The Yang Research Group
Precise Synthesis Lab at Tongji University

# Josep课题组的研究工作

汇报人：李蔚鹏

2025年5月9日

# 目录

# 一、Josep Cornella

•2008, graduated in chemistry from the University of Barcelona, M.S.;

•2008-2012, Queen Mary University of London, Ph.D., Advisor: Igor Larrosa ;

•2012-2015,加泰罗尼亚化学研究所(ICIQ), Postdoc, Advisor: Ruben Martin ;

•2015-2017, The Scripps Research Institute, Postdoc, Advisor: Phil S. Baran;

•2017春, Max-Planck-Institut für Kohlenforschung, Max Planck Group Leader;

•2017夏, Max-Planck-Institut für Kohlenforschung, Max Planck Research Group Leader;

# 二、Bi(I)/Bi(III)

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Communication
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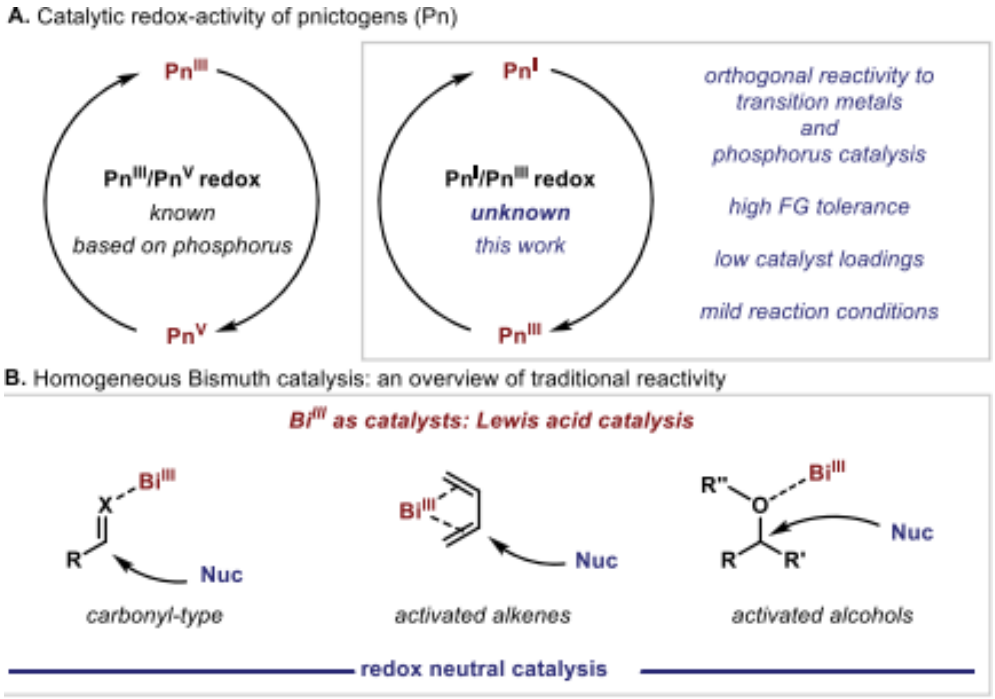
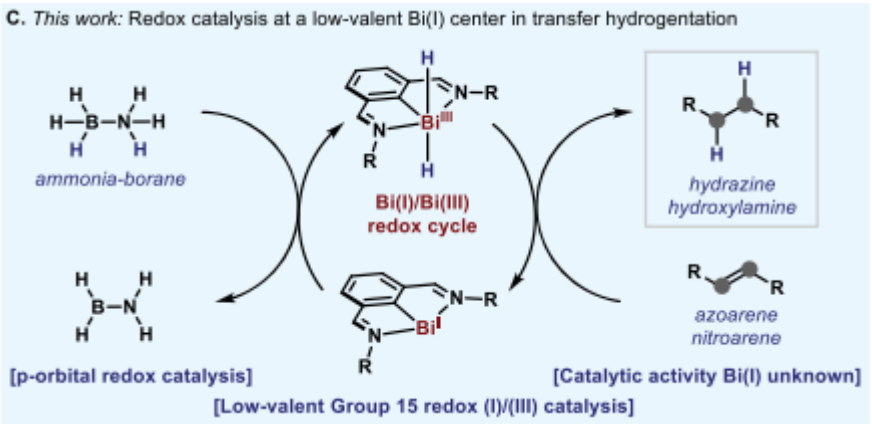
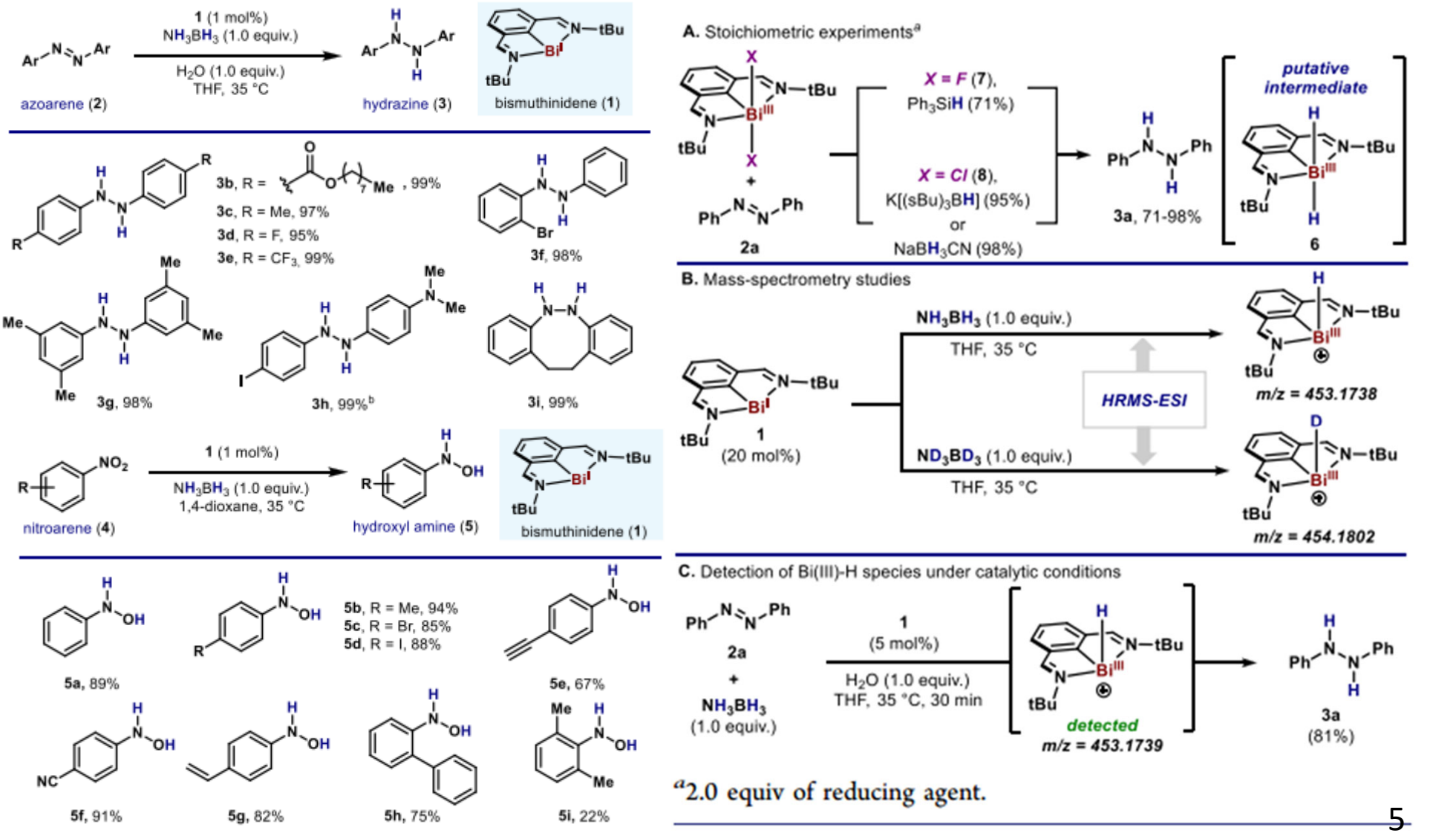
## Bi(I)-Catalyzed Transfer-Hydrogenation with Ammonia-Borane

