Seminar

Bismuth Redox Catalysis

报告人：何俊雄

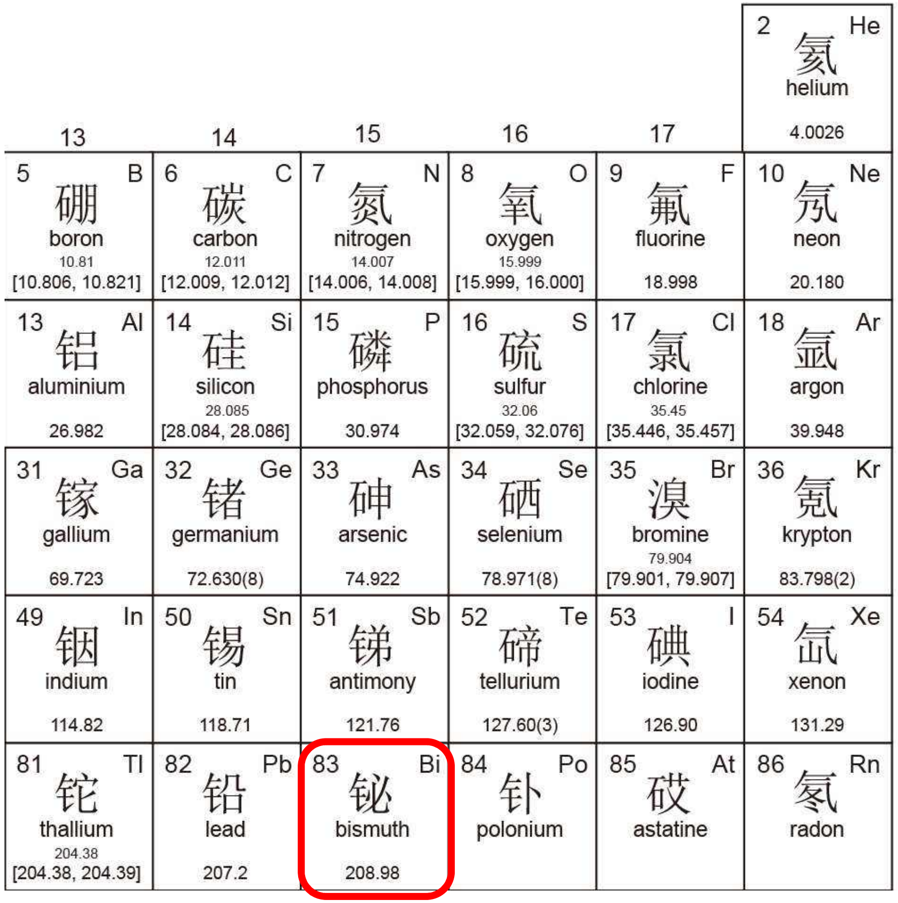
导　师：蔡　泉 青年研究员

2022.10.08

目录

- **背景介绍**
- **Bi(II)/Bi(III) 催化**
- **Bi(I)/Bi(III) 催化**
- **Bi(III)/Bi(V) 催化**
- **总结和展望**

铋的化学性质

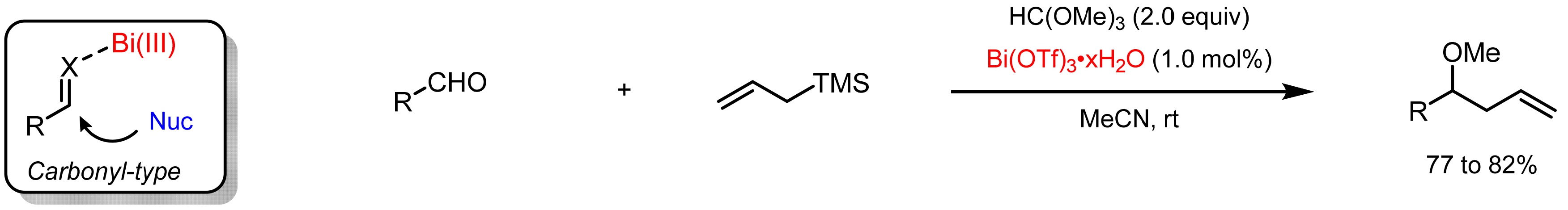


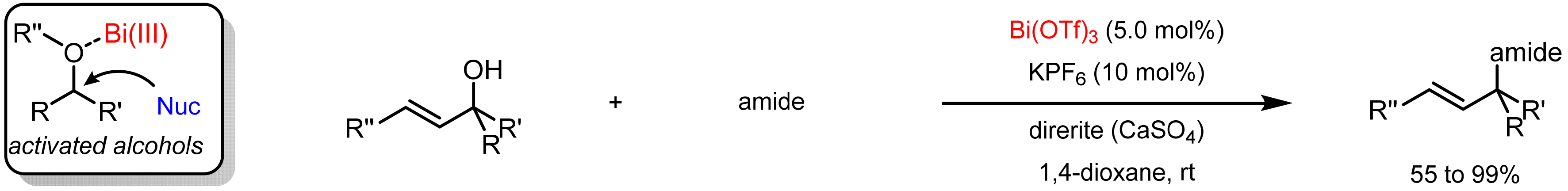
13	14	15	16	17	
					2 He 氦 helium 4.0026
5 B 硼 boron 10.81 [10.806, 10.821]	6 C 碳 carbon 12.011 [12.009, 12.012]	7 N 氮 nitrogen 14.007 [14.006, 14.008]	8 O 氧 oxygen 15.999 [15.999, 16.000]	9 F 氟 fluorine 18.998	10 Ne 氖 neon 20.180
13 Al 铝 aluminium 26.982	14 Si 硅 silicon 28.085 [28.084, 28.086]	15 P 磷 phosphorus 30.974	16 S 硫 sulfur 32.06 [32.059, 32.076]	17 Cl 氯 chlorine 35.45 [35.446, 35.457]	18 Ar 氩 argon 39.948
31 Ga 镓 gallium 69.723	32 Ge 锗 germanium 72.630(8)	33 As 砷 arsenic 74.922	34 Se 硒 selenium 78.971(8)	35 Br 溴 bromine 79.904 [79.901, 79.907]	36 Kr 氪 krypton 83.798(2)
49 In 铟 indium 114.82	50 Sn 锡 tin 118.71	51 Sb 锑 antimony 121.76	52 Te 碲 tellurium 127.60(3)	53 I 碘 iodine 126.90	54 Xe 氙 xenon 131.29
81 Tl 铊 thallium 204.38 [204.38, 204.39]	82 Pb 铅 lead 207.2	83 Bi 铋 bismuth 208.98	84 Po 钋 polonium	85 At 砹 astatine	86 Rn 氡 radon

- 位于第六周期第五主族，最外层电子排布$6s^2 6p^3$
- 有多种氧化态，如Bi(I)、Bi(II)、 Bi(III)和Bi(V)
- 相比于低价态的第三、四主族元素易发生氧化，高价态的第六、七主族元素易发生还原的性质，第五主族元素不同氧化态间既能发生氧化也可以还原，具有作为氧化还原催化剂的潜力

a) J. V. Crivello. *J. Polym. Sci., Part A: Polym. Chem*. **2009**, *47*, 5639-5651; b) Y. Peng, J.-D. Guo, B. D. Ellis, Z. Zhu, J. C. Fettinger, S. Nagase, P. P. Power. *J. Am. Chem. Soc*. **2009**, *131*, 16272-16282; c) A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge. *J. Am. Chem. Soc*. **2012**, *134*, 6500-6503; d) M. R. Crimmin, M. J. Butler, A. J. P. White. *Chem. Commun*. **2015**, *51*, 15994-15996; e) D. Kaiser, I. Klose, R. Oost, J. Neuhaus, N. Maulide. *Chem. Rev*. **2019**, *119*, 8701-8780.

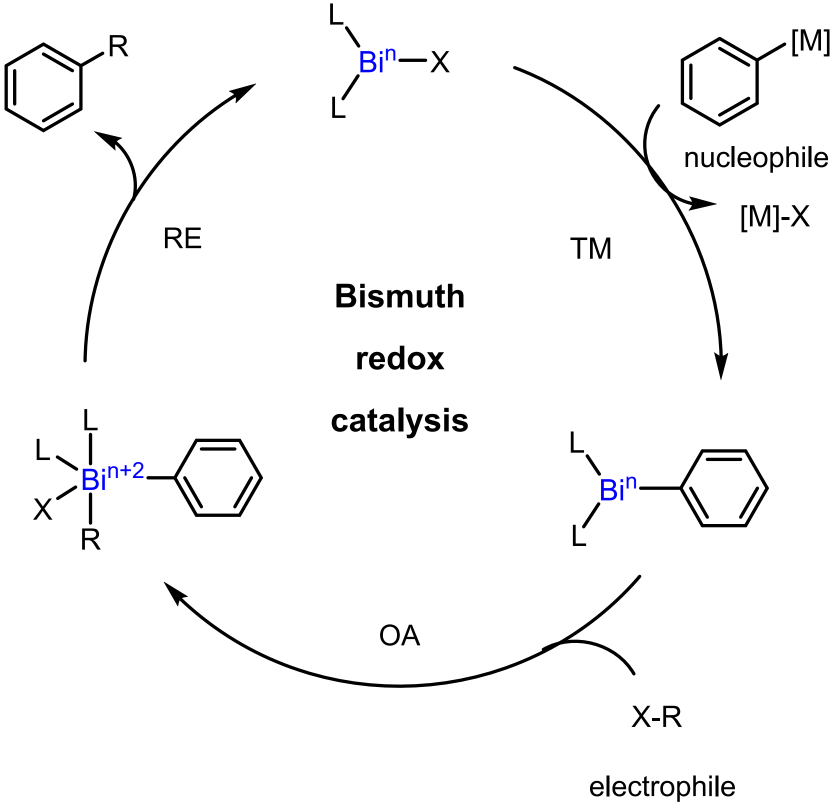
铋(III)作为路易斯酸催化剂





a) P. W. Anzalone, A. R. Baru, E. M. Danielson, P. D. Hayes, M. P. Nguyen, A. F. Panico, R. C. Smith, R. S. Mohan, *J. Org. Chem*. **2005**, *70*, 2091-2096; b) H. Qin, N. Yamagiwa, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc*. **2006**, *128*, 1611-1614; c) H. Qin, N. Yamagiwa, S. Matsunaga, M. Shibasaki, *Angew. Chem. Int. Ed*. **2007**, *46*, 409-413.

铋的氧化还原催化循环



♣ **优势：**

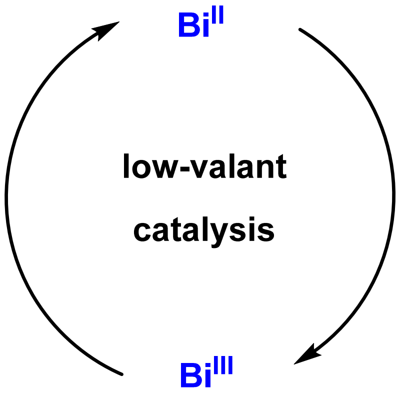
- 无毒
- 含量丰富，廉价易得

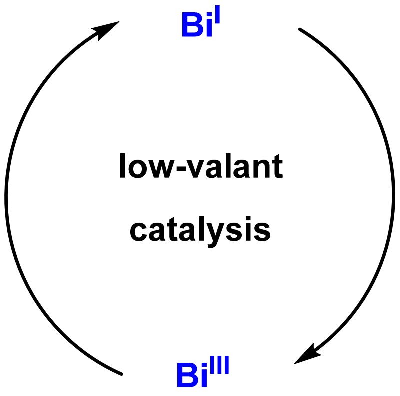
♣ **挑战：**

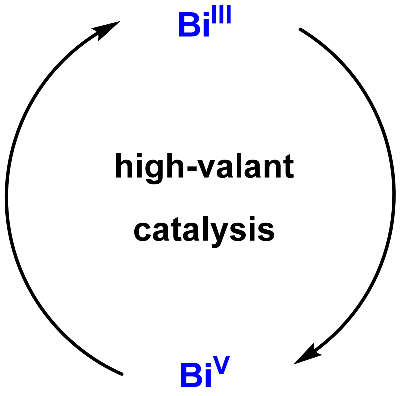
- 氧化还原闭环
- p区元素前线轨道能差大
- Bi-X的转金属化

a) P. de Marcillac, N. Coron, G. Dambier, J. Leblanc, J.-P. Moalic, *Nature* **2003**, *422*, 876-878;
b) M. Mehring, *Coord. Chem. Rev*. **2007**, *251*, 974-1006; c) R. Mohan, *Nat. Chem*. **2010**, *2*, 336.

目前发展的Bi的氧化还原催化循环







Bi(II)具有自由基性质

可以催化自由基类型的反应

Bi(I)具有较强的还原性

可以直接用作还原试剂

Bi(V)具有较强的氧化性

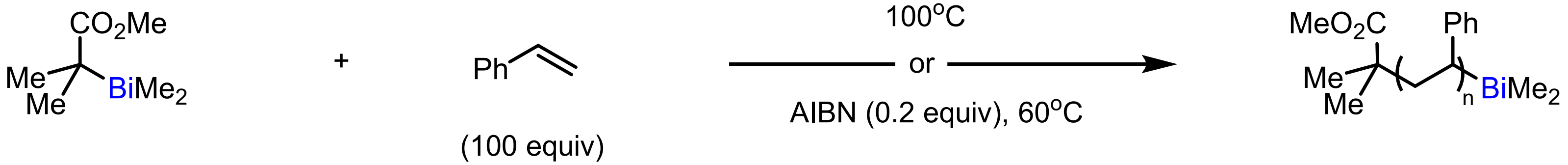
芳基Bi(V)可用作氧化剂

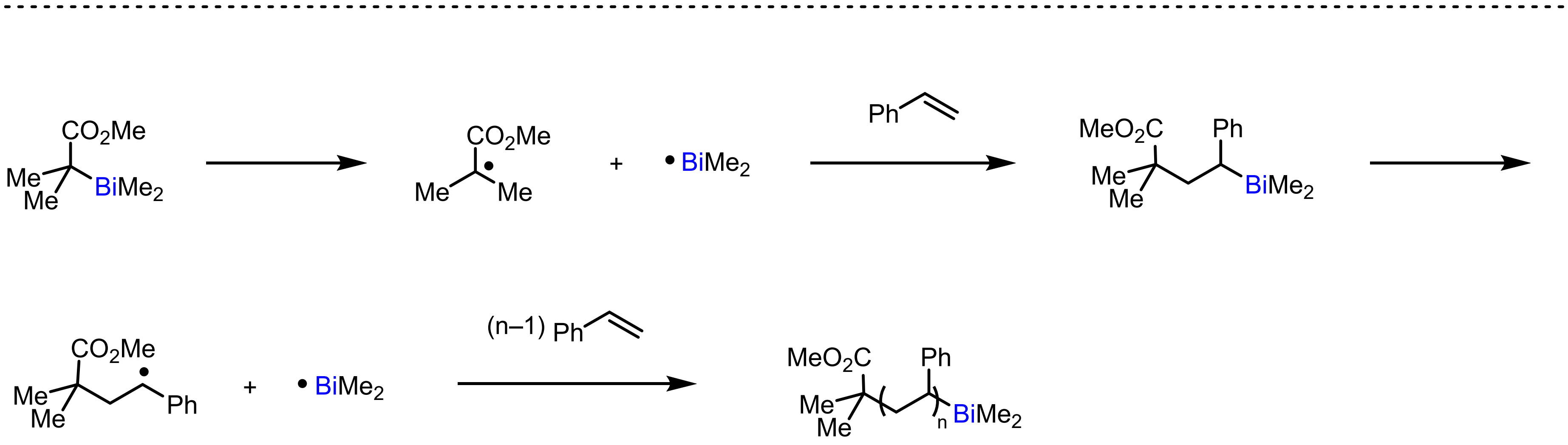
和芳基化试剂

目录

- 背景介绍
- **Bi(II)/Bi(III) 催化**
- Bi(I)/Bi(III) 催化
- Bi(III)/Bi(V) 催化
- 总结和展望

铋(II)的自由基性质

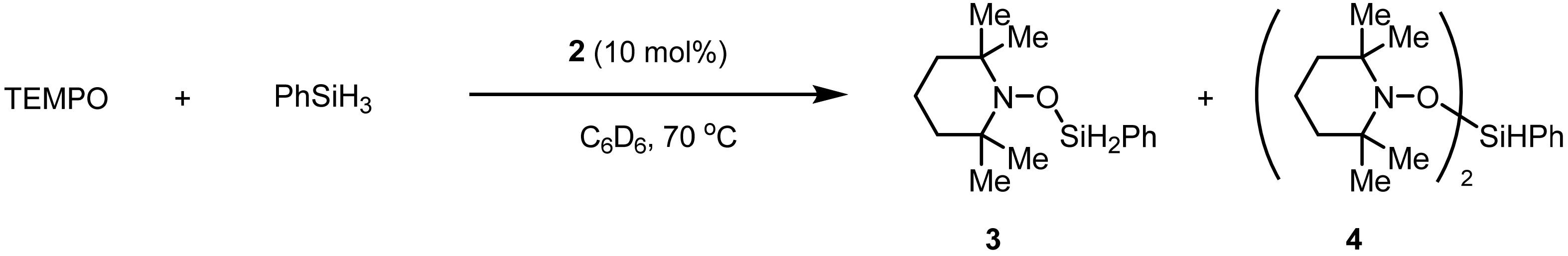


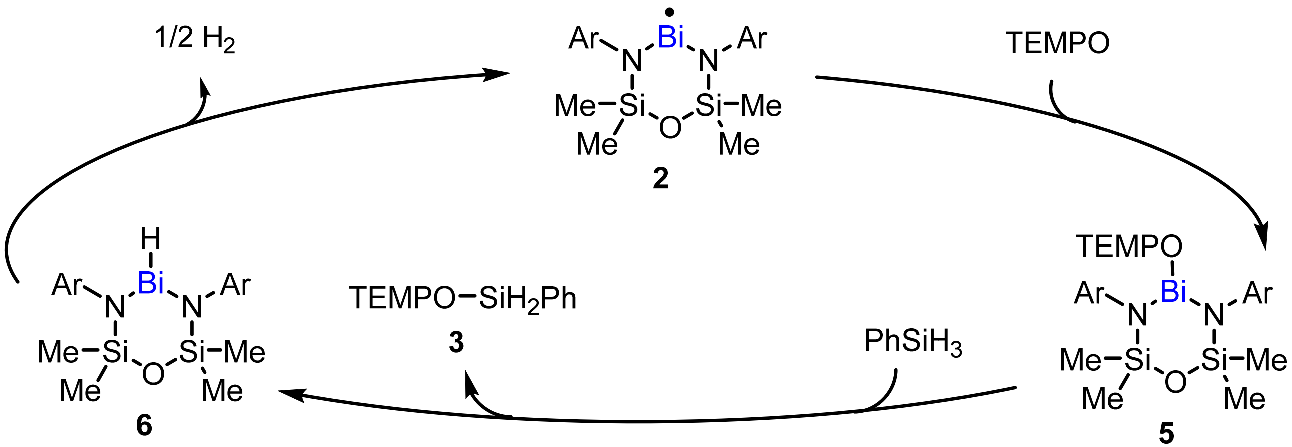


Bi(III)经过热解或AIBN引发均裂形成自由基性质的Bi(II)，介导了苯乙烯参与的多聚反应

S. Yamago, E. Kayahara, M. Kotani, B. Ray, Y. Kwak, A. Goto, T. Fukuda, *Angew. Chem. Int. Ed.* **2007**, *46*, 1304-1306.

