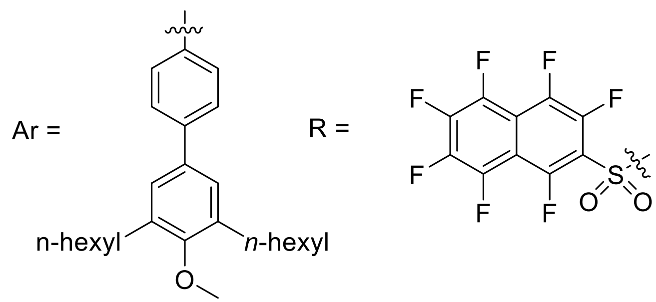


11

12
49%, 76:24 er

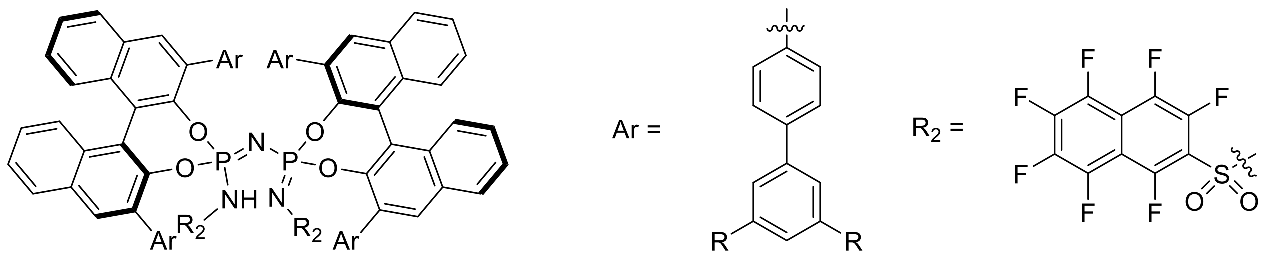


6c

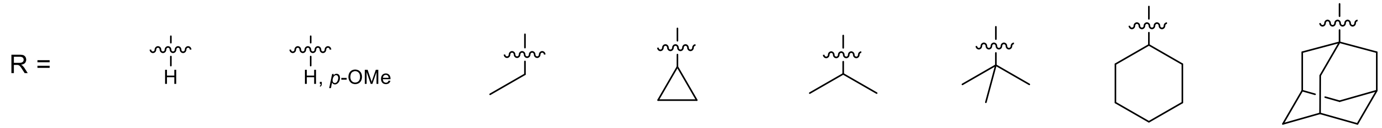


P. Zhang, N. Tsuji, J. Quyang, B. List, *J. Am. Chem. Soc*. **2021**, *143*, 675−680.

Scope of DED-bearing Catalysts

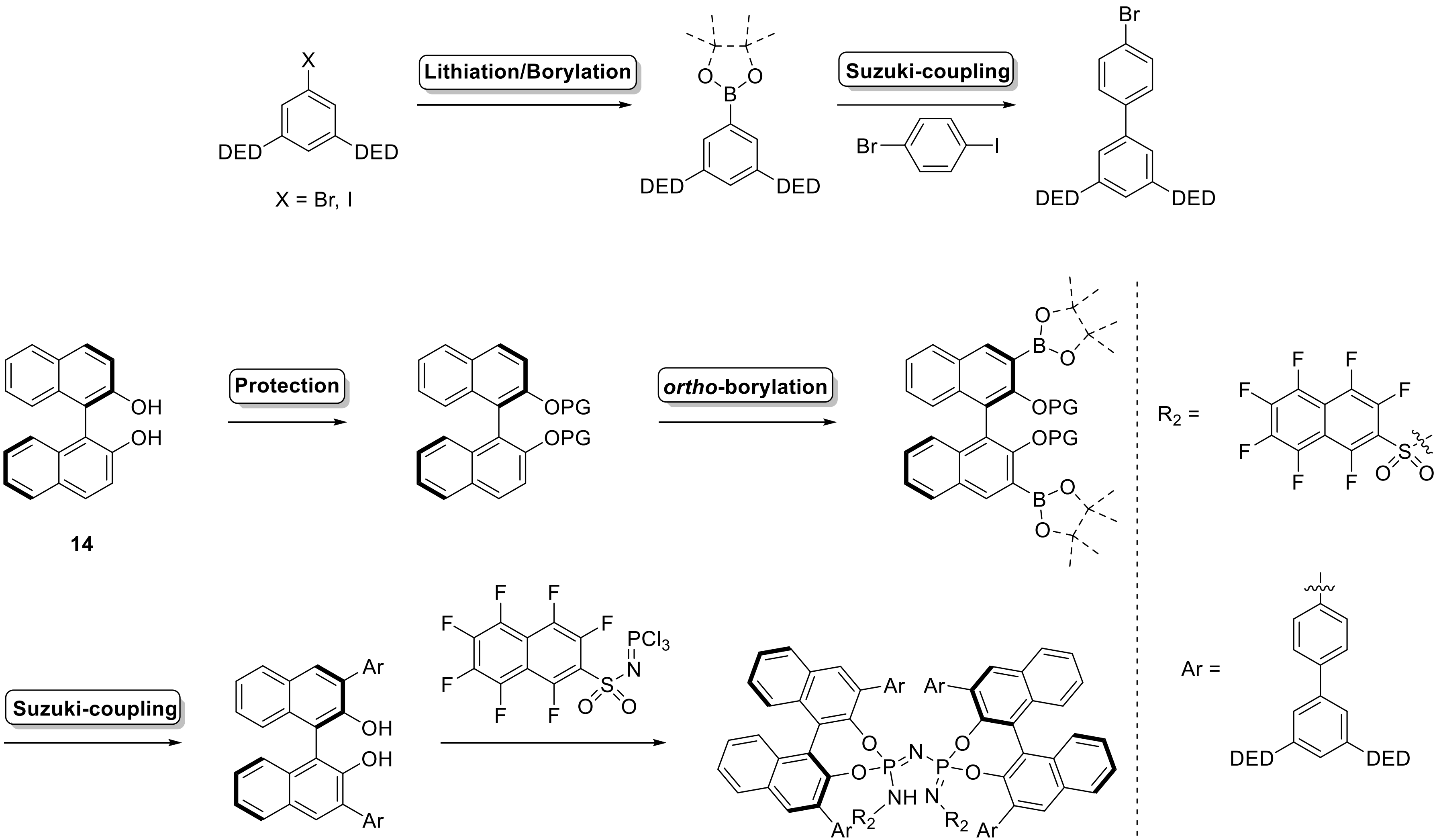


13(a-h)