Feng Wang,[†] Oriol Planas,[†] and Josep Cornella*



# 二、Bi(I)/Bi(III)


1 (1 mol%)
NH3BH3 (1.0 equiv.)
H2O (1.0 equiv.)
THF, 35 °C
azoarene (2)
hydrazine (3)
bismuthinidene (1)
3b, R = , 99%
3c, R = Me, 97%
3d, R = F, 95%
3e, R = CF3, 99%
3f, 98%
3g, 98%
3h, 99%b
3i, 99%
1 (1 mol%)
NH3BH3 (1.0 equiv.)
1,4-dioxane, 35 °C
nitroarene (4)
hydroxyl amine (5)
bismuthinidene (1)
5a, 89%
5b, R = Me, 94%
5c, R = Br, 85%
5d, R = I, 88%
5e, 67%
5f, 91%
5g, 82%
5h, 75%
5i, 22%
A. Stoichiometric experiments[a]
X = F (7),
Ph3SiH (71%)
X = Cl (8),
K[(sBu)3BH] (95%)
or
NaBH3CN (98%)
2a
3a, 71-98%
putative intermediate
6
B. Mass-spectrometry studies
NH3BH3 (1.0 equiv.)
THF, 35 °C
ND3BD3 (1.0 equiv.)
THF, 35 °C
HRMS-ESI
1
(20 mol%)
m/z = 453.1738
m/z = 454.1802
C. Detection of Bi(III)-H species under catalytic conditions
2a
+
NH3BH3
(1.0 equiv.)
1
(5 mol%)
H2O (1.0 equiv.)
THF, 35 °C, 30 min
detected
m/z = 453.1739
3a
(81%)
[a]2.0 equiv of reducing agent.

# 二、Bi(I)/Bi(III)

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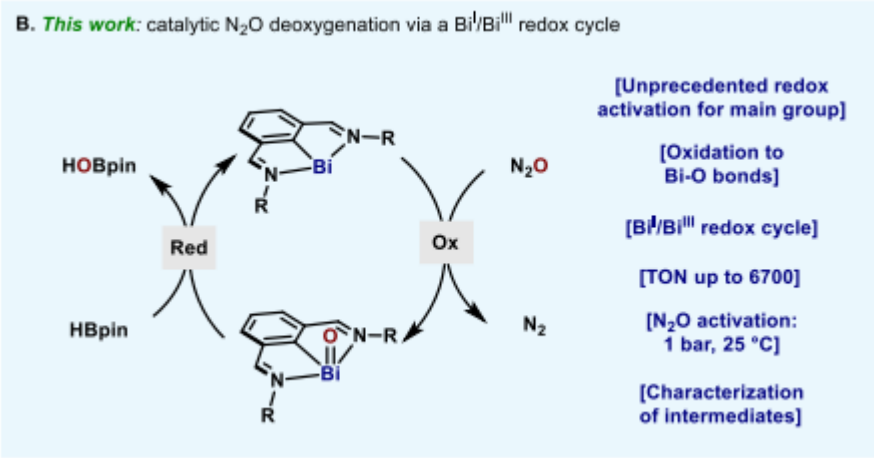
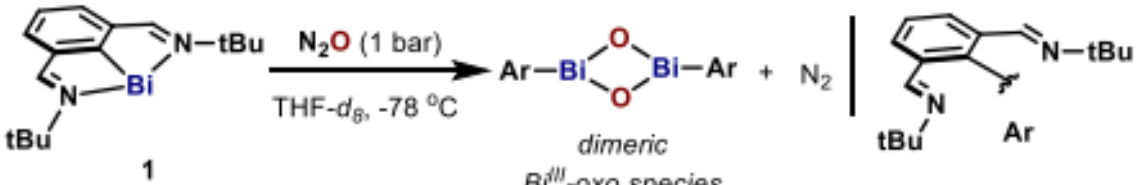
Communication