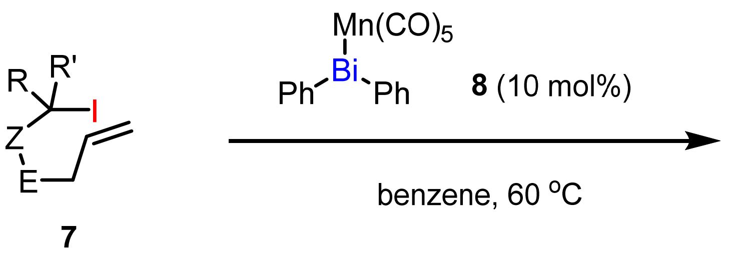
Bi(II)催化的TEMPO与苯基硅烷的脱氢偶联

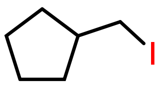




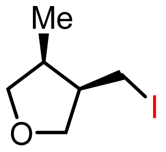
a) R. J. Schwamm, J. R. Harmer, M. Lein, C. M. Fitchett, S. Granville, M. P. Coles. *Angew. Chem., Int. Ed*. **2015**, *54*, 10630-10633;
b) R. J. Schwamm, M. Lein, M. P. Coles, C. M. Fitchett, *Chem. Commun*. **2018**, *54*, 916-919.

Bi催化的δ-碘代烯烃的环化反应



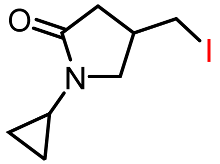


9a, 96%

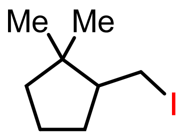


9b, 99%

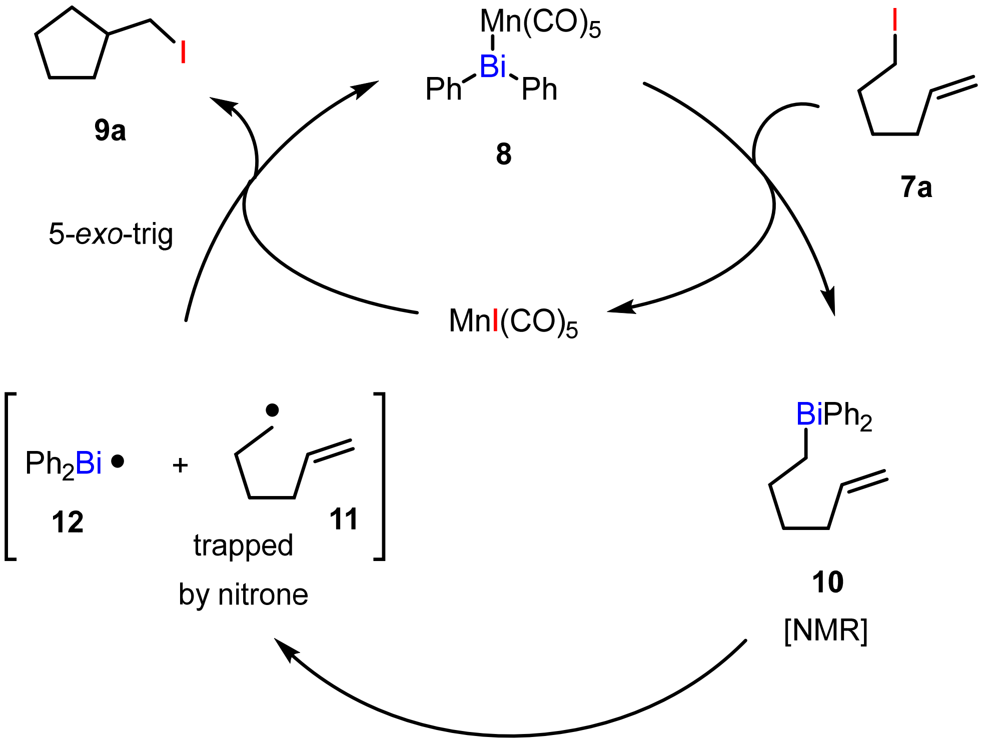
cis/trans = 2.7:1



9c, 95%



9d, 96%

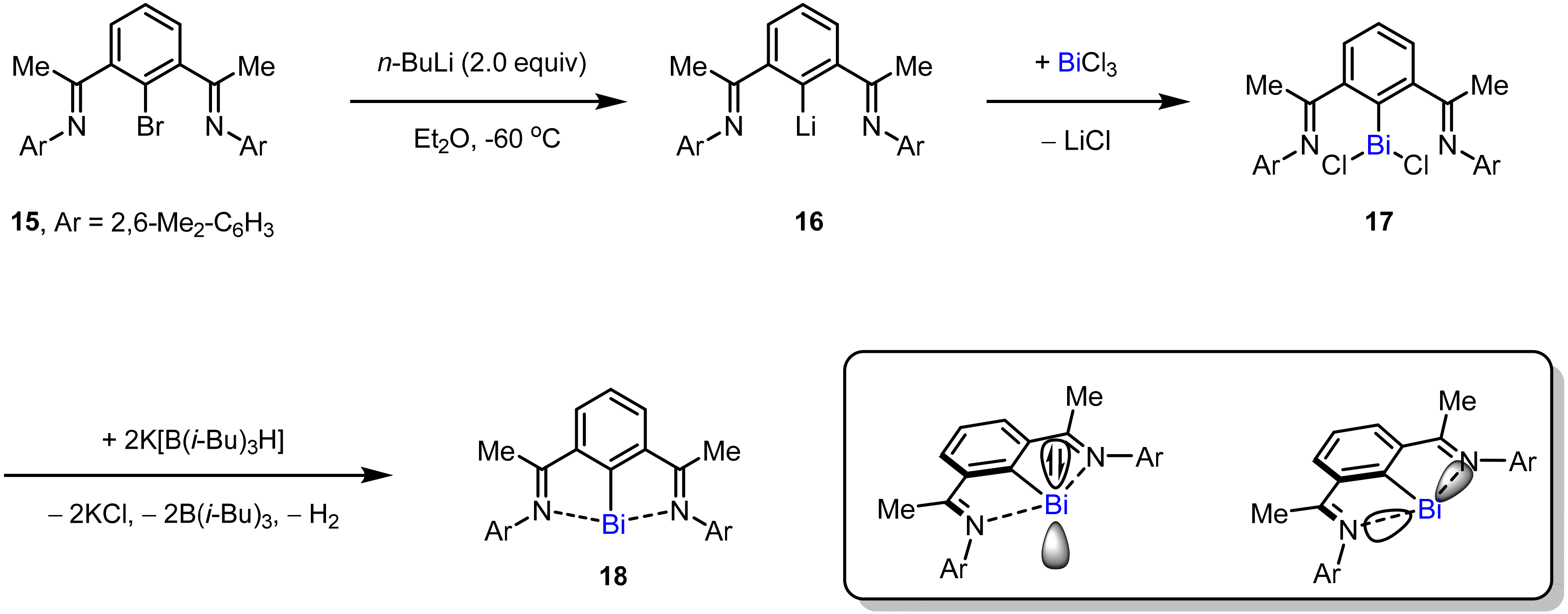


核磁共振氢谱监测到烷基Bi(III)的形成，烷基自由基可以被硝酮捕获

J. Ramler, I. Krummenacher, C. Lichtenberg. *Angew. Chem. Int. Ed*. **2019**, *58*, 12924-12929.

目录

Bi(I)单体的合成



15, Ar = 2,6-Me_2-C_6H_3

16

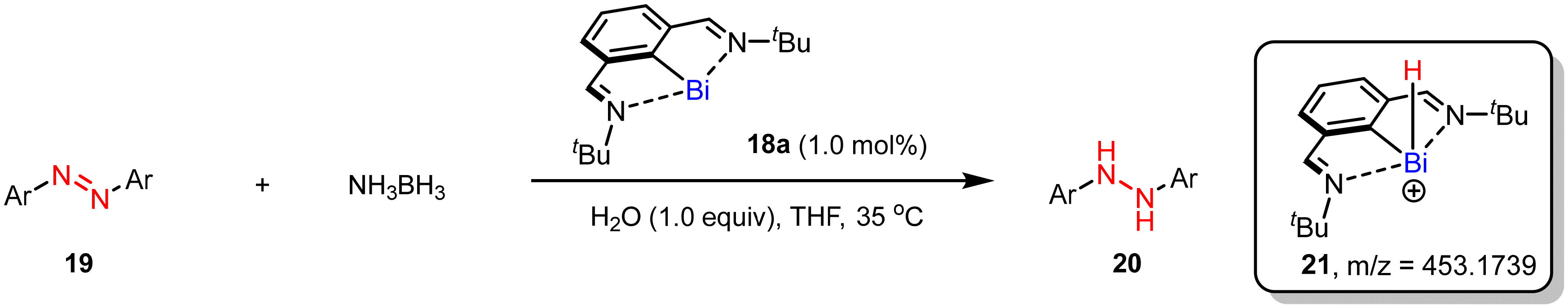
17

18

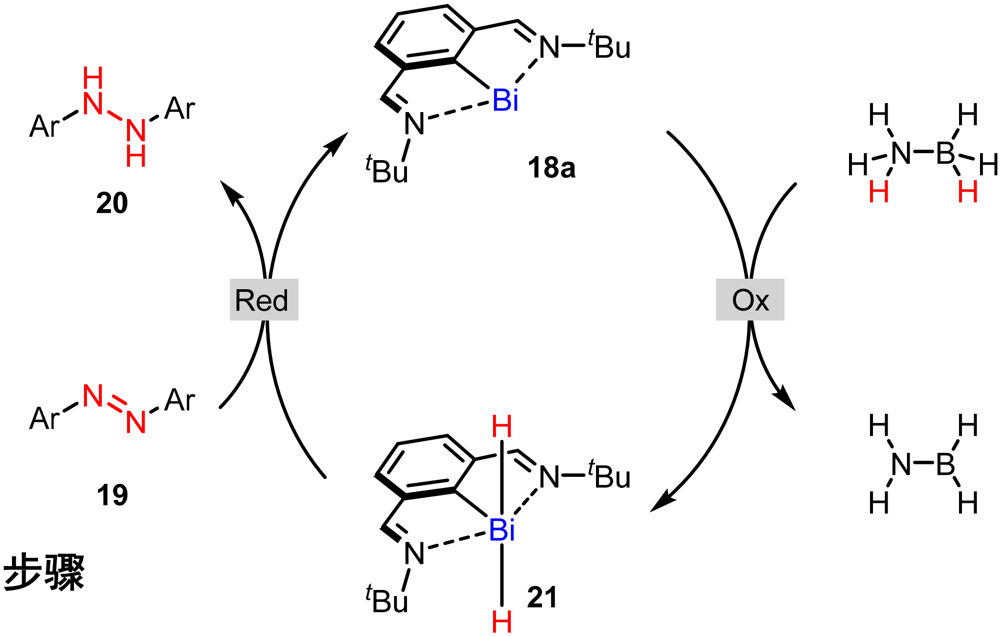
Bi(I)的孤对电子通过与配体上π键的离域作用稳定，空轨道则与配体上的N原子通过配位作用来稳定Bi(I)

P. Šimon, F. de Proft, R. Jambor, A. Růžička, L. Dostál, *Angew. Chem. Int. Ed.* **2010**, *49*, 5468-5471.

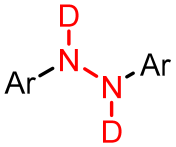
Bi(I)催化的氨基硼烷和重氮芳烃转移氢化反应



21, m/z = 453.1739



ND_3BD_3 instead of NH_3BH_3

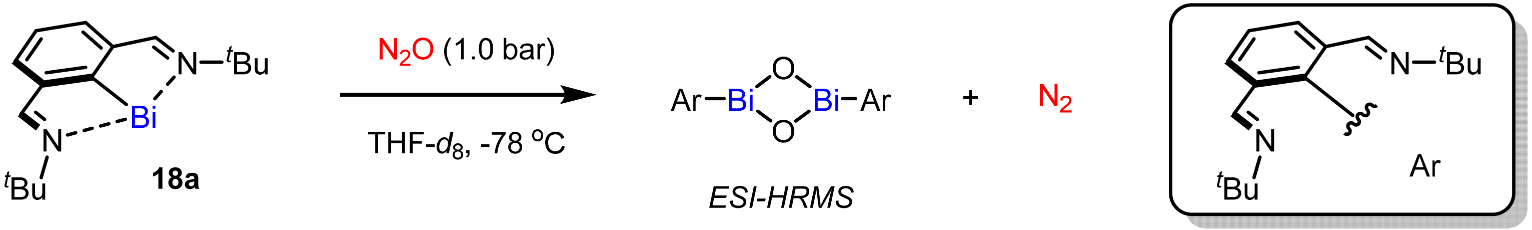


KIE = 7.05

Bi(I)被氨基硼烷氧化是反应的决速步骤

F. Wang, O. Planas, J. Cornella, *J. Am. Chem. Soc.* **2019**, *141*, 4235-4240.

Bi(I)催化N_2O的还原反应



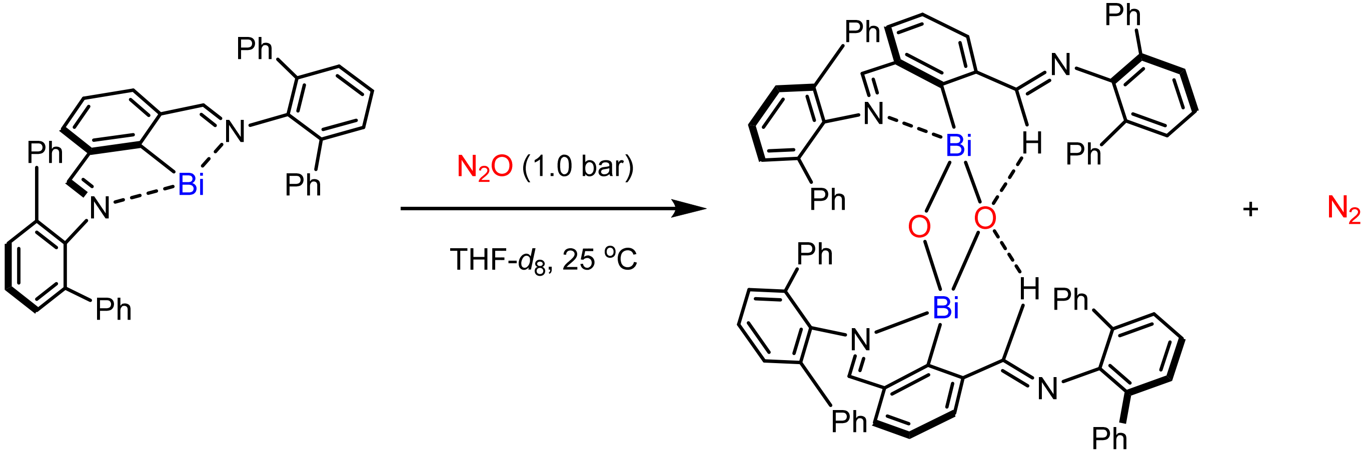
18a

N_2O (1.0 bar)