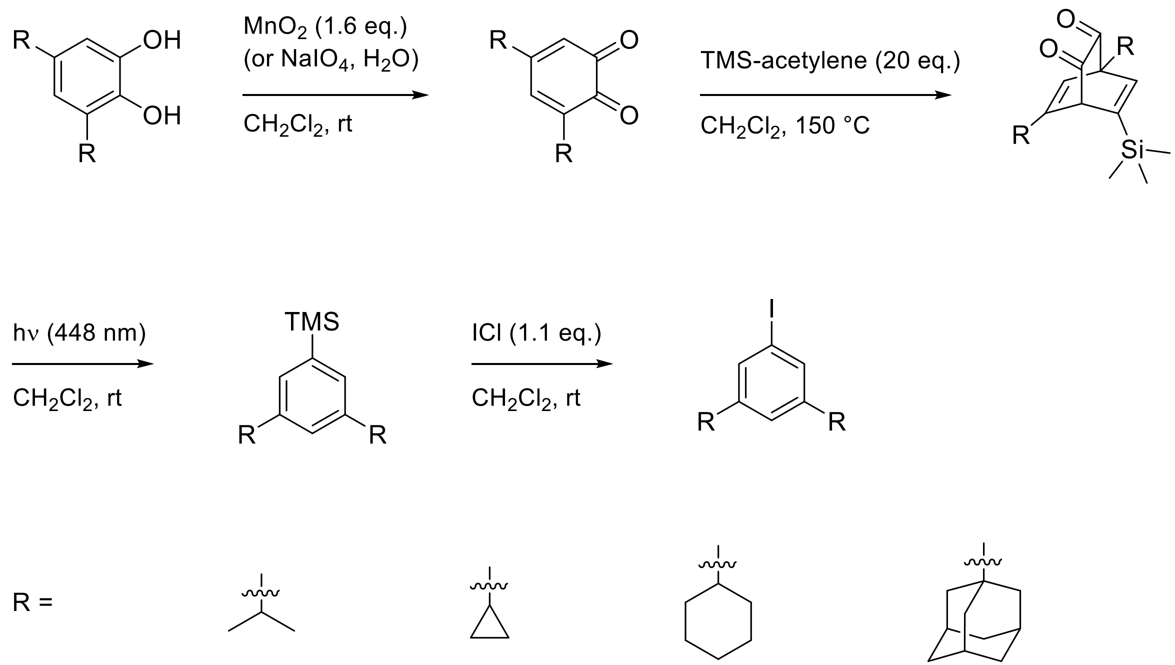
a **b** **c** **d** **e** **f** **g** **h**

Overview of the IDPi Synthesis

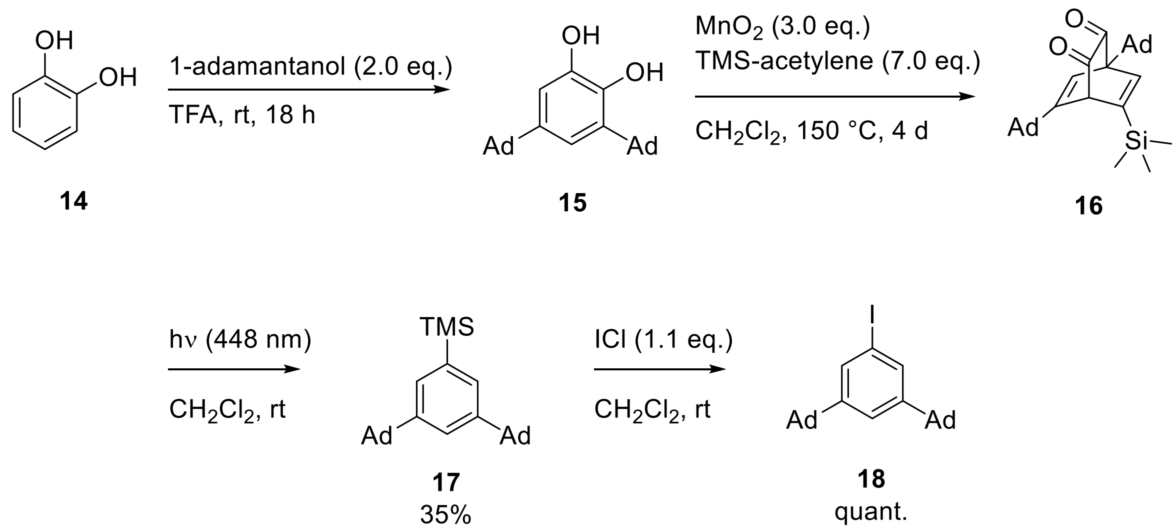


P. Zhang, N. Tsuji, J. Quyang, B. List, *J. Am. Chem. Soc*. **2021**, *143*, 675−680*;* H. Zhou, H. Y. Bae, M. Leutzsch, J. L. Kennemur, D. B. Bécart, B. List, *J. Am. Chem. Soc.* **2020**, *142*, 13695–13700.