## Catalytic Activation of $N_2O$ at a Low-Valent Bismuth Redox Platform

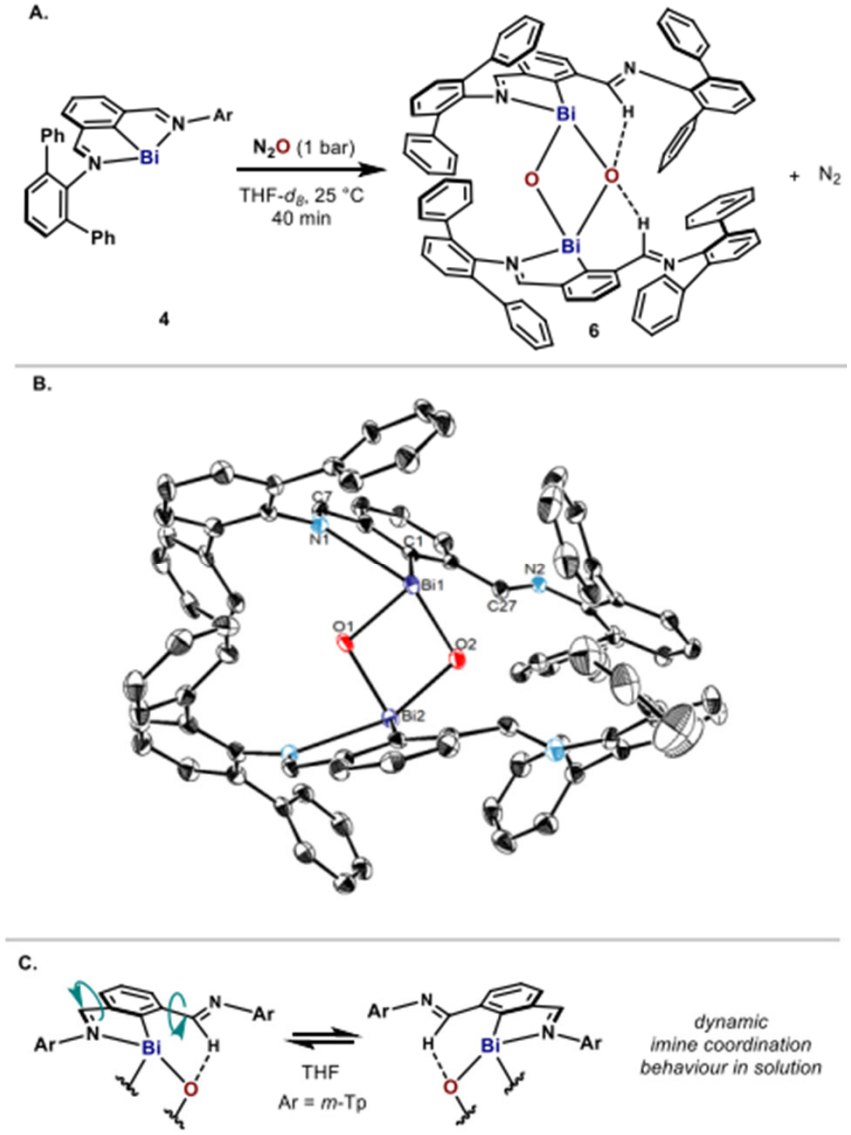
Yue Pang, Markus Leutzsch, Nils Nöthling, and Josep Cornella*