THF-d_8, -78 °C

ESI-HRMS

无法确定具体结构

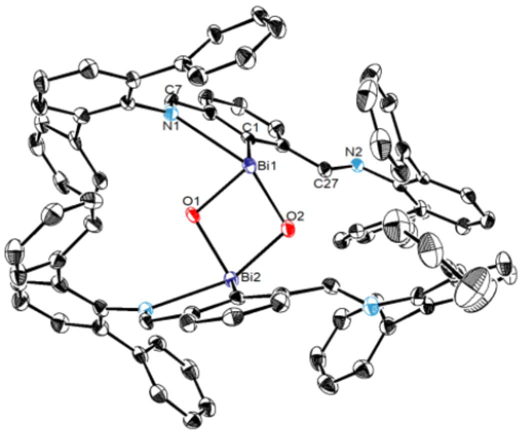


N_2O (1.0 bar)

THF-d_8, 25 °C

18b

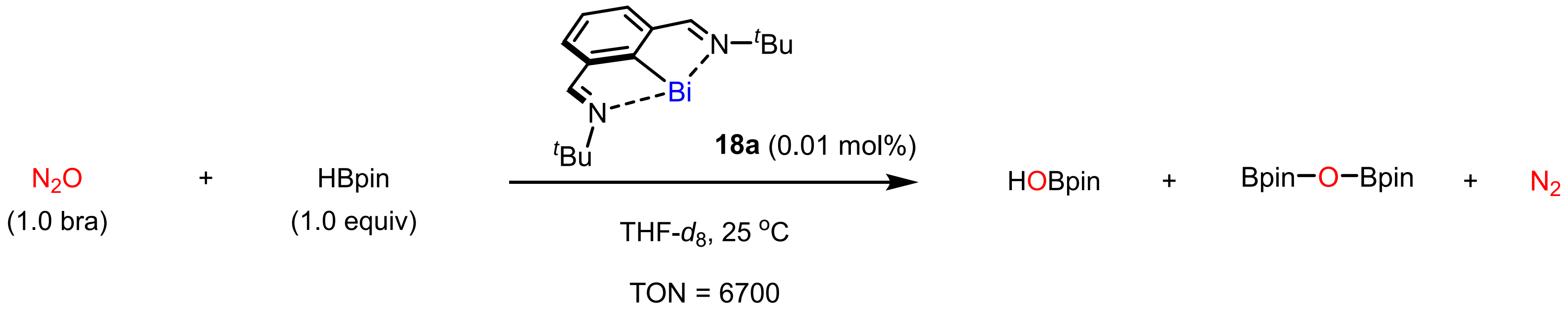
22

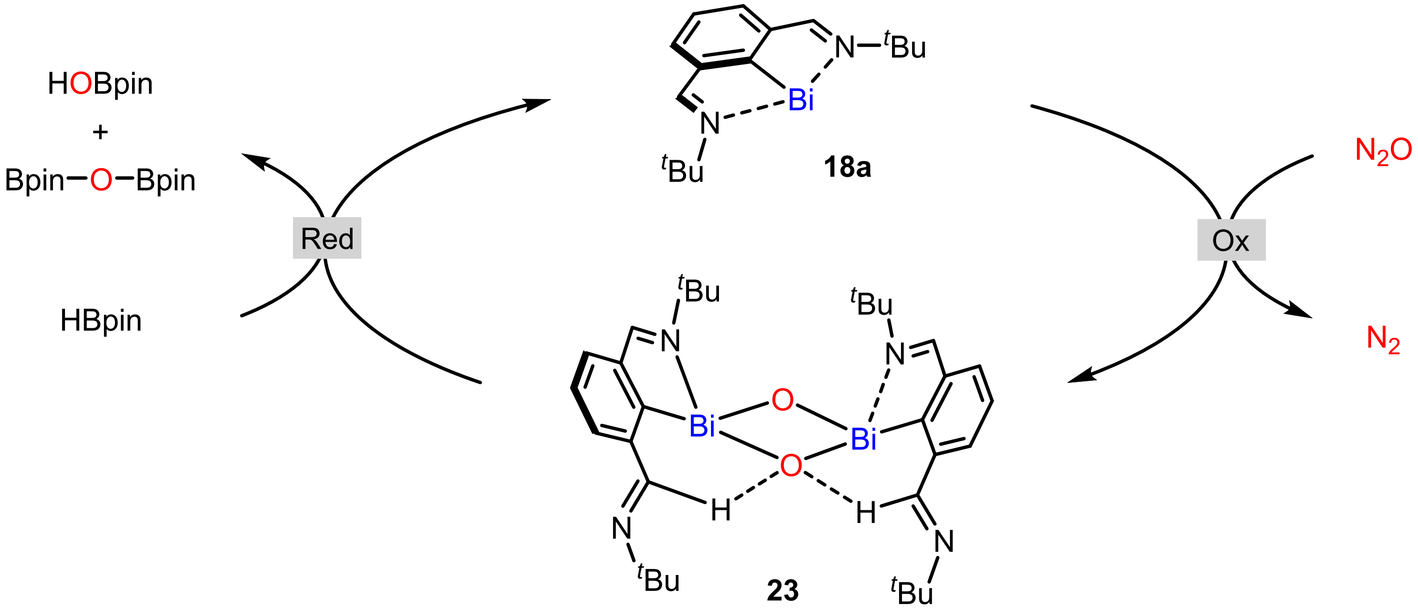


X-ray of **22**

Y. Pang, M. Leutzsch, N. Nöthling, J. Cornella, *J. Am. Chem. Soc.* **2020**, *142,* 19473-19479.

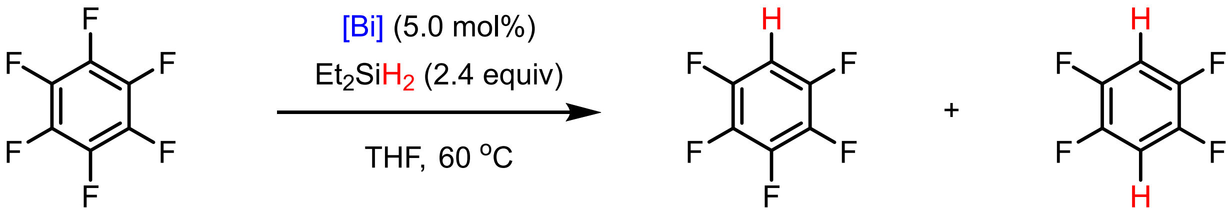
Bi(I)催化N_2O的还原反应



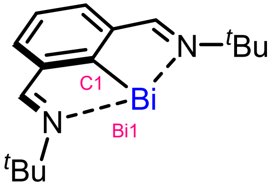
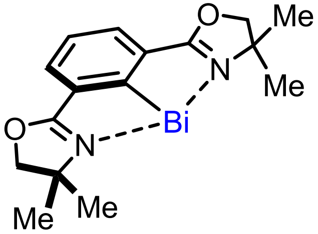
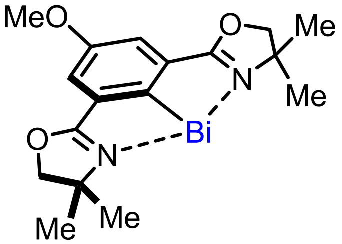


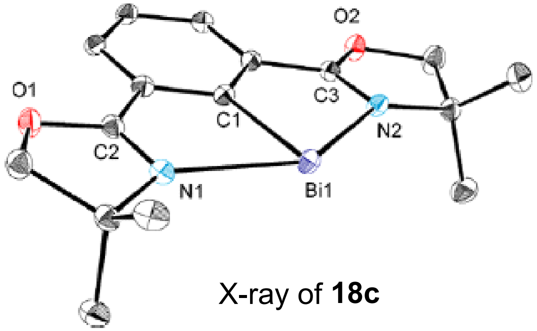
Y. Pang, M. Leutzsch, N. Nöthling, J. Cornella, *J. Am. Chem. Soc.* **2020**, *142,* 19473-19479.

Bi(I) 催化氟代芳烃的脱氟氢化反应

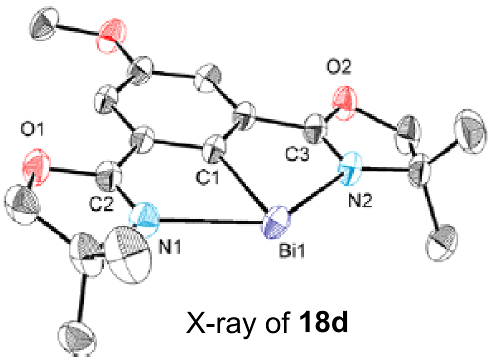


24 **25** **25'**

[Bi]	 **18a**	 **18c**	 **18d**
yield of **25**	<1%	40%	74% (16% of **25'**)
C1-Bi1 (Å)	2.146	2.193	2.201