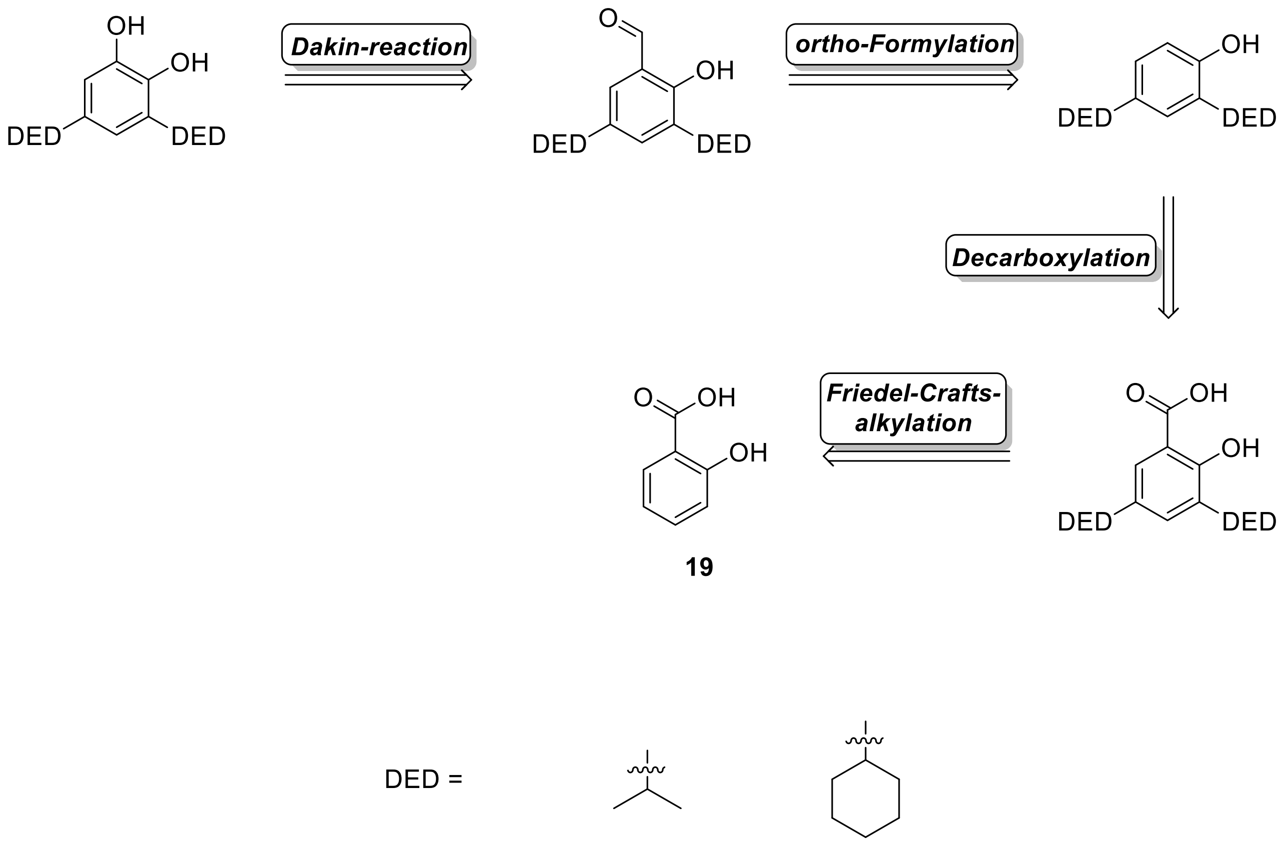
Ochmann's Synthetic Route to all-*meta*-Substituted Iodobenzenes



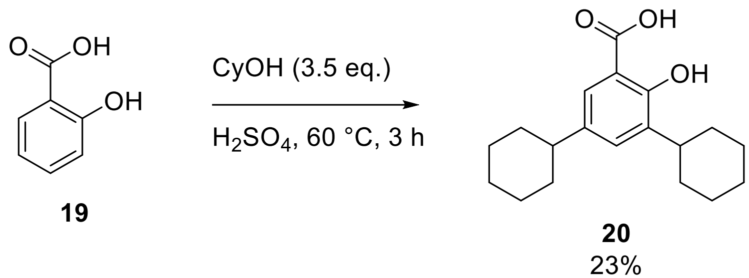
Synthesis of all-*meta*-Adamantyl Iodobenzene

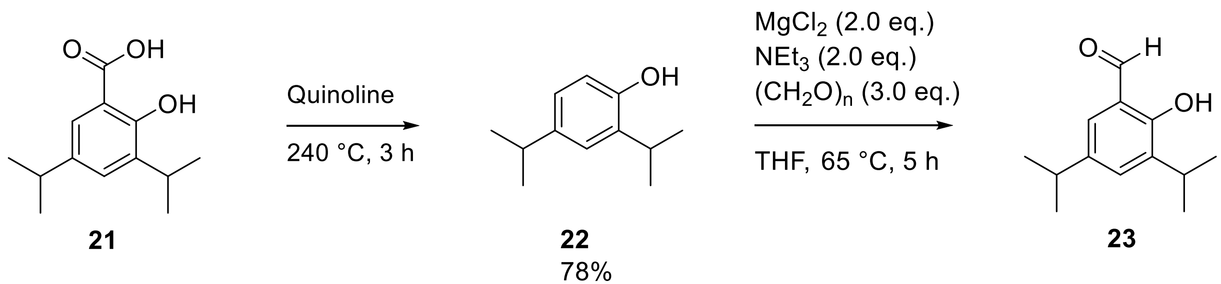


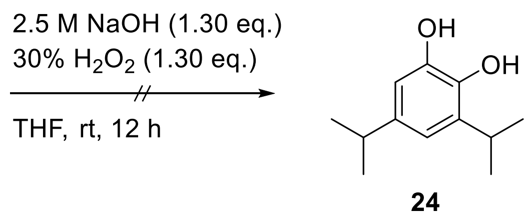
Retrosynthetic Route to 3,5-DiDED Catechols