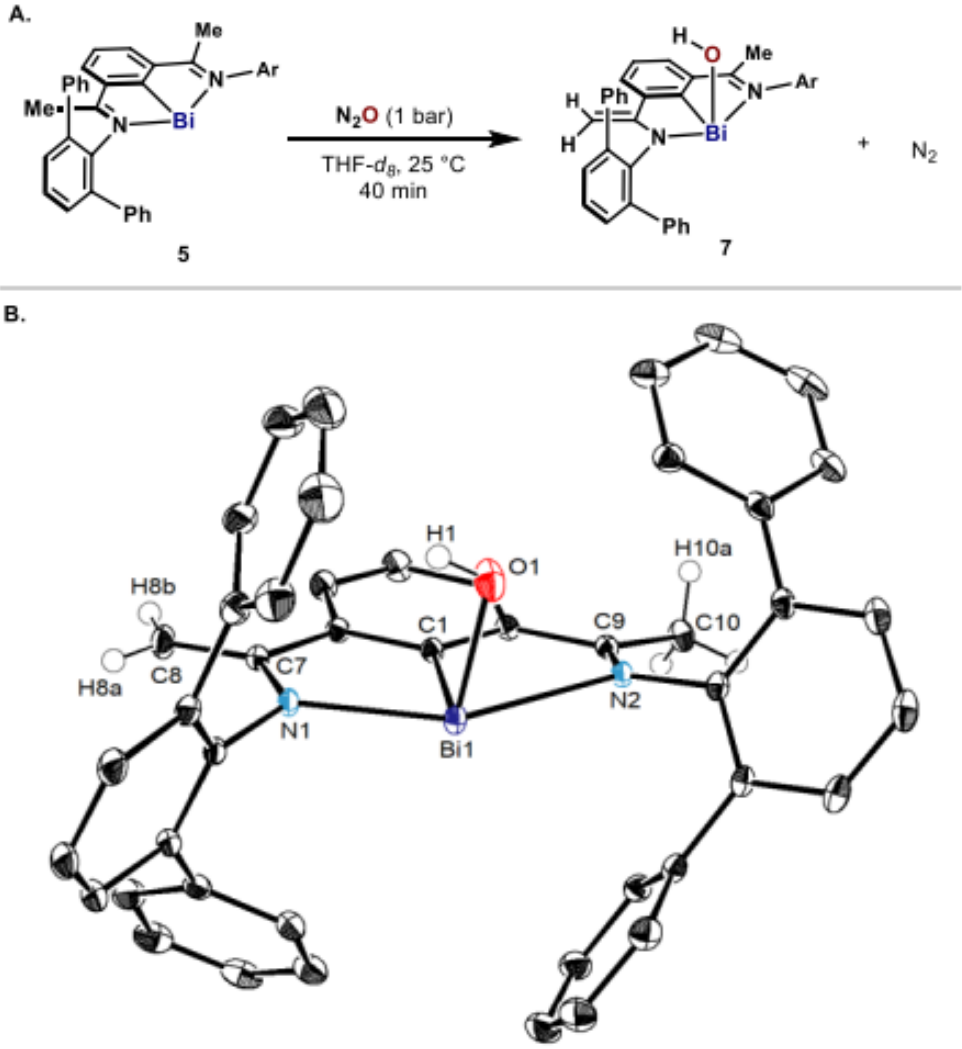



### Scheme 1. Oxidation of Bismuthinidene 1 with $N_2O$



# 二、Bi(I)/Bi(III)


A.
Ph
N
Ar
Bi
Ph
4
N2O (1 bar)
THF-d8, 25 °C
40 min
N
Bi
H
O
O
Bi
H
N
N
6
+ N2
B.
C7
N1
C1
Bi1
N2
C27
O1
O2
Bi2
C.
Ar
N
Ar
Bi
H
O
THF
Ar = m-Tp
dynamic
imine coordination
behaviour in solution


A.
Me
Ph
N
Ar
Me
N
Bi
Ph
5
N2O (1 bar)
THF-d8, 25 °C
40 min
H
O
Me
H
Ph
N
Ar
H
N
Bi
Ph
7
+ N2
B.
H1
O1
H10a
H8b
C1
C9
C10
H8a
C8
C7
N2
N1
Bi1