X-ray of **18c**

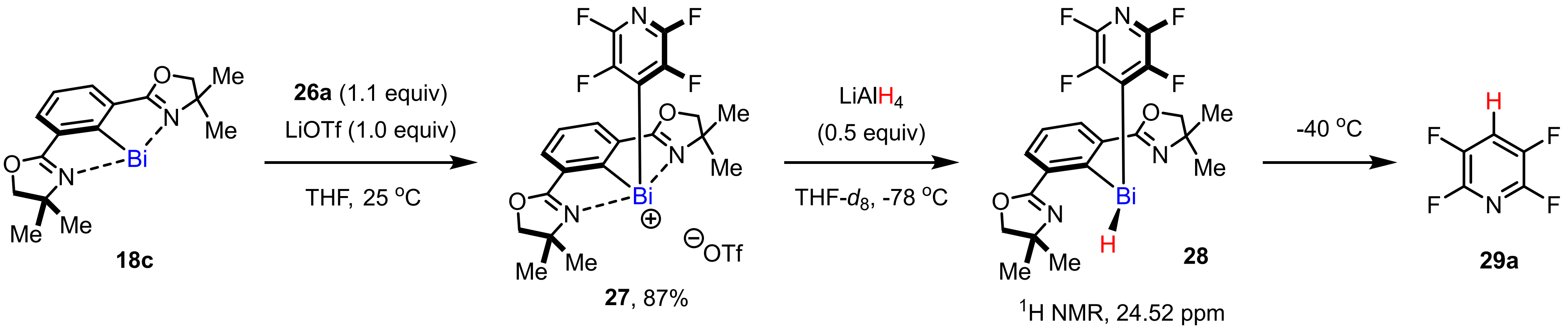


X-ray of **18d**

脱氟氢化反应产率与催化剂的C1-Bi1键长成正比，当碳铋键增长时，Bi(I)与苯环之间的离域作用减弱，增大Bi的电荷密度，提高了与C-F键氧化加成的活性

Y. Pang, M. Leutzsch, N. Nöthling, F. Katzenburg, J. Cornella, *J. Am. Chem. Soc.* **2021**, *143*, 12487-12493.

Bi(I) 催化氟代芳烃的脱氟氢化反应



18c

26a (1.1 equiv)
LiOTf (1.0 equiv)
THF, 25 °C

27, 87%

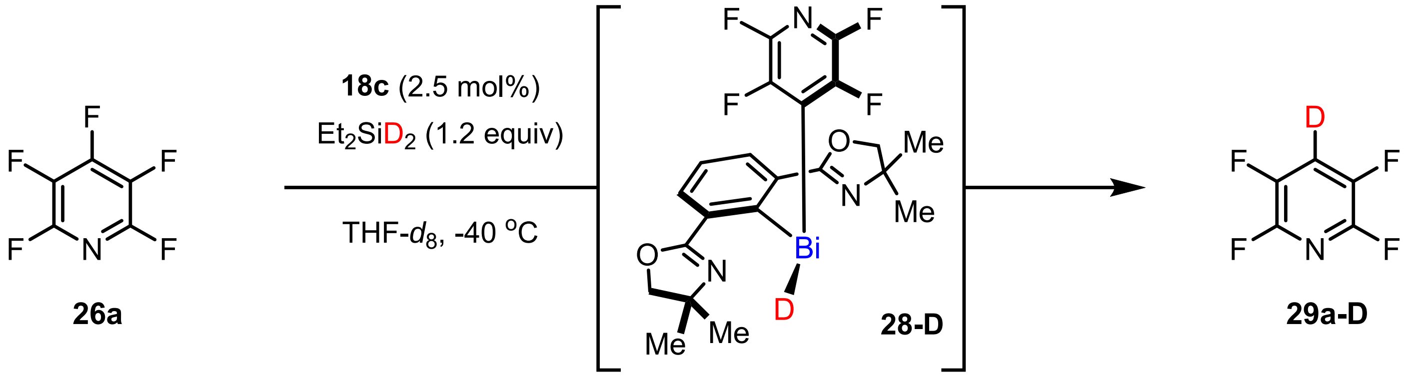
LiAlH$_4$
(0.5 equiv)
THF-d_8, -78 °C

28

^{1}H NMR, 24.52 ppm

-40 °C

29a



26a

18c (2.5 mol%)
Et$_2$SiD$_2$ (1.2 equiv)
THF-d_8, -40 °C

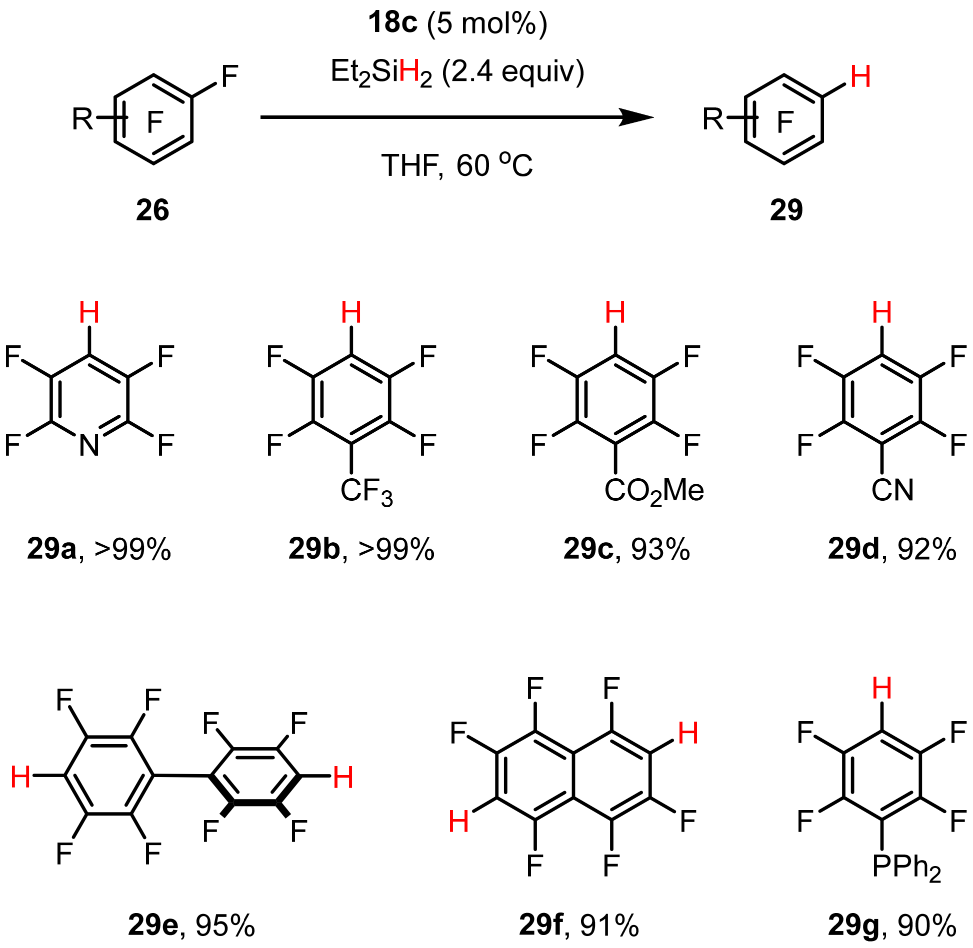
28-D

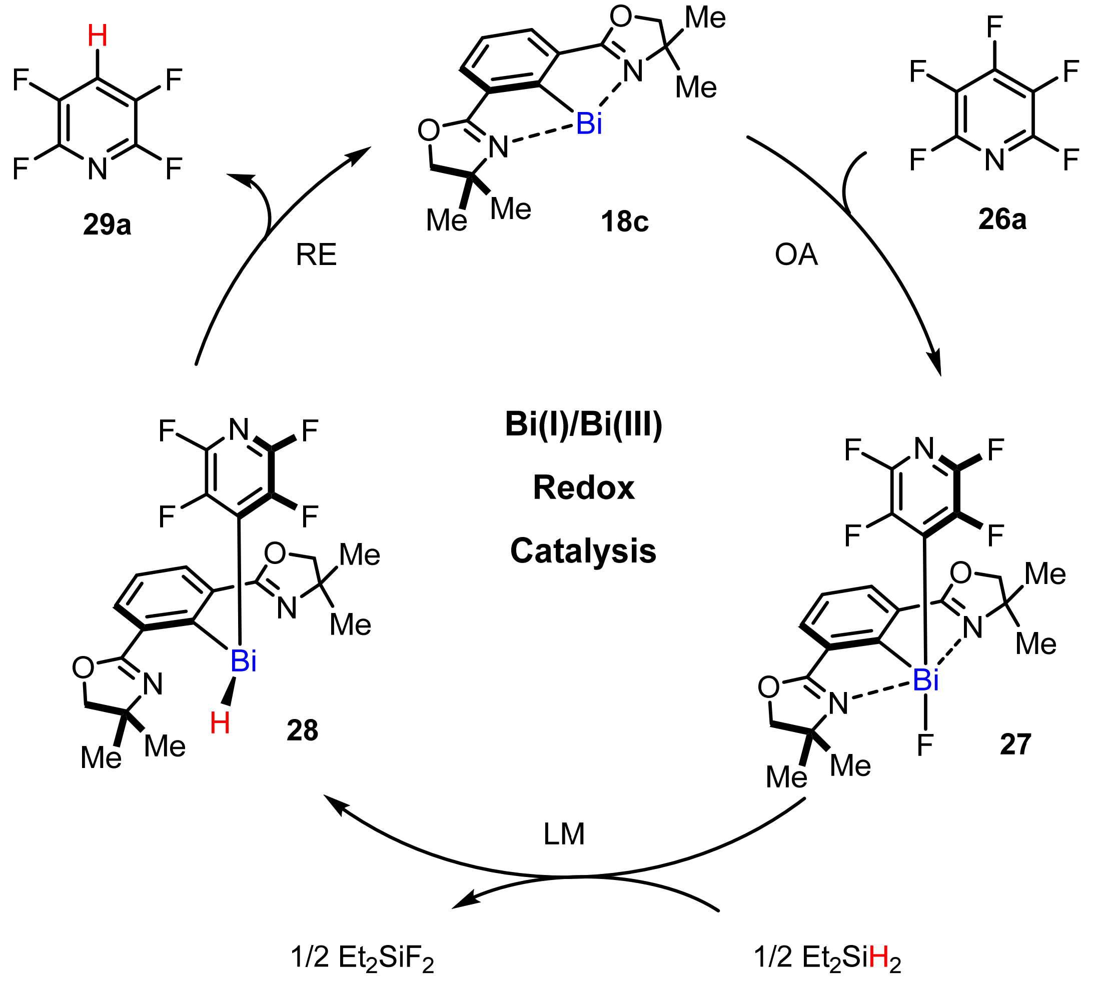
29a-D

反应经过Bi(III)-H中间体，氢来源于二乙基硅烷

Y. Pang, M. Leutzsch, N. Nöthling, F. Katzenburg, J. Cornella, *J. Am. Chem. Soc.* **2021**, *143*, 12487-12493.

Bi(I) 催化氟代芳烃的脱氟氢化反应

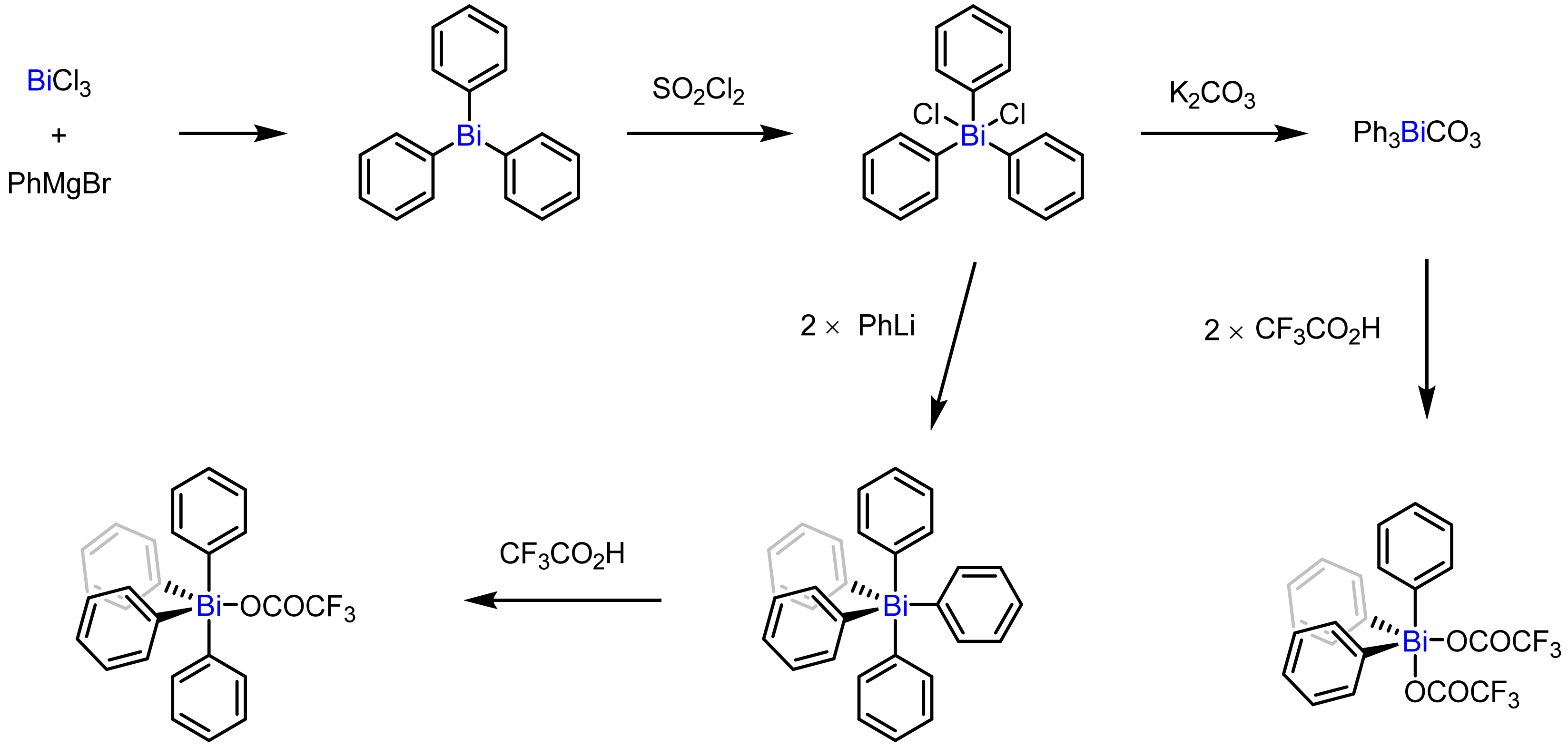




Y. Pang, M. Leutzsch, N. Nöthling, F. Katzenburg, J. Cornella, *J. Am. Chem. Soc.* **2021**, *143*, 12487-12493.

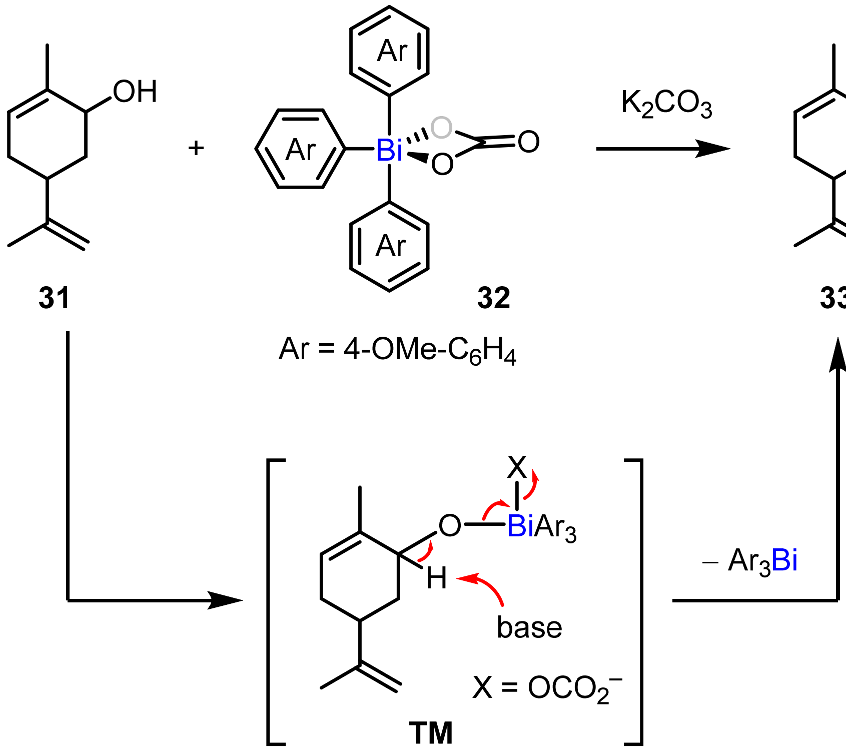
目录

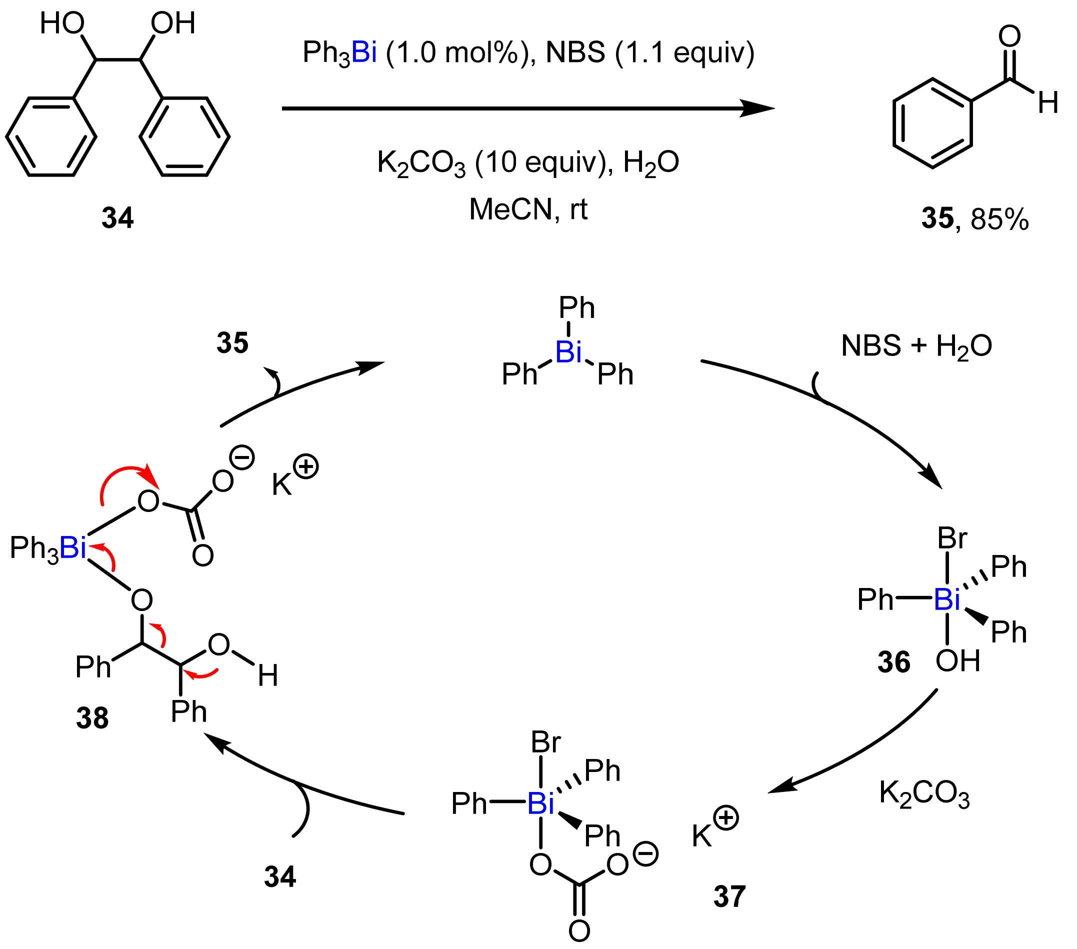
Bi(V) 化合物的合成



D. H. R. Barton, B. Charpiot, K. U. Ingold, L. J. Johnston, W. B. Motherwell, J. C. Scaiano, S. P. Stanforth, *J. Am. Chem. Soc*. **1985**, *107*, 3607-3611.

铋(V)化合物作为氧化剂

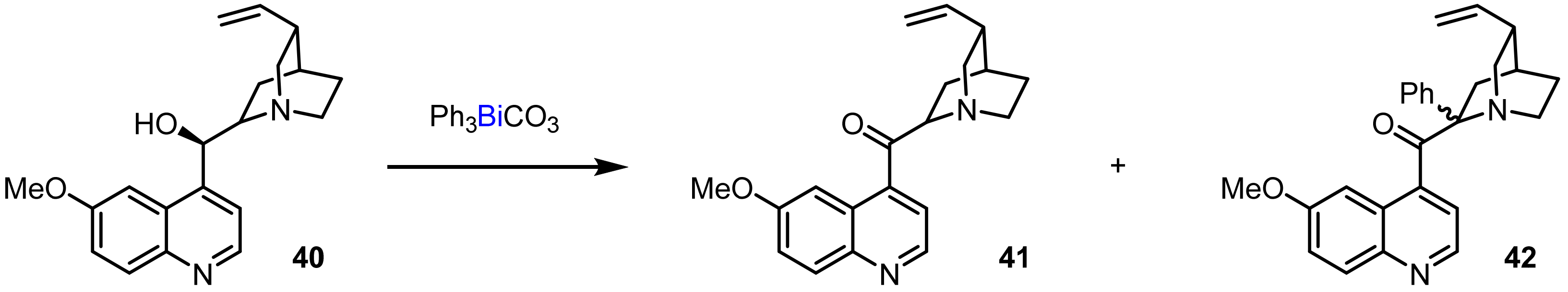




Bi(V)化合物可以作为氧化剂氧化羟基

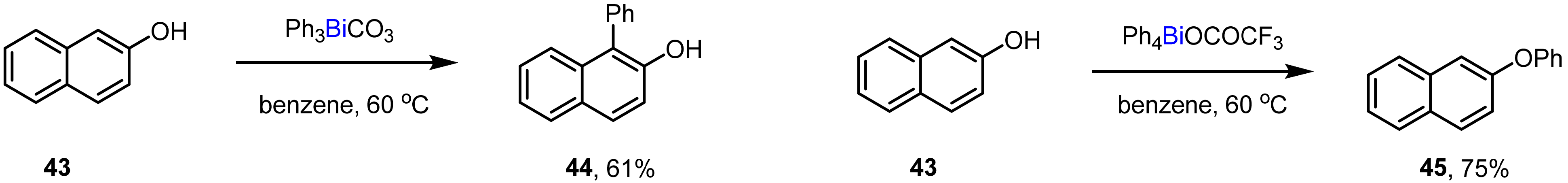
a) D. H. R. Barton, J. P. Kitchin, D. J. Lester, W. B. Motherwell, M. T. B. Papoula. *Tetrahedron.* **1981**, *37*, 73-79;
b) D. H. R. Barton, W. B. Motherwell, A. Stobie. *J. Chem. Soc. Chem. Commun.* **1981**, 1232-1233.

Bi(V) 化合物作为芳基化试剂



38% with 1.0 equiv Ph_3BiCO_3

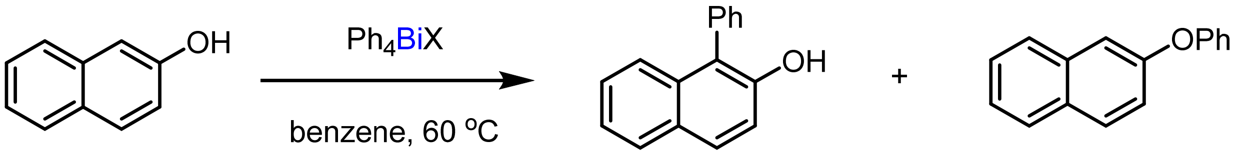
with 3.0 equiv Ph_3BiCO_3



Bi(V)化合物的配体会影响芳基化的选择性

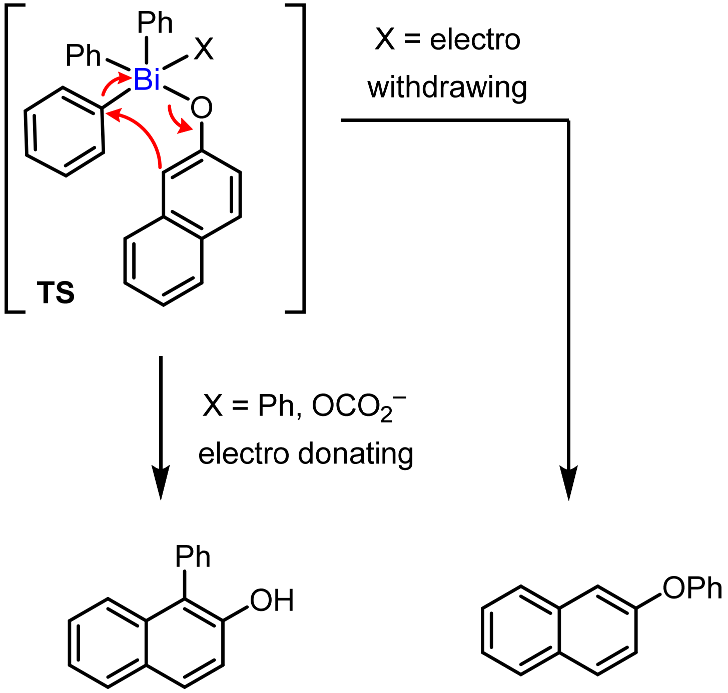
a) D. H. R. Barton, D. J. Lester, W. B. Motherwell, M. T. B. Papoula. *J. Chem. Soc. Chem. Comm.* **1981**, 246-247;
b) D. H. R. Barton, B. Charpiot, W. B. Motherwell, *Tetrahedron Lett*. **1982**, *23*, 3365-3368.