Synthesis of 3,5-Dicyclohexyl- and 3,5-Diisopropyl Catechol

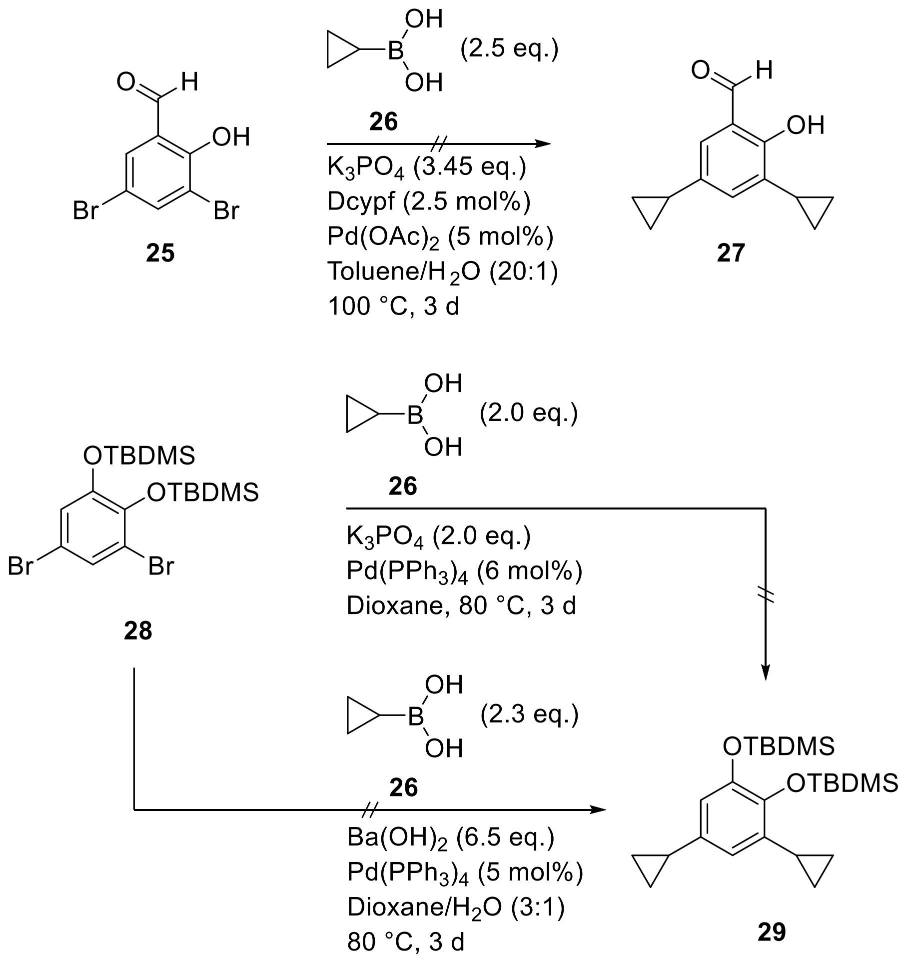






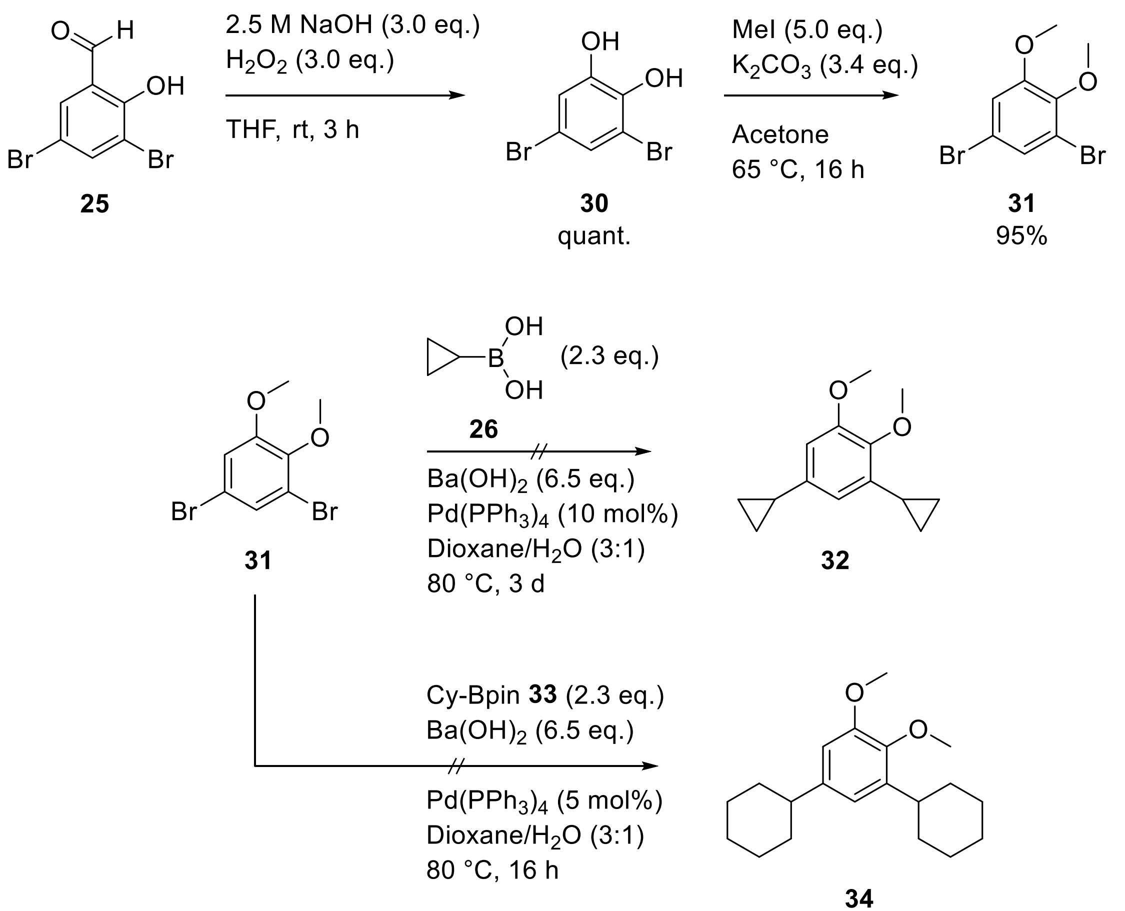
Y. Dai, L. Zheng, D. Chakraborty, B. Borhan, W. D. Wulff, *Chem. Sci.* **2021**, *12*, 12333–12345.