# 二、Bi(I)/Bi(III)

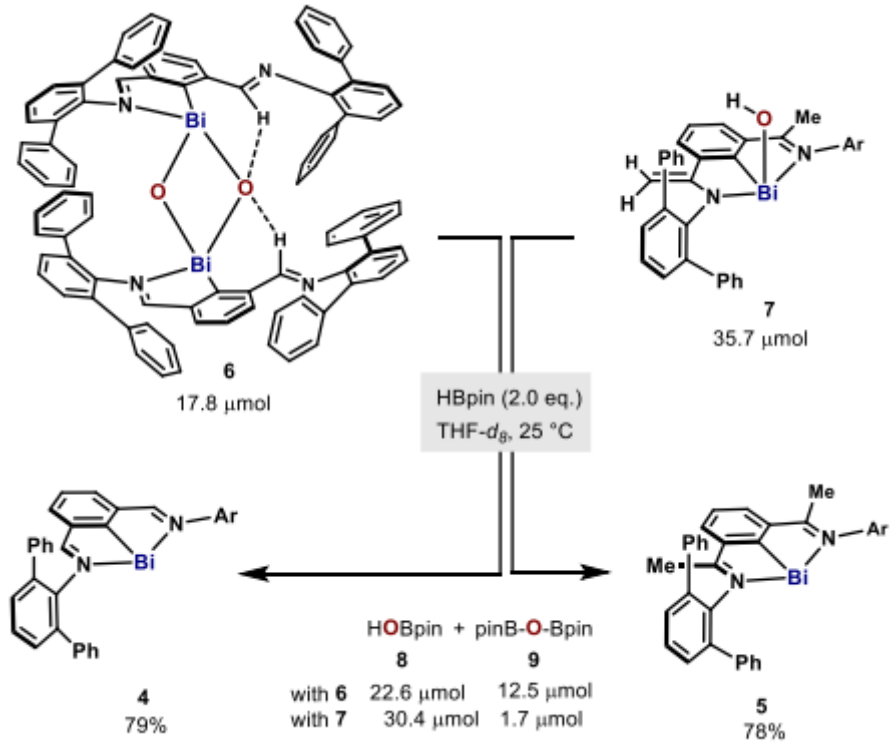



**Table 1. Bi(I)-Catalyzed $N_2O$ Deoxygenation with HBpin**

HBpin + $N_2O$ (1 bar) —[x mol% Bi(I)], THF-$d_8$, 25 °C→ HOBpin (**8**) + pinB-O-Bpin (**9**) + $N_2$

| Entry | Bi(I) (x mol%) | time | conv. (%)[a] | 8 / 9 ratio (%)[b] | TON[b] |
|---|---|---|---|---|---|
| 1 | - | 15 h | 0 | - | - |
| 2 | **4** (1.0) | 15 h | 79 | 27 / 27 | 54 |
| 3 | **5** (1.0) | 15 h | 100 | 79 / 10 | 89 |
| 4 | **1** (1.0) | ~3 min[c] | 100 | 60 / 20 | 80 |
| 5 | **1** (0.1) | ~15 min[c] | 100 | 57 / 21 | 780 |
| 6 | **1** (0.05) | ~30 min[c] | 100 | 53 / 23 | 1520 |
| 7 | **1** (0.01) | 11 h | 97 | 36 / 31 | 6700 |

[a]Based on HBpin. [b]Calculated by $^1$H NMR using mesitylene as internal standard. [c]Determined by disappearance of the characteristic color of Bi(I).

# 二、Bi(I)/Bi(III)

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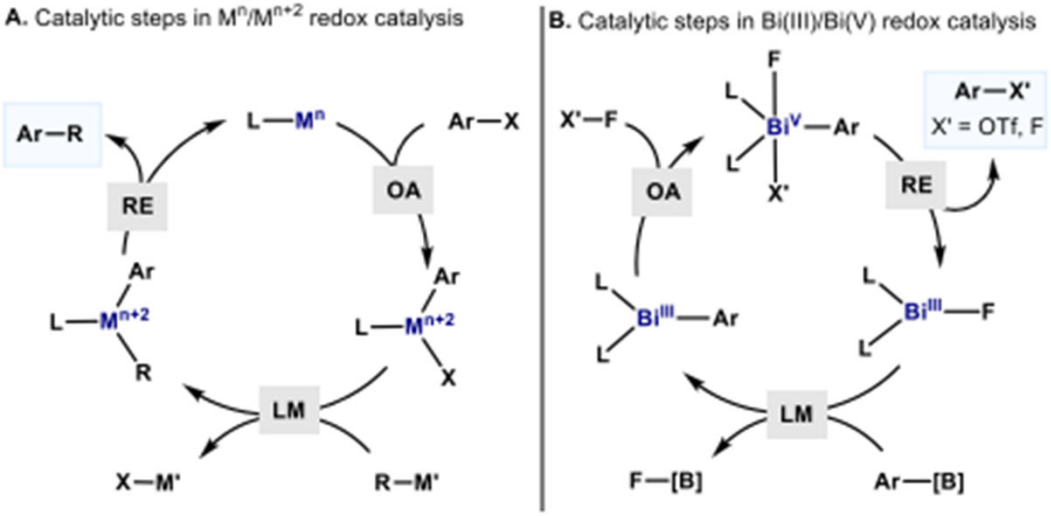
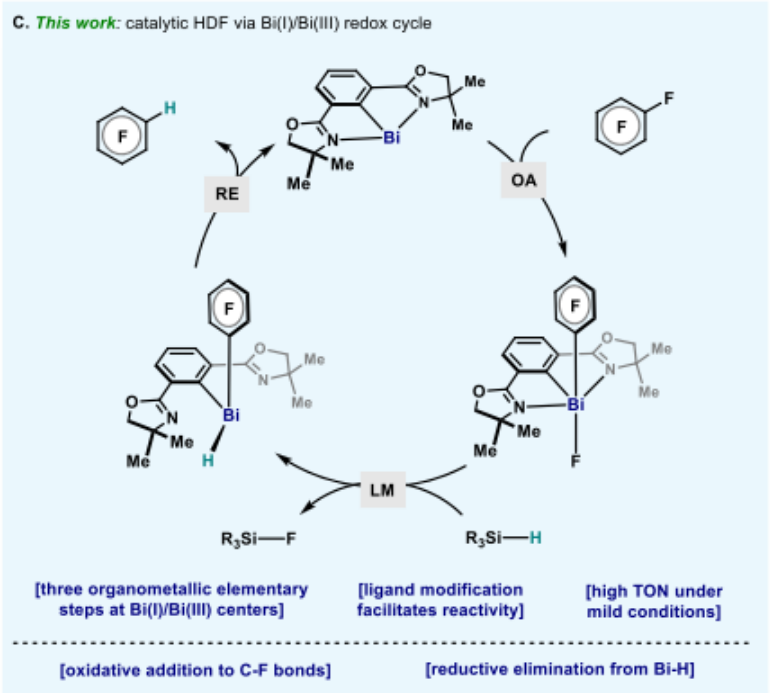
## Catalytic Hydrodefluorination via Oxidative Addition, Ligand Metathesis, and Reductive Elimination at Bi(I)/Bi(III) Centers