Bi(V) 配体对芳基化反应的影响



43 **44** **45**

Ph_4BiX	yield of **43** (%)	yield of **44** (%)	yield of **45** (%)
X = $OCOCH_3$	19	25	26
X = $OCOCF_3$	-	-	75
X = OSO_2-C_6H_4-*p*-Me	58	-	42
X = OSO_2CF_3	95	-	-
X = Ph	-	77	-
X = OCO_2^-	-	75	-

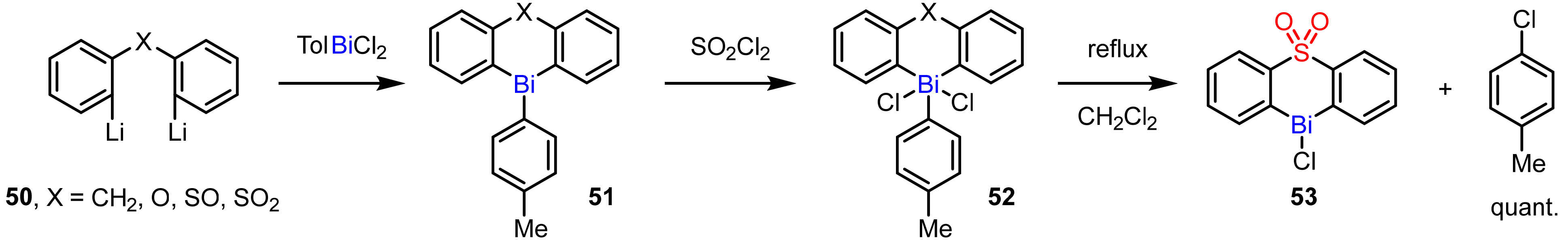


X = electro withdrawing

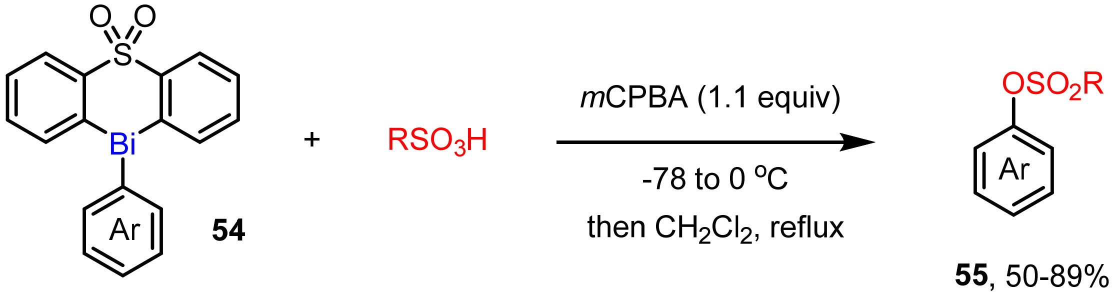
X = Ph, OCO_2^- electro donating

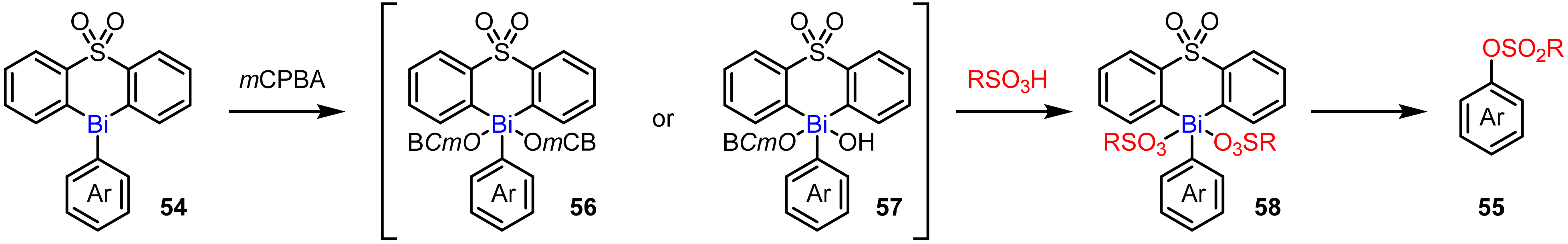
D. H. R. Barton, B. Charpiot, W. B. Motherwell, *Tetrahedron Lett*. **1982**, *23*, 3365-3368.

Bi(V)化合物的还原消除



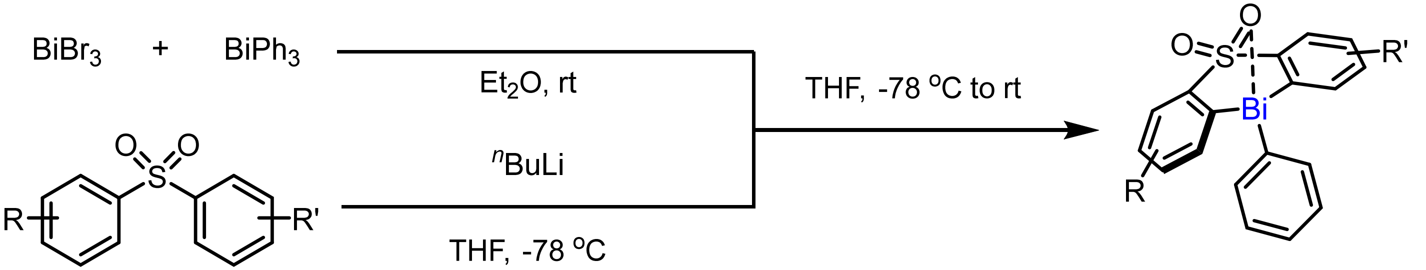
H. Suzuki, T. Murafuji, N. Azuma. *J. Chem. Soc. Perkin Trans. 1*, **1992**, 1593-1600.

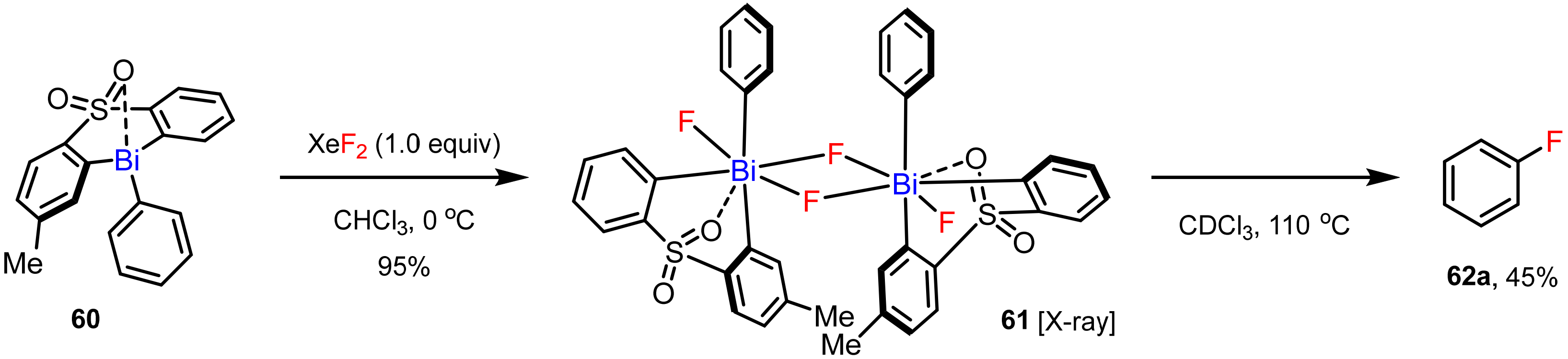




N. Sakurai, T. Mukaiyama. *Heterocycles* **2007**, *74*, 771-790.

Bi(V)氟化物的还原消除





60

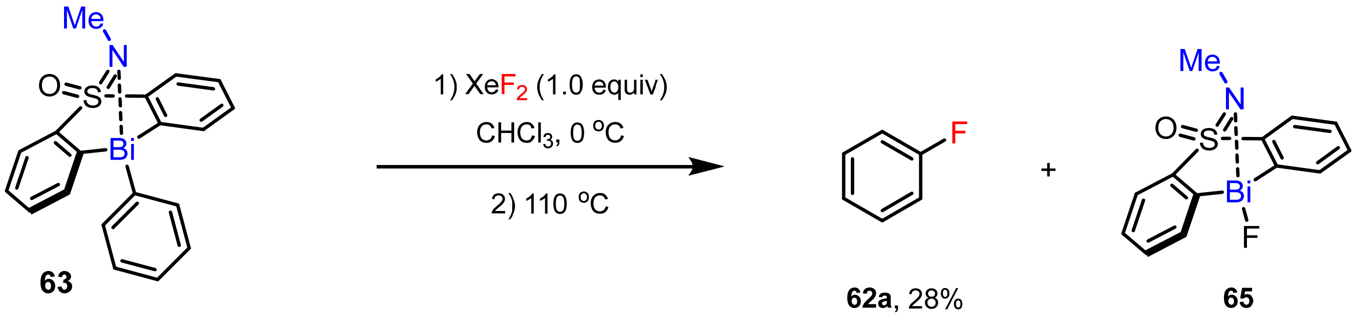
61 [X-ray]

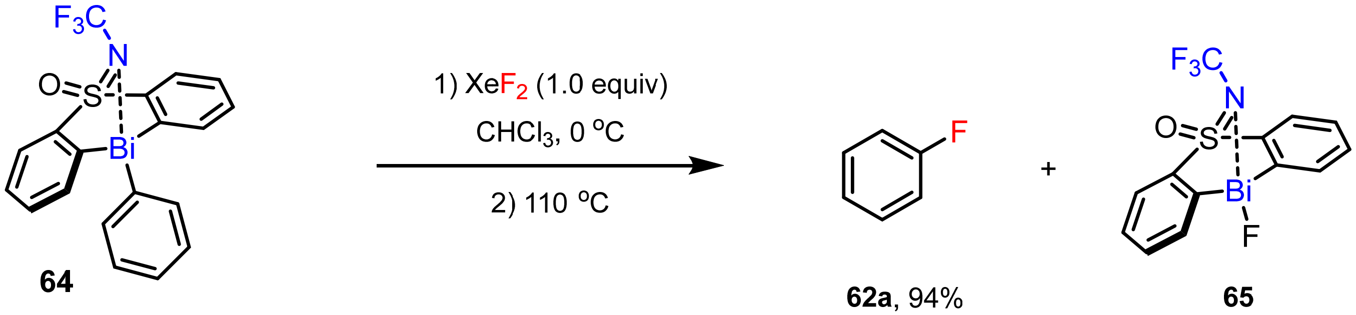
62a, 45%

Ph$_3$BiF$_2$在加热条件下未观察到氟苯的生成，砜基引入促进了Bi(V)氟化物发生还原消除

O. Planas, F. Wang, M. Leutzsch, J. Cornella. *Science* **2020**, *367*, 313-317.

芳基Bi(III)化合物的改造

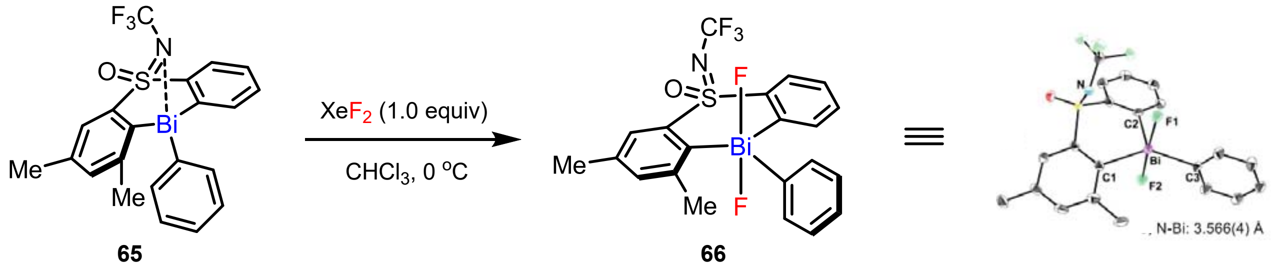


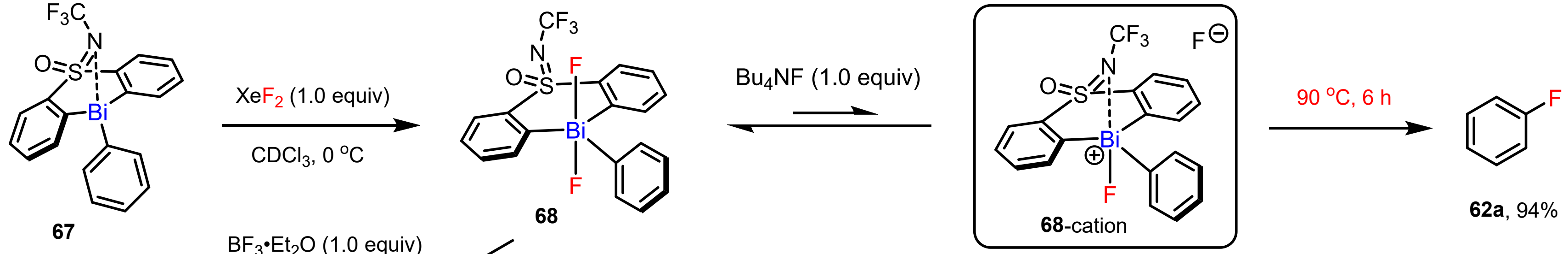


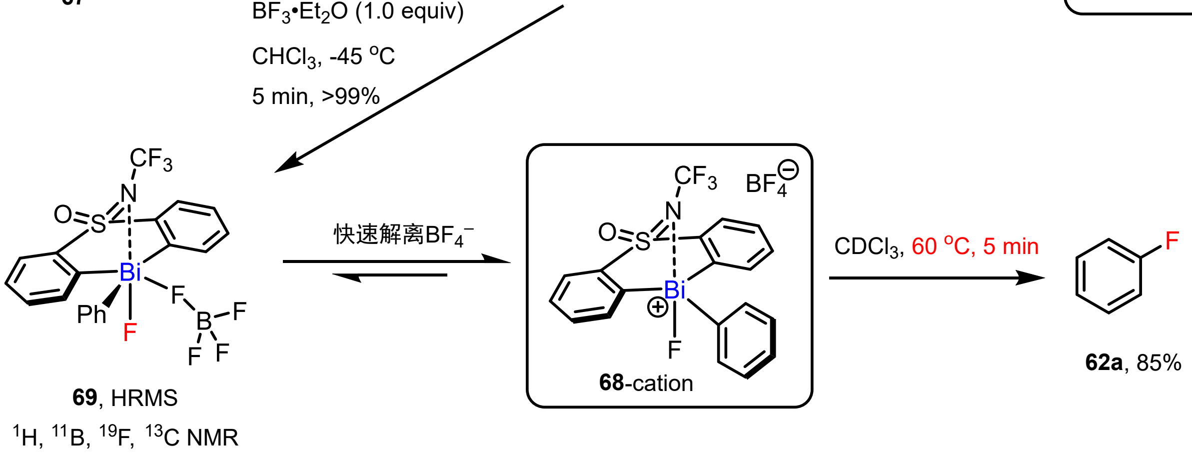
吸电性的三氟甲基进一步促进Bi(V)发生还原消除

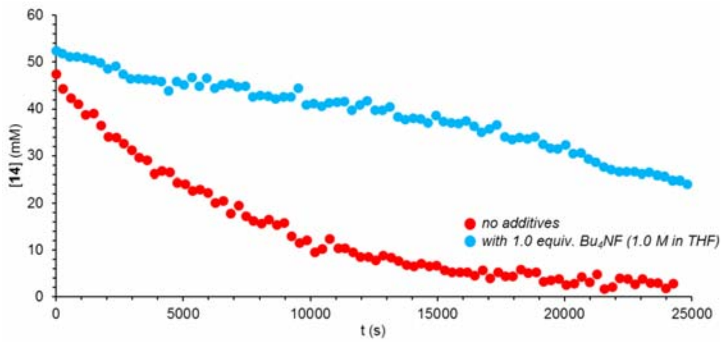
O. Planas, F. Wang, M. Leutzsch, J. Cornella. *Science* **2020**, *367*, 313-317.