Synthesis of 3,5-Dicyclopropyl Catechol

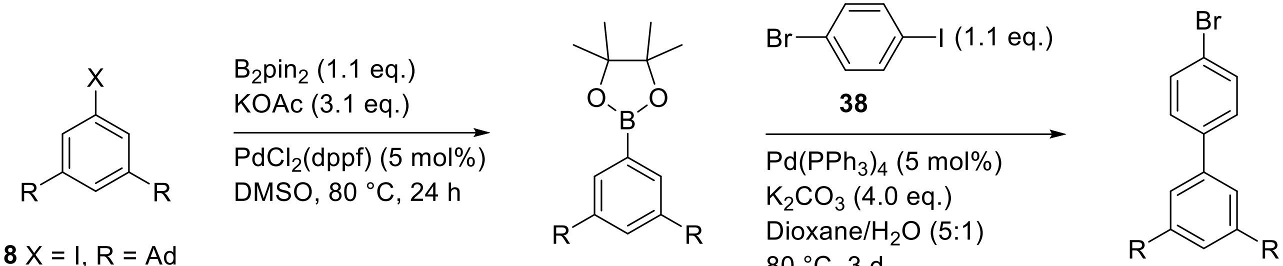


D. Wallace, C. Chen, *Tetrahedron Lett*. **2002**, *43*, 6987−6990.

Synthesis of 3,5-Dicyclopropyl Catechol



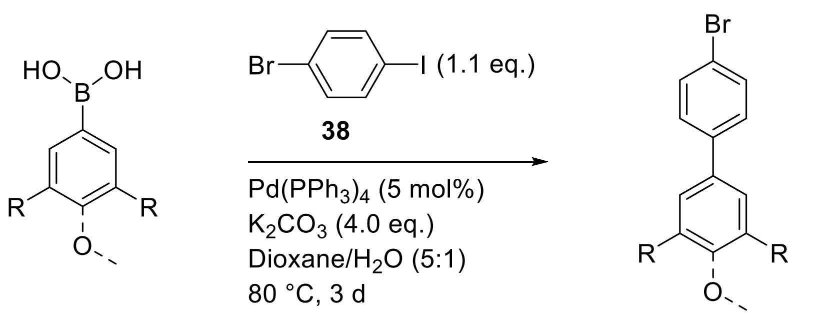
Synthesis of Biphenyl Bromides



18 X = I, R = Ad
35 X = Br, R= *t*Bu

36 R = Ad 75%
37 R= *t*Bu 64%

39 R= *t*Bu 85%
40 R= Ad 46%

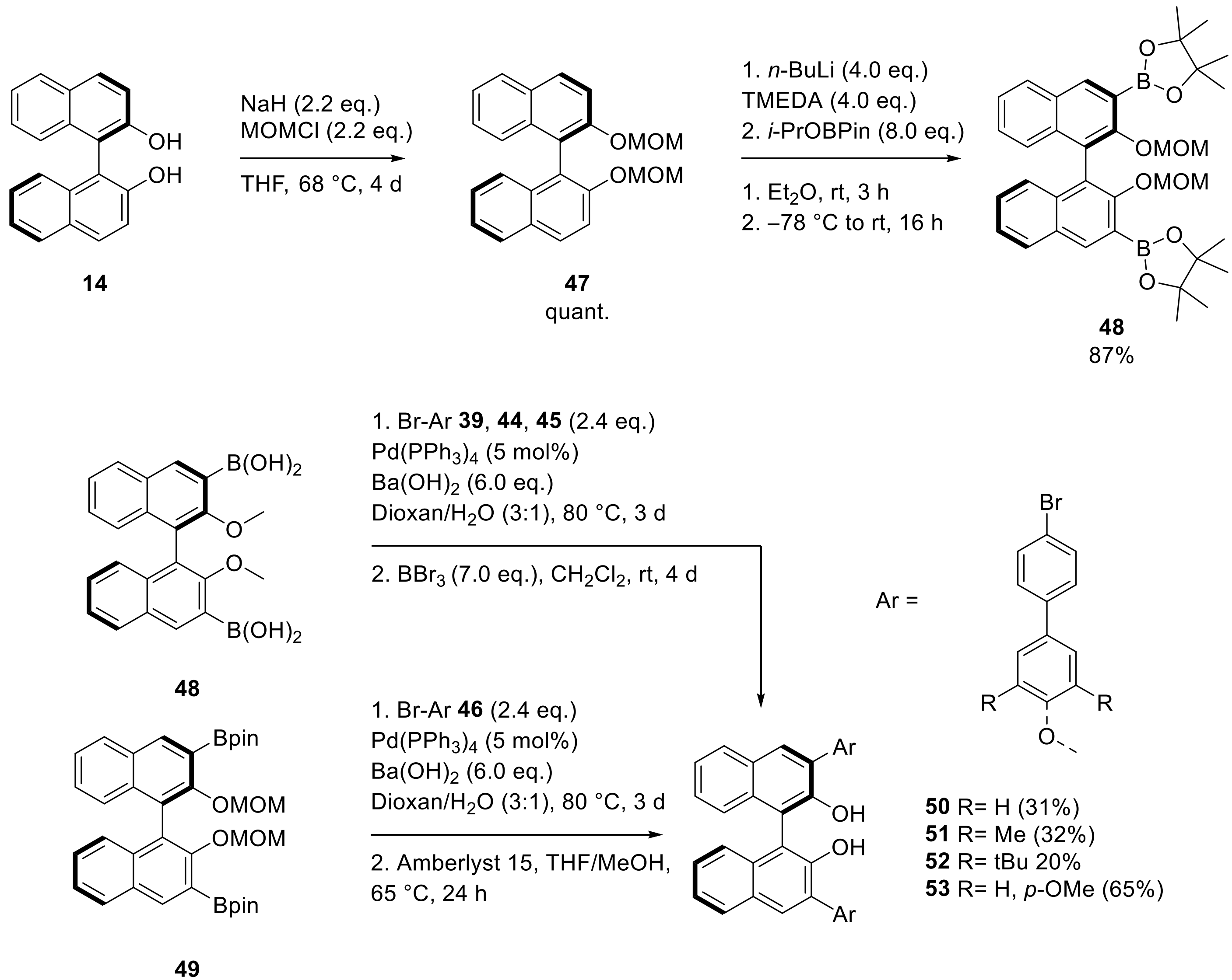


41 R = H
42 R= Me
43 R = H, *p*-OMe

44 R = H 73%
45 R= Me 94%
46 R = H, *p*-OMe 83%

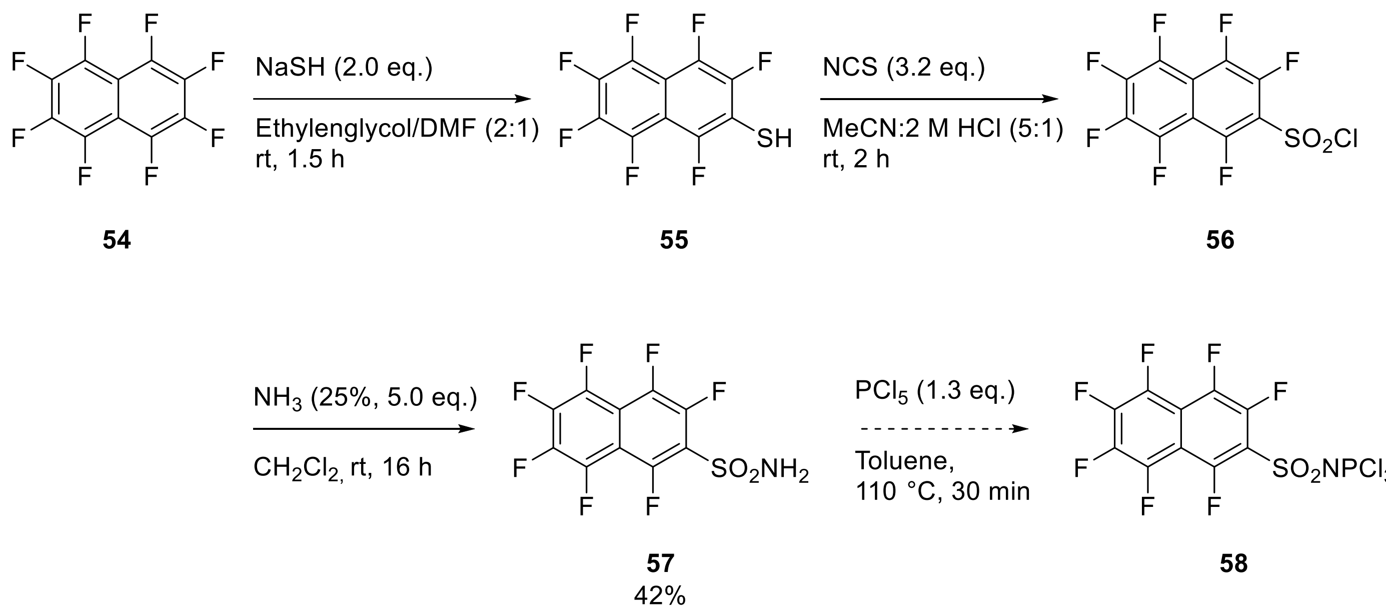