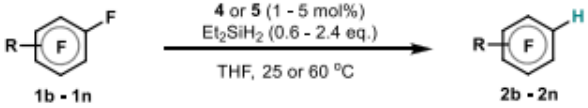
Yue Pang, Markus Leutzsch, Nils Nöthling, Felix Katzenburg, and Josep Cornella*



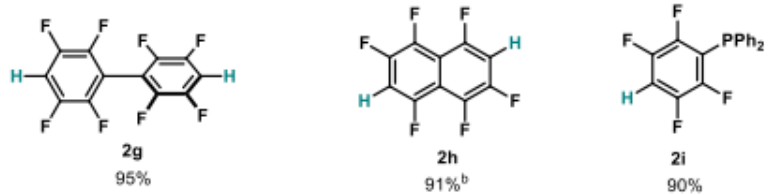
# 二、Bi(I)/Bi(III)

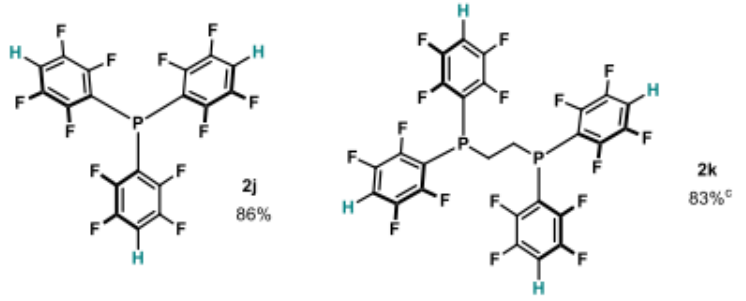
lyzed HDF[a]