Bi(V)氟化物还原消除的机理



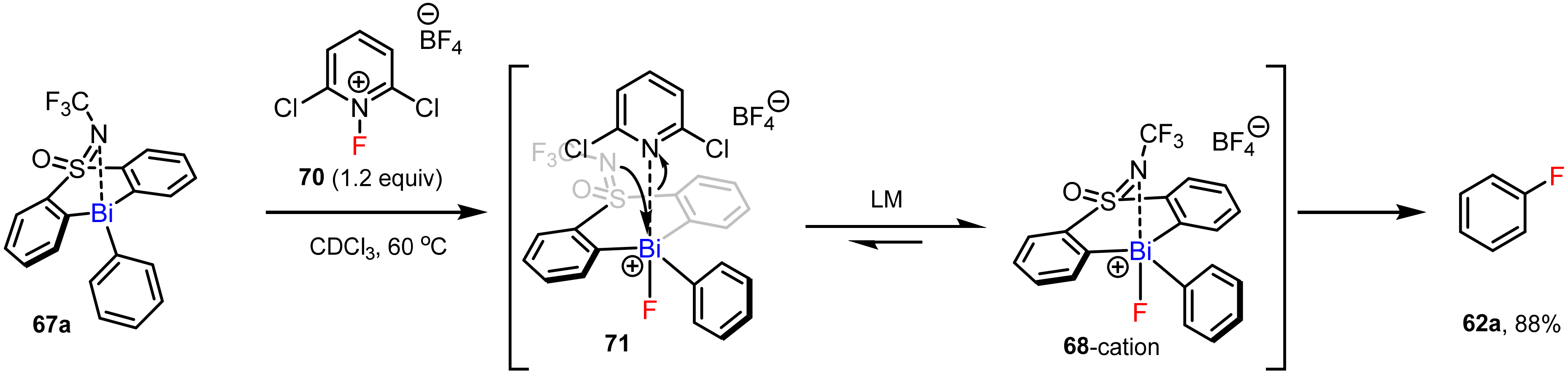


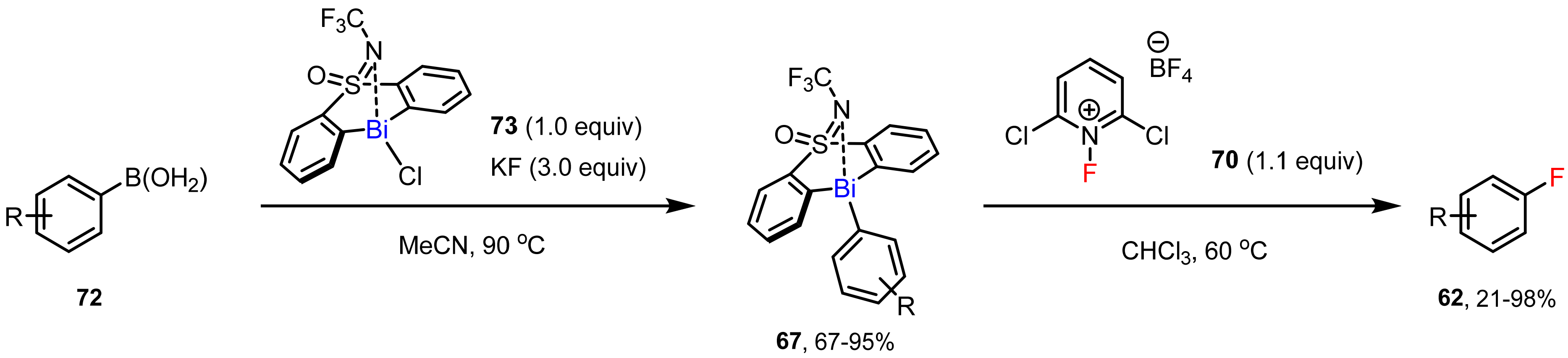




O. Planas, F. Wang, M. Leutzsch, J. Cornella. *Science* **2020**, *367*, 313-317.

Bi介导芳基硼酸的氟化反应

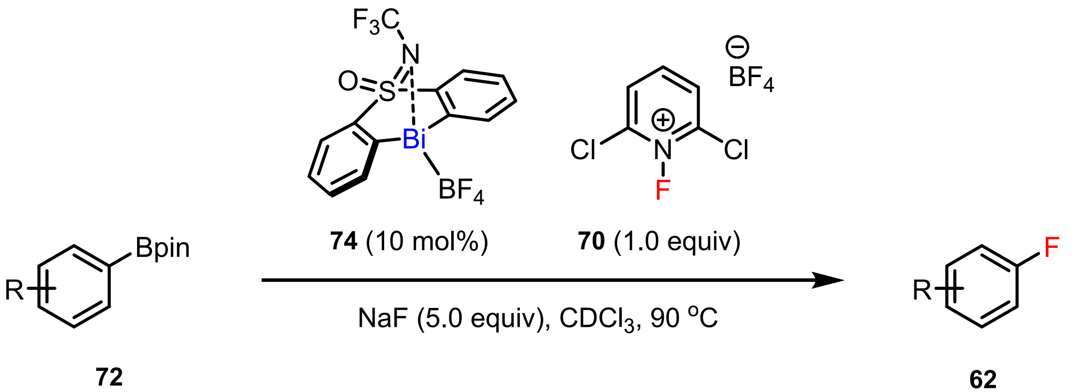


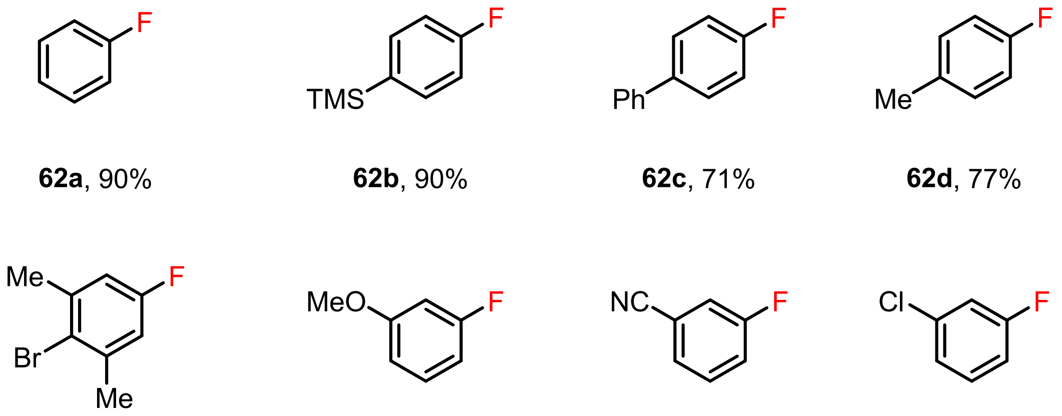


通过分步的方法实现了铋介导的芳基硼酸的氟化反应

O. Planas, F. Wang, M. Leutzsch, J. Cornella. *Science* **2020**, *367*, 313-317.

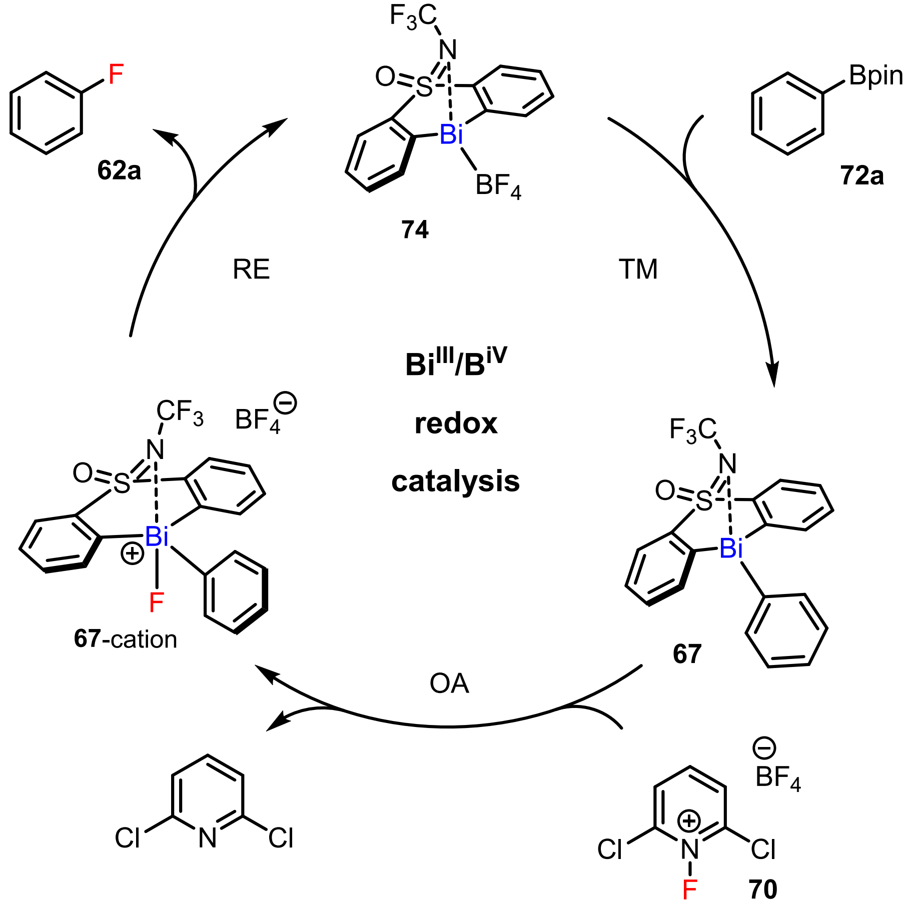
Bi催化芳基硼酸酯的氟化反应





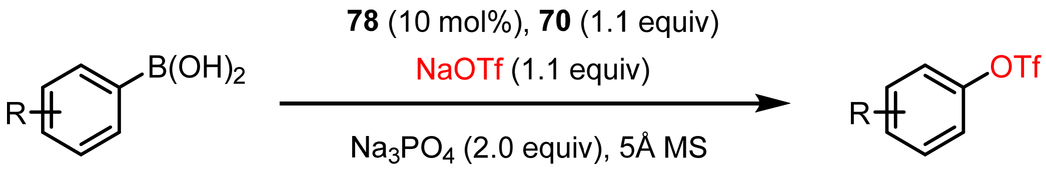
62a, 90% **62b**, 90% **62c**, 71% **62d**, 77%

62e, 84% **62f**, 55% **62g**, 28% **62h**, 36%



O. Planas, F. Wang, M. Leutzsch, J. Cornella. *Science* **2020**, *367*, 313-317.

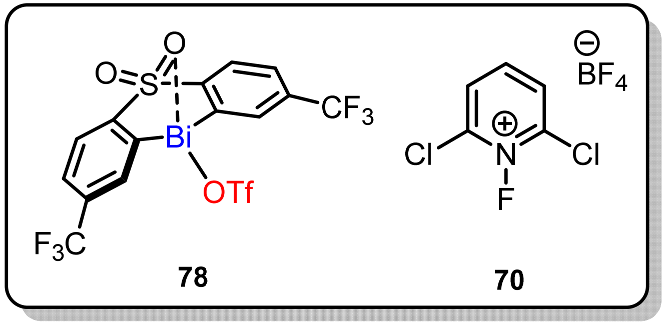
Bi催化芳基硼酸的三氟甲磺酸酯化



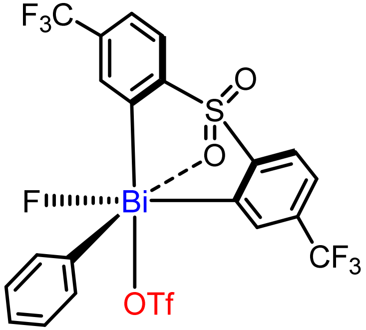
78 (10 mol%), **70** (1.1 equiv)
NaOTf (1.1 equiv)

Na_3PO_4 (2.0 equiv), 5Å MS
$CHCl_3$, 60 °C

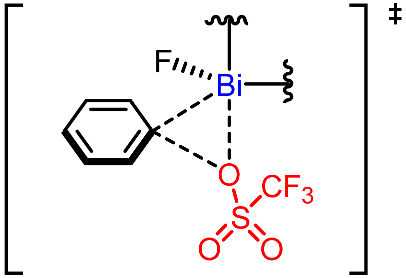
72 **79**



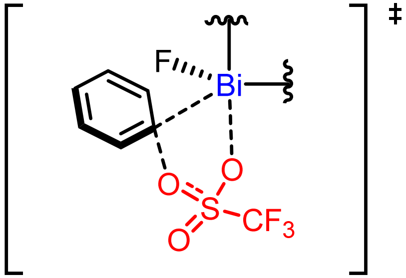
78 **70**



$[\mathbf{80}+Na]^+$ = 828.9576



3-membered ring (**TS1**)
$\Delta G^{\ddagger}$ = 24.8 kcal/mol

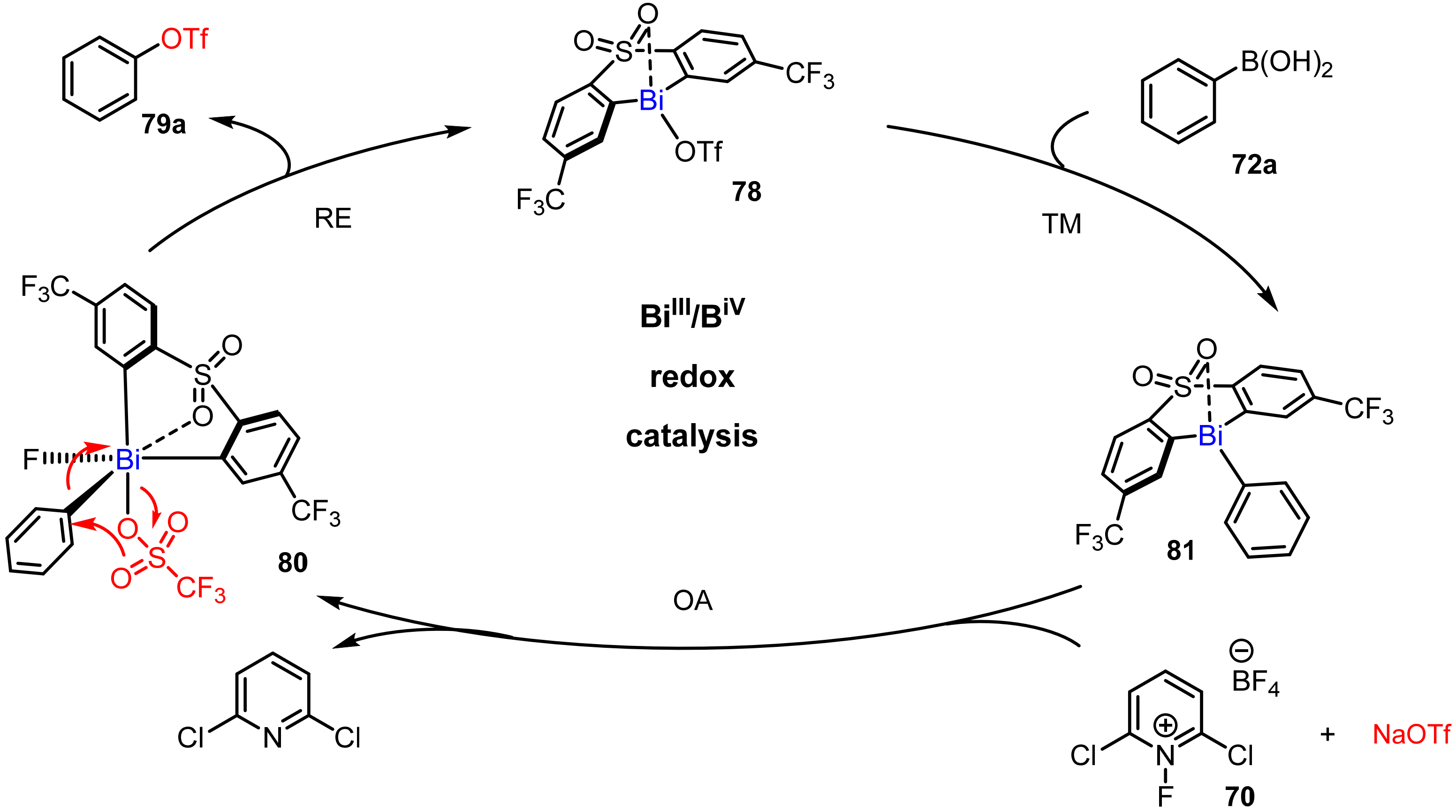


5-membered ring (**TS2**)
$\Delta G^{\ddagger}$ = 21.2 kcal/mol

Bi(V)与三氟甲磺酸负离子配位形成中间体80，还原消除时，经历五元环过渡态

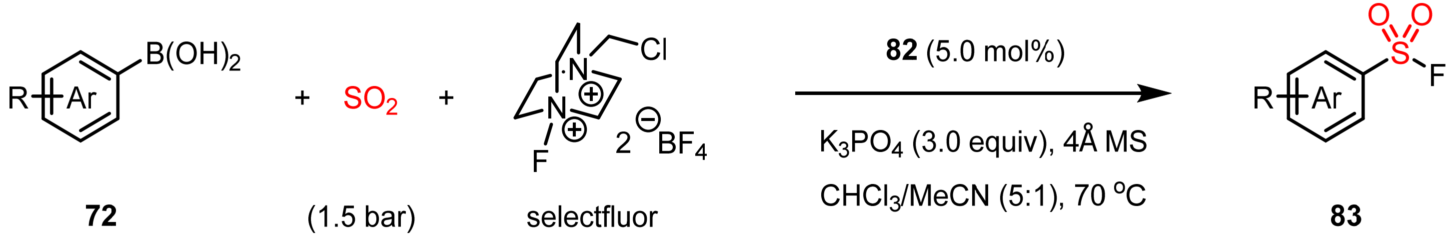
O. Planas, V. Peciukenas, J. Cornella. *J. Am. Chem. Soc.* **2020**, *142,* 11382-11387.