P. Zhang, N. Tsuji, J. Quyang, B. List, *J. Am. Chem. Soc*. **2021**, *143*, 675−680; J. Ranta, T. Kumpulainen, H. Lemmetyinen, A. Efimov, *J. Org. Chem.* **2010**, *75*, 5178–5194.

Synthesis of DED-bearing BINOLs



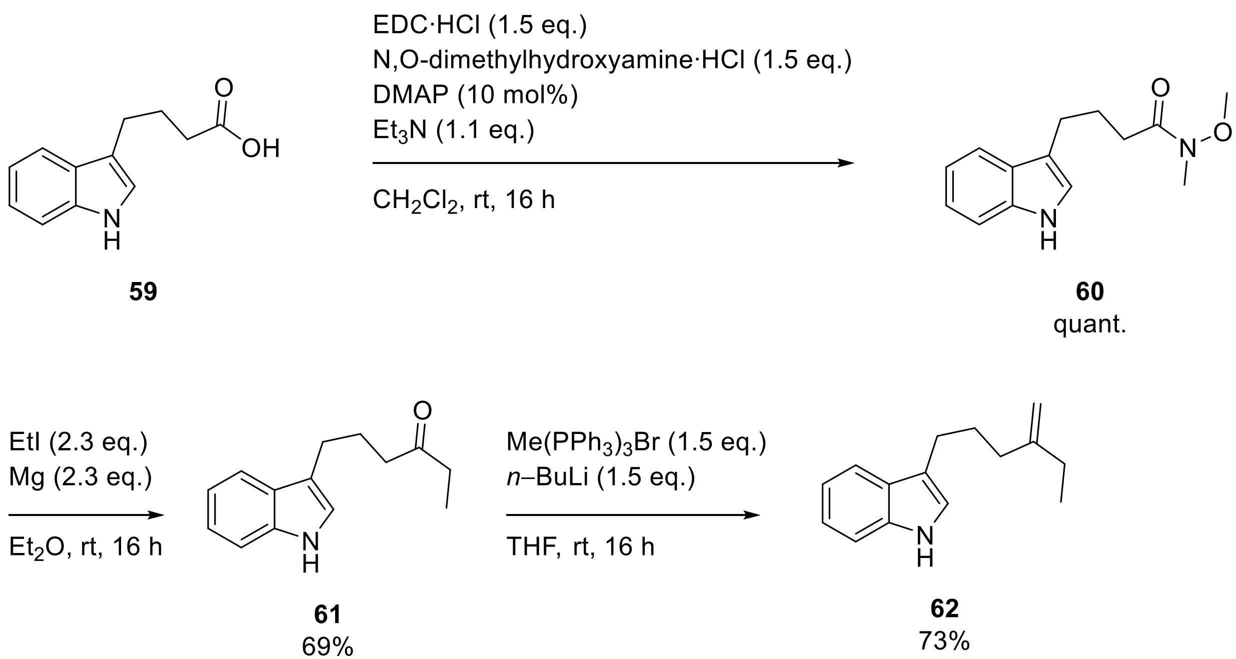
C. Simonin, M. Awale, M. Brand, R. Van Deursen, J. Schwartz, M. Fine, G. Kovacs, P. Häfliger, G. Gyimesi, A. Sithampari, R. P. Charles, M. A. Hediger, J. L. Reymond, *Angew. Chemie Int. Ed.* **2015**, *54*, 14748–14752; Y. He, Z. Bian, C. Kang, L. Gao, *Chem. Commun.* **2010**, *46*, 5695–5697.