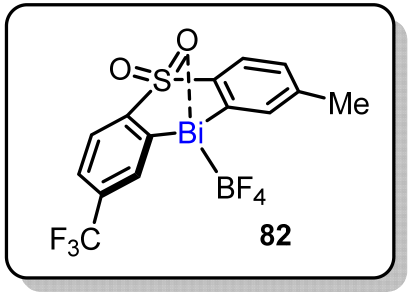
Bi催化芳基硼酸的三氟甲磺酸酯化反应机理

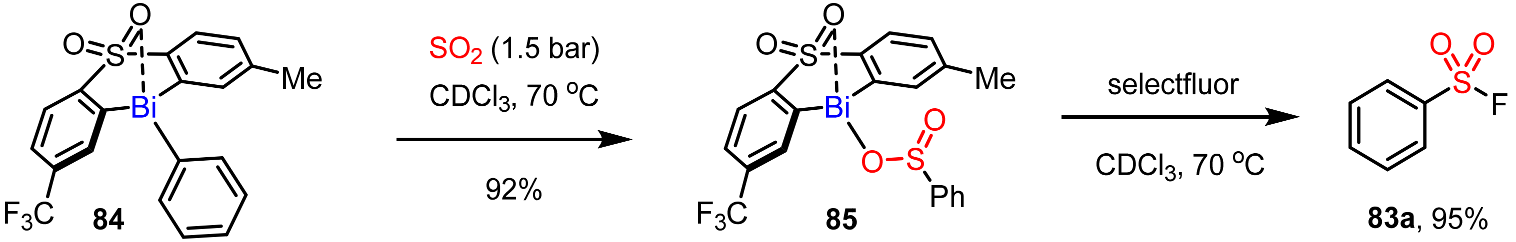


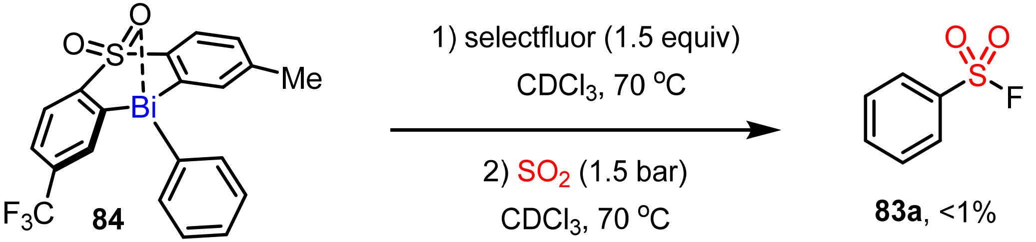
O. Planas, V. Peciukenas, J. Cornella. *J. Am. Chem. Soc.* **2020**, *142,* 11382-11387.

Bi(III)催化芳基硼酸的磺酰氟化反应芳基化反应





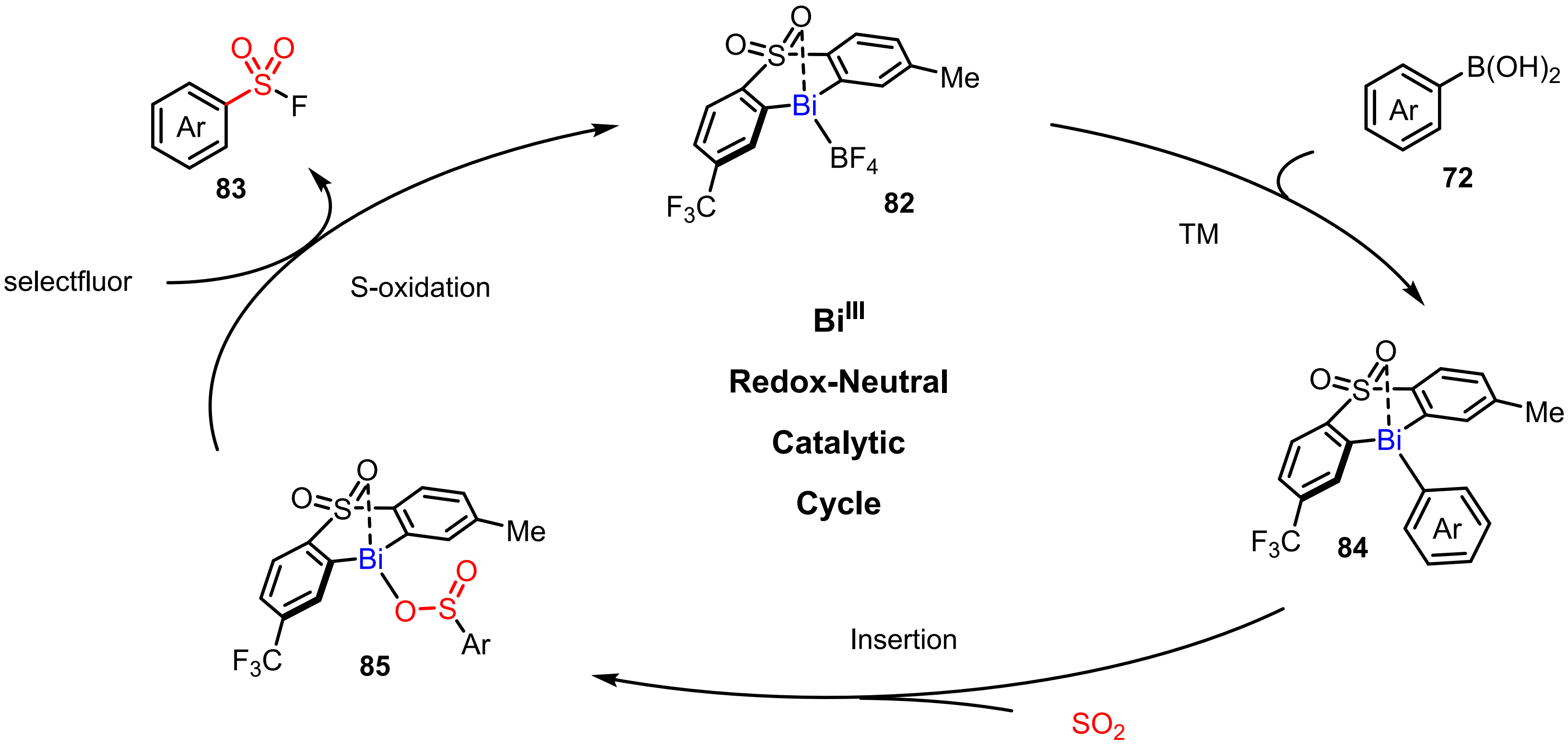




反应不经过Bi(V)中间体，SO_2直接插入Bi(III)

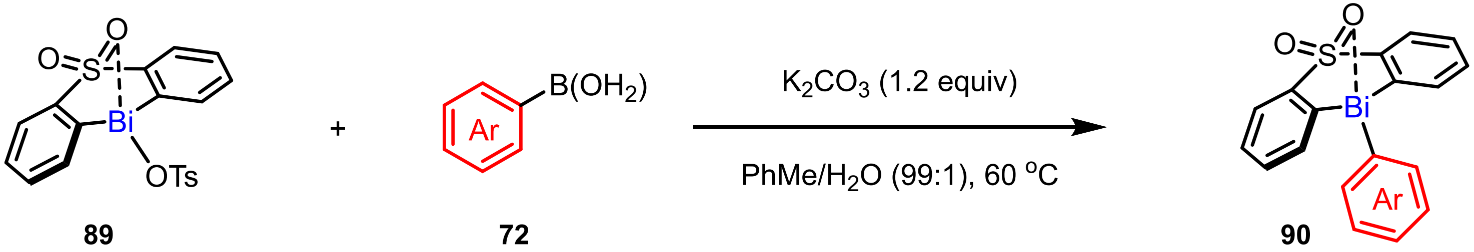
M. Magre, J. Cornella, *J. Am. Chem. Soc.* **2021**, *143*, 21497-21502.

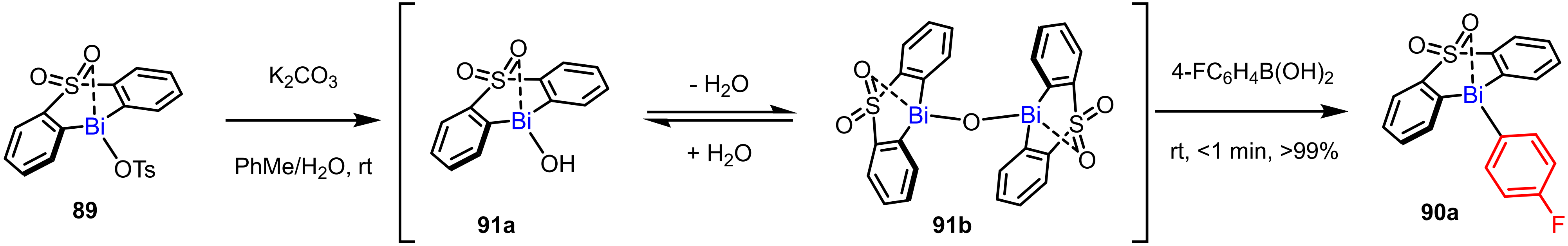
Bi(III)催化芳基硼酸的磺酰氟化反应机理



M. Magre, J. Cornella, *J. Am. Chem. Soc.* **2021**, *143*, 21497-21502.

Bi(III)与芳基硼酸的转金属化

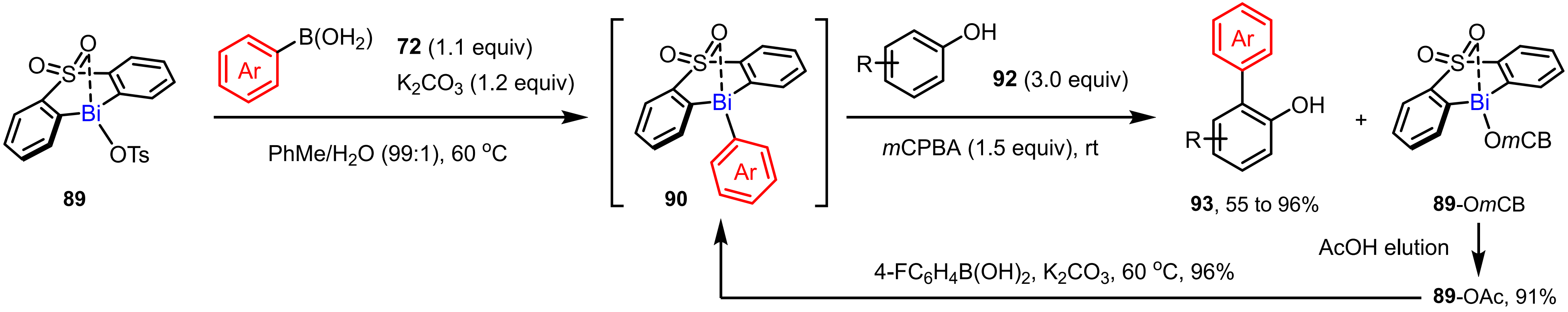


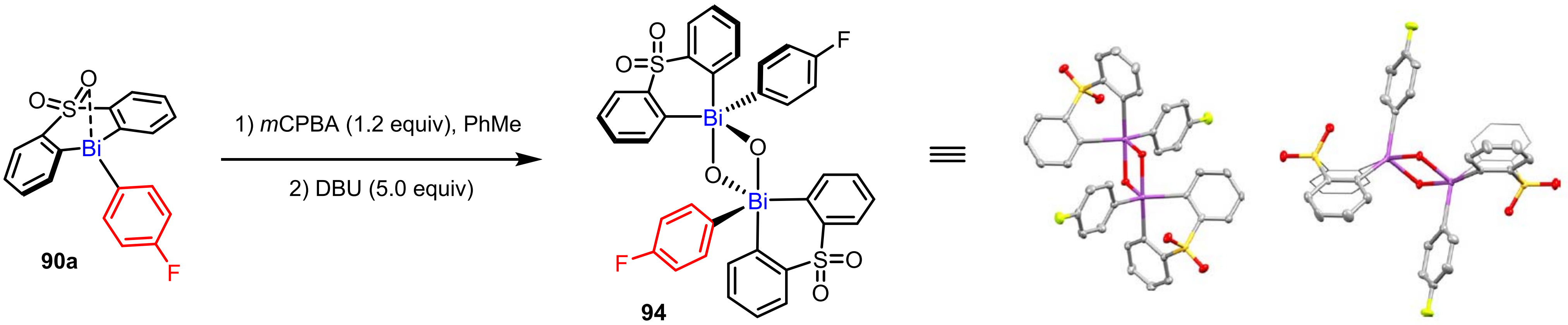


实际上发生转金属化的中间体是91a/91b

M. Jurrat, L. Maggi, W. Lewis, L. T. Ball. *Nat. Chem.* **2020**, *12,* 260-269.

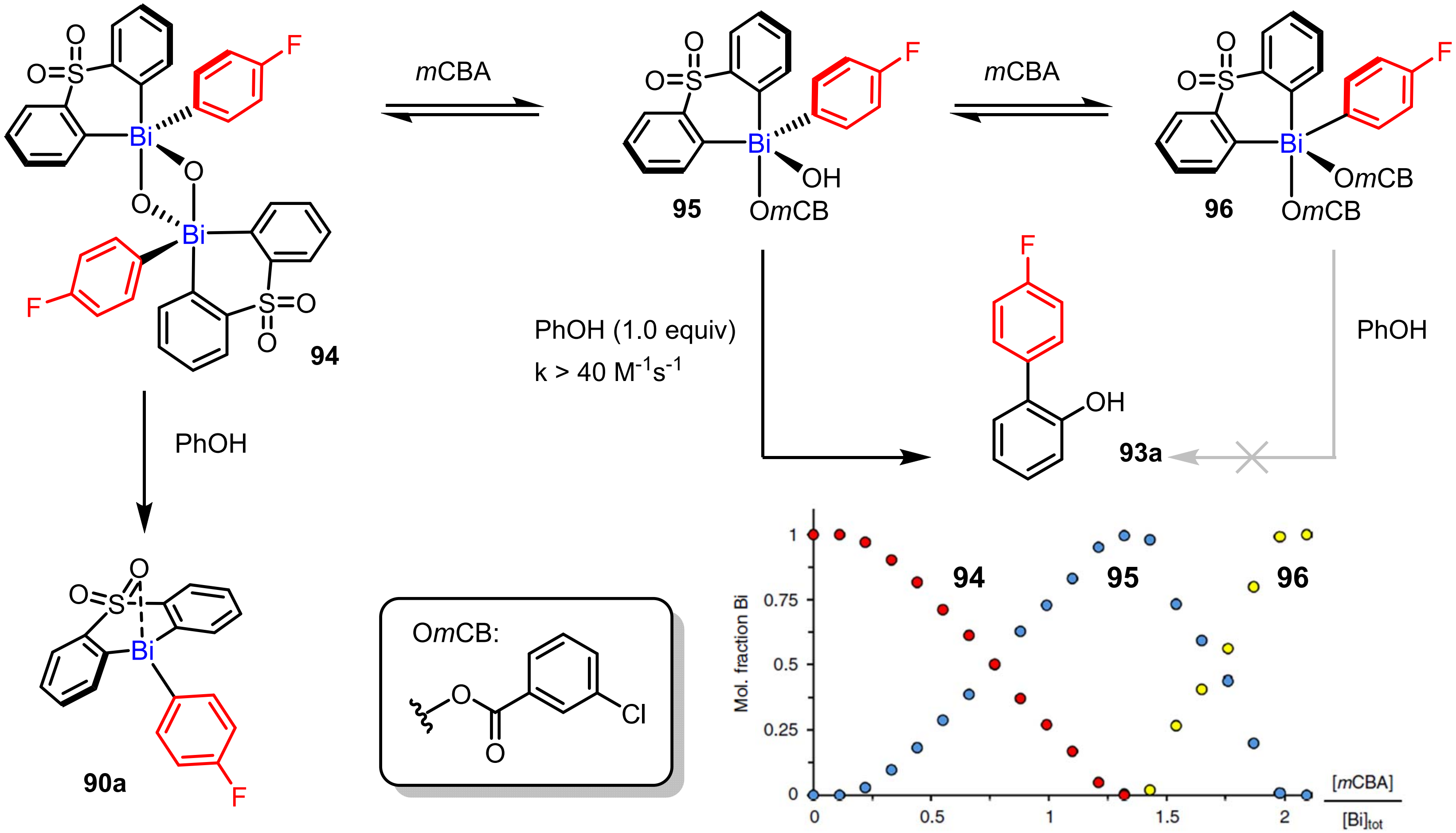
Bi介导的苯酚/萘酚的邻位C-H芳基化反应





M. Jurrat, L. Maggi, W. Lewis, L. T. Ball. *Nat. Chem.* **2020**, *12,* 260-269.

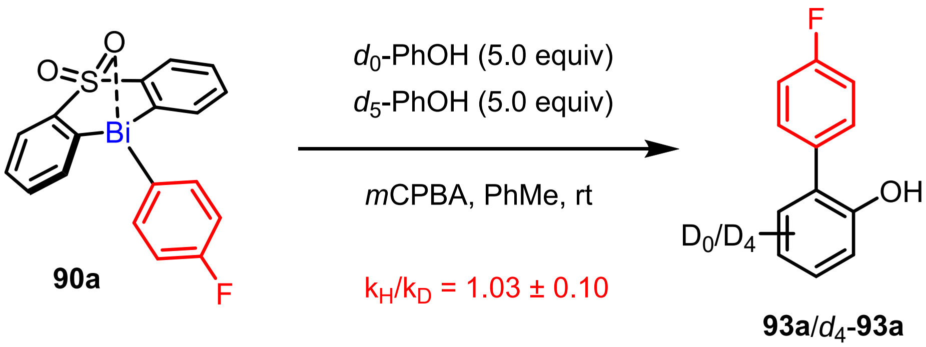
Bi介导的苯酚/萘酚的邻位C-H芳基化反应

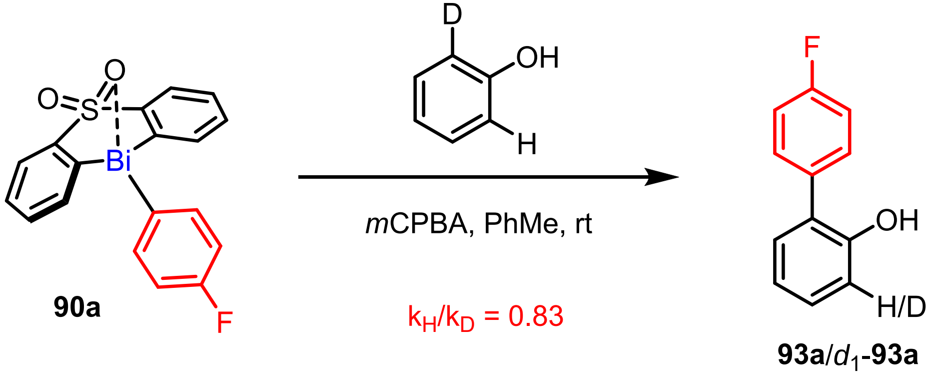


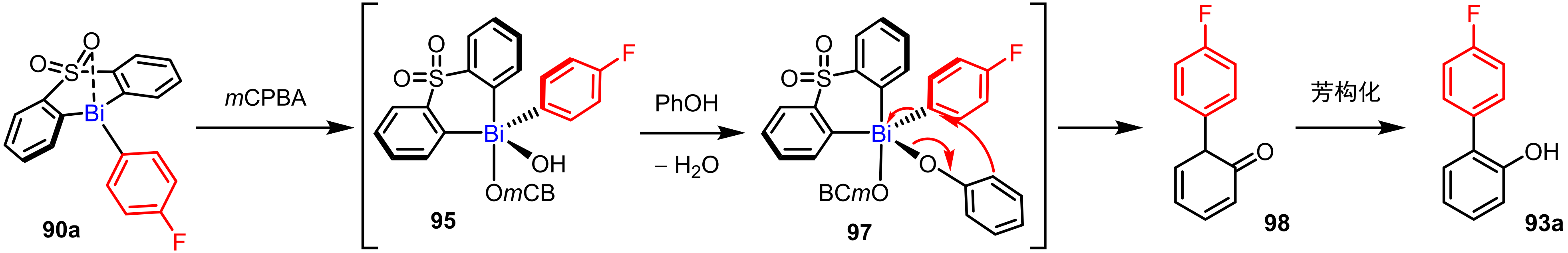
芳基Bi(III)被*m*CPBA氧化后，只有形成的**Bi(V) 95**才能进一步与苯酚发生反应