Synthesis of the Phosphorimidoyl Trichloride



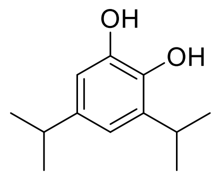
H. Zhou, H. Y. Bae, M. Leutzsch, J. L. Kennemur, D. B. Bécart, B. List, *J. Am. Chem. Soc.* **2020**, *142*, 3695–13700; G. M. Brooke, *J. Fluor. Chem*. **1989**, *43*, 393–403; A. Nishiguchi, K. Maeda, S. Miki, *Synthesis* **2006**, *24*, 4131–4134; M, Shimizu, J. Kikuchi, A. Kondoh, M. Terada, *Chem. Sci*. **2018**, 9, 5747–5757.

Synthesis of the Substrate

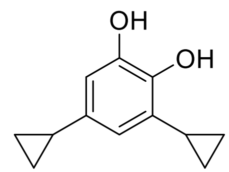


P. Zhang, N. Tsuji, J. Quyang, B. List, *J. Am. Chem. Soc*. **2021**, *143*, 675−680.

Conclusion



64



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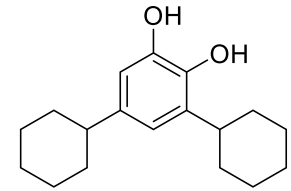
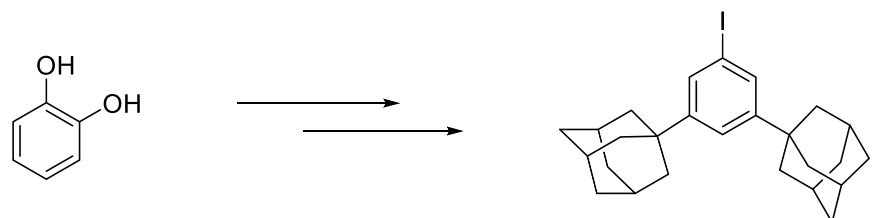
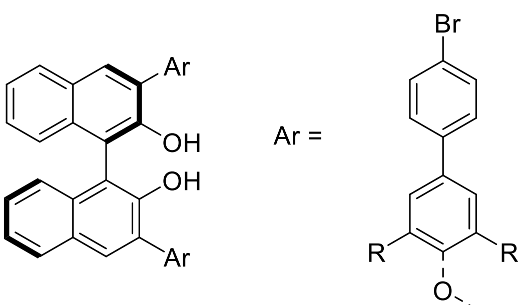


66

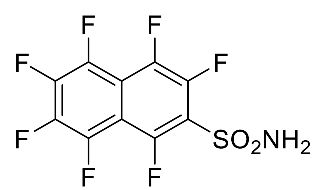


14

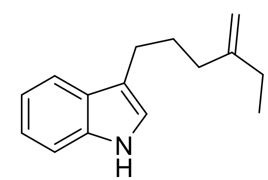
18
35%



50 R= H (31%)
51 R= Me (32%)
52 R= tBu 20%
53 R= H, *p*-OMe (65%)

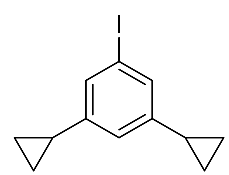


58
42%



62
50%

Outlook



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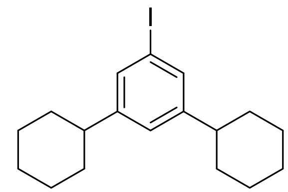
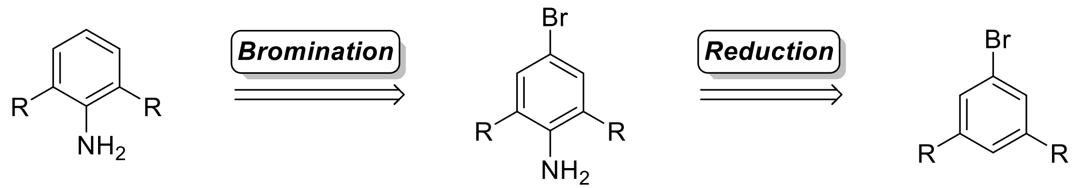


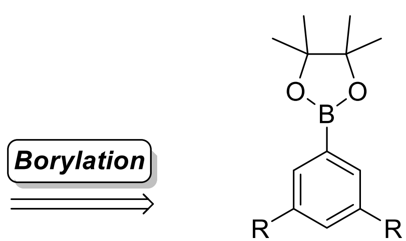
68



69 R = Et
70 R = *i*-Pr

71 R = Et
72 R = *i*-Pr

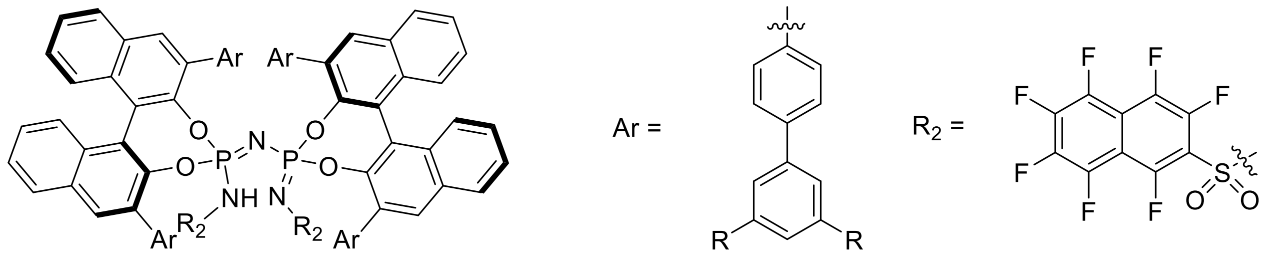
73 R = Et
74 R = *i*-Pr



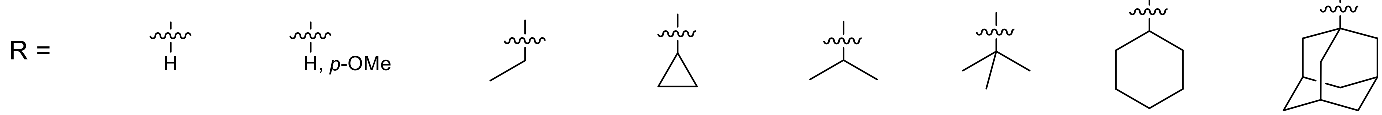
75 R = Et
76 R = *i*-Pr

V. Diemer, H. Chaumeil, A. Defoin, A. Fort, A. Boeglin, C. Carré*, Eur. J. Org. Chem*. **2006**, *12*, 2727–2738; A. Chow, M. So, W. Lu, N. Zhu, C. Che, *Chem. Asian J*. **2011**, *6*, 544–553.

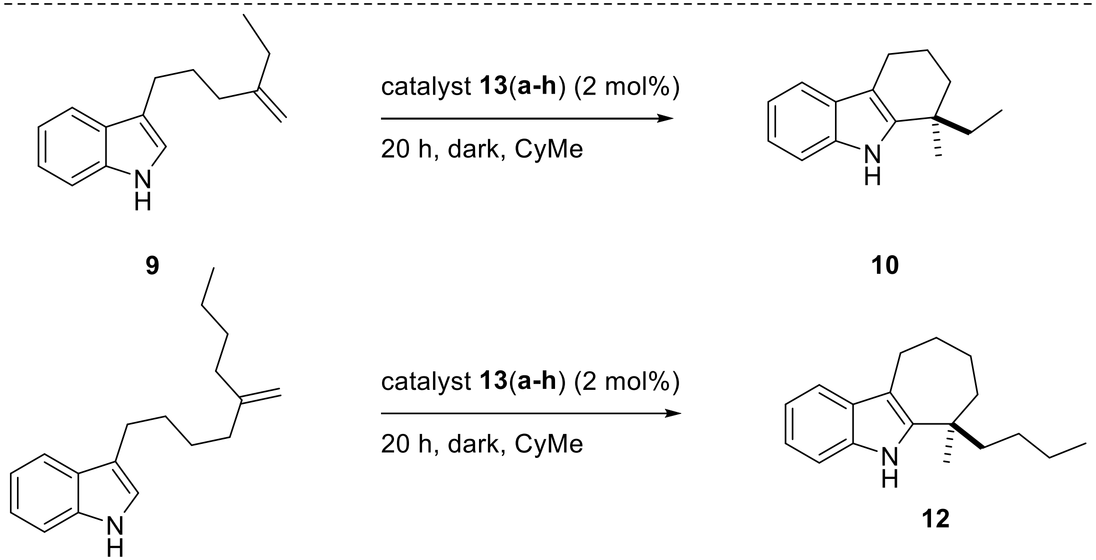
Outlook



13(a-h)



a **b** **c** **d** **e** **f** **g** **h**



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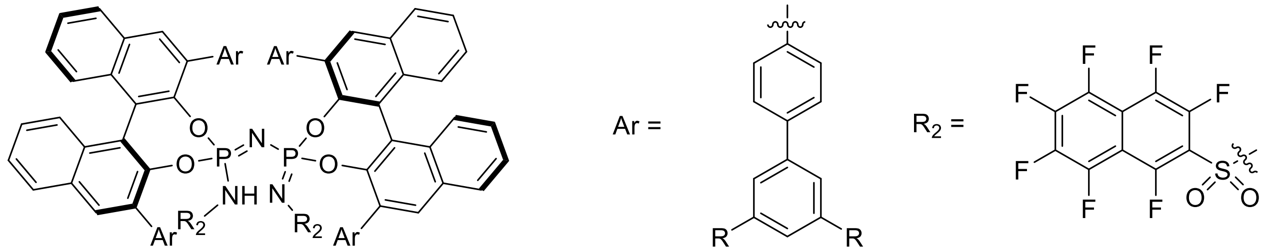
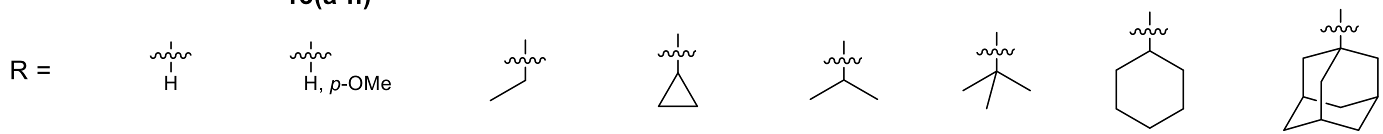
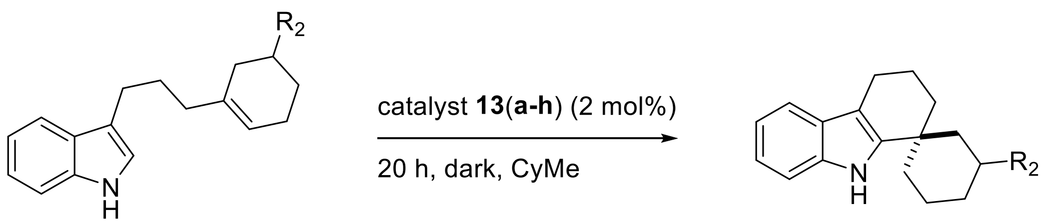
Outlook



13(a-h)



a **b** **c** **d** **e** **f** **g** **h**



77 **78**

P. Zhang, N. Tsuji, J. Quyang, B. List, *J. Am. Chem. Soc.* **2021**, *143*, 675−680.

Thank you!

Prof. Peter R. Schreiner

Friedhelm

Subgroup Friedhelm

PRS Group