M. Jurrat, L. Maggi, W. Lewis, L. T. Ball. *Nat. Chem.* **2020**, *12*, 260-269.

Bi介导的苯酚/萘酚的邻位C-H芳基化反应



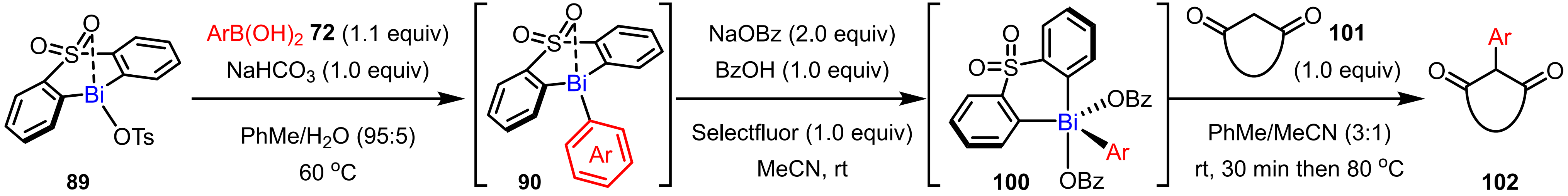




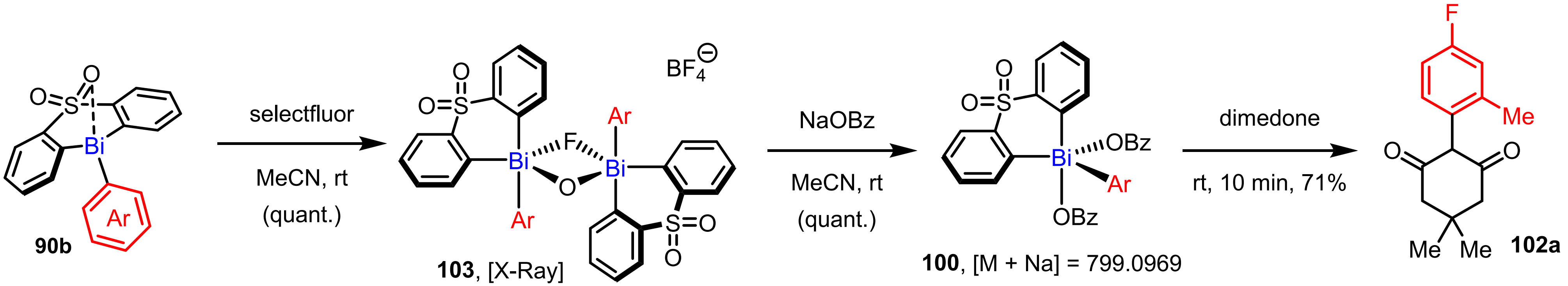
形成的中间体97发生分子内亲核取代，sp2碳转化为sp3碳，故测出逆二级同位素效应(k_H/k_D = 0.83)，随后发生芳构化得到邻位碳氢键芳基化产物

M. Jurrat, L. Maggi, W. Lewis, L. T. Ball. *Nat. Chem.* **2020**, *12,* 260-269.

Bi介导的1,3-二酮的α-芳基化反应



89 **90** **100** **102**

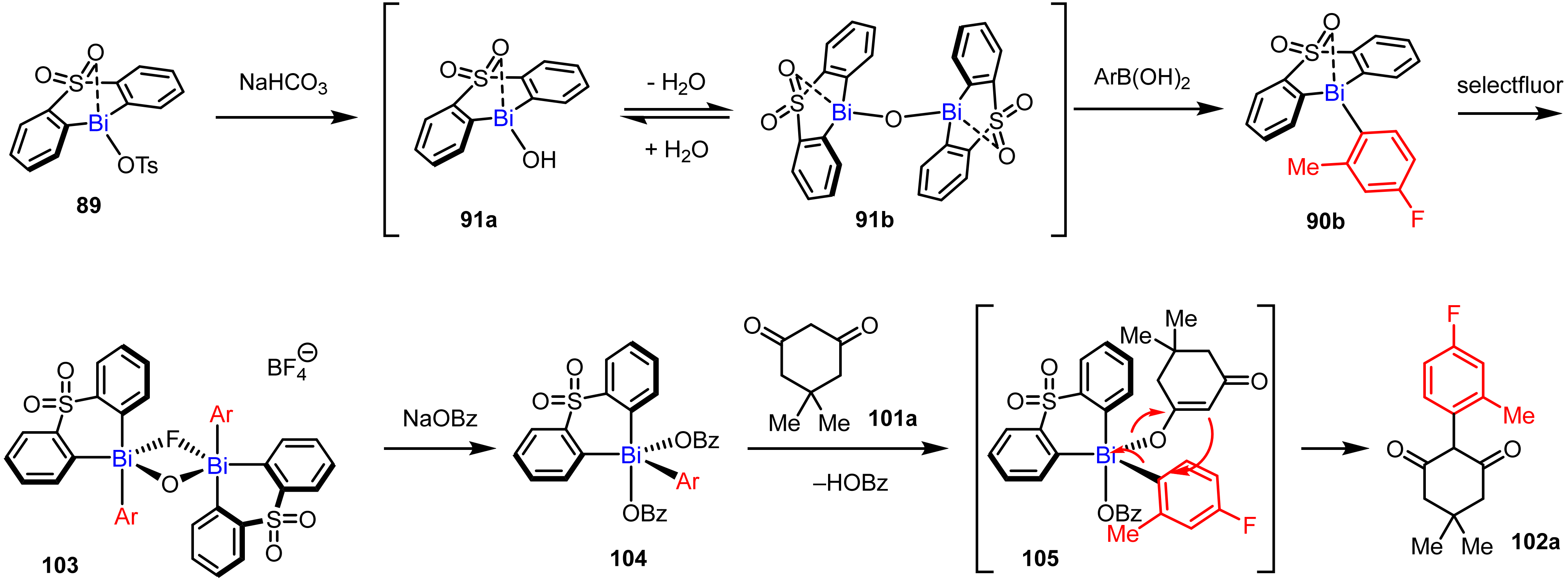


90b **103**, [X-Ray] **100**, [M + Na] = 799.0969 **102a**

芳基Bi(III)被selectfluor氧化后，与苯甲酸负离子发生配体交换

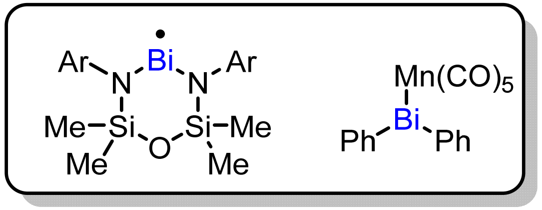
K. Ruffell, S. P. Argent, K. B. Ling, L. T. Ball. *Angew. Chem. Int. Ed.* **2022**, e202210840.

Bi介导的1,3-二酮的α-芳基化反应历程

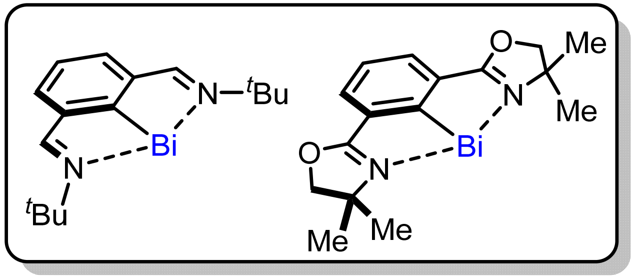


K. Ruffell, S. P. Argent, K. B. Ling, L. T. Ball. *Angew. Chem. Int. Ed.* **2022**, e202210840.

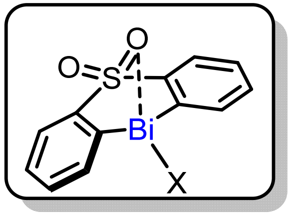
总结



目前已发展的两例催化反应均为自由基类型反应

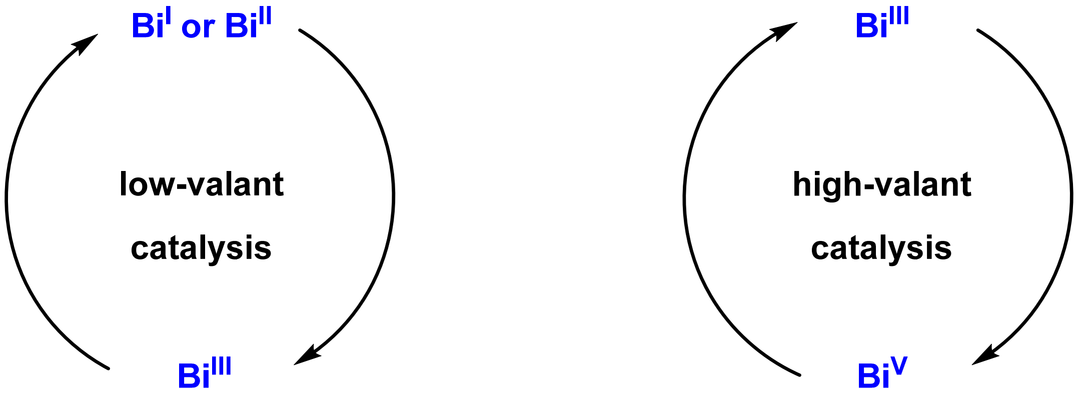


Cornella教授利用Bi(I)的还原性催化了氨基硼烷与芳基偶氮的转移氢化、N_2O的还原，实现了全氟取代芳烃的脱氟氢化反应



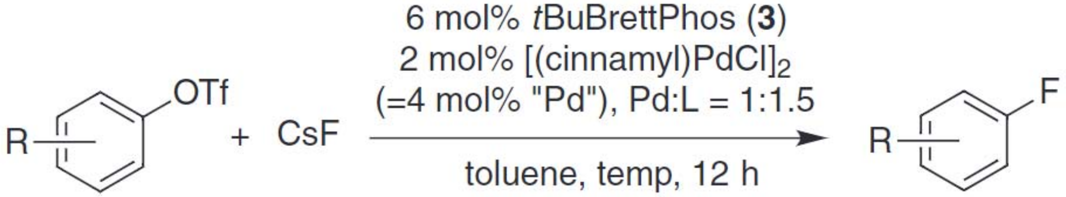
Cornella教授利用砜基稳定的Bi(III)化合物实现了芳基硼酸的氟化和三氟甲磺酸酯化反应，随后在研究磺酰氟化反应时发现Bi(III)也可以作为氧化还原中性的催化剂。Liam. T. Ball教授则将Bi(V)作为芳基化试剂，串联Bi(III)的转金属化、氧化和Bi(V)芳基化，实现了Bi介导的苯酚邻位芳基化反应和1,3-二酮α位芳基化反应

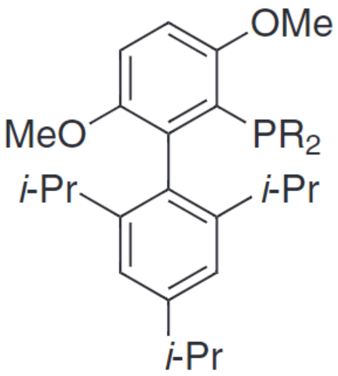
展望



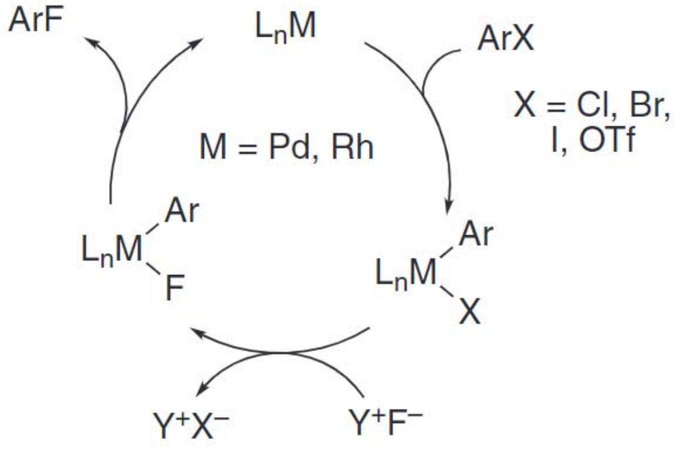
- 相较于氧化加成、还原消除和配体交换，涉及到Bi迁移插入的报道仍是少数
- Bi(II)化合物仅少数几例报道， Bi(IV)化合物目前还未有报道
- 将稳定的Bi化合物运用到电催化或光催化反应中
- 合成手性Bi催化剂实现对映选择性的转化

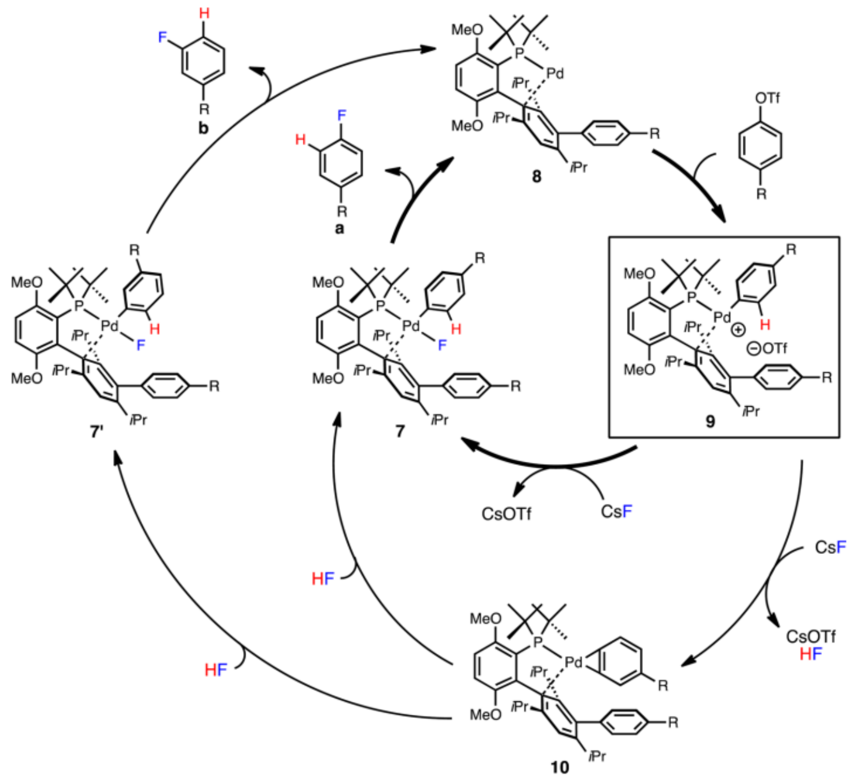
Thanks for your
kind attention!





BrettPhos (**2**, R = Cyclohexyl)
*t*BuBrettPhos (**3**, R = *t*-Bu)





a) D. A. Watson, M. Su, G. Teverovskiy, Y. Zhang, J. García-Fortanet,T. Kinzel, S. L. Buchwal, *Science* **2009**, *325*, 1661-1664;
b) P. J. Milner, T. Kinzel, Y. Zhang, S. L. Buchwald. *J. Am. Chem. Soc*. **2014**, *136*, 15757-15766.