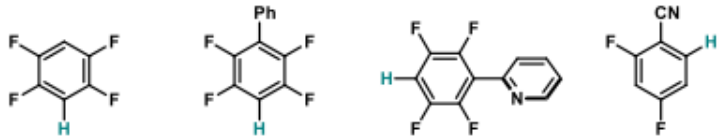

**Conditions A**: **4** (1 mol%), 25 °C, 2 min - 2 h


**Conditions B**: **4** (1- 5 mol%), 60 °C, 20 h

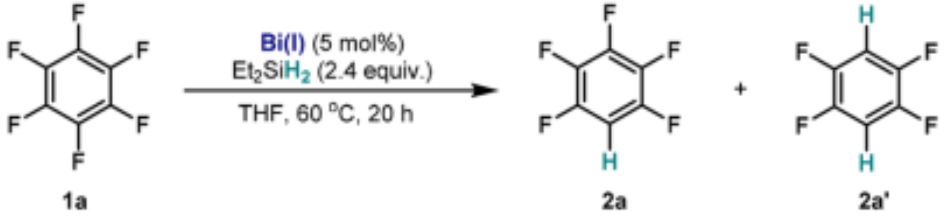


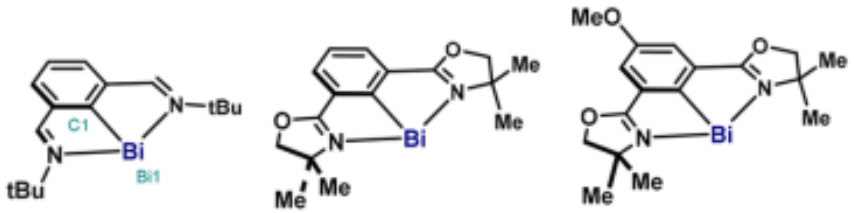




**Conditions C**: **5** (5 mol%), 60 °C, 3 d



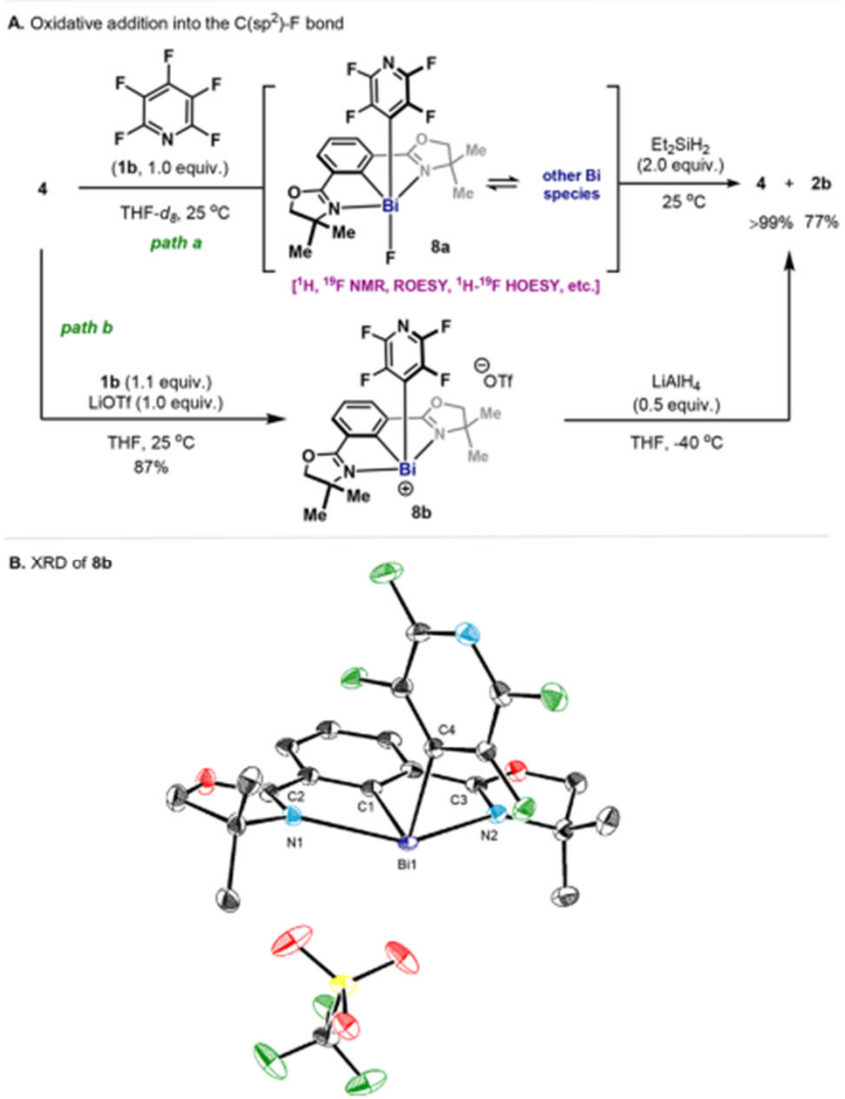

A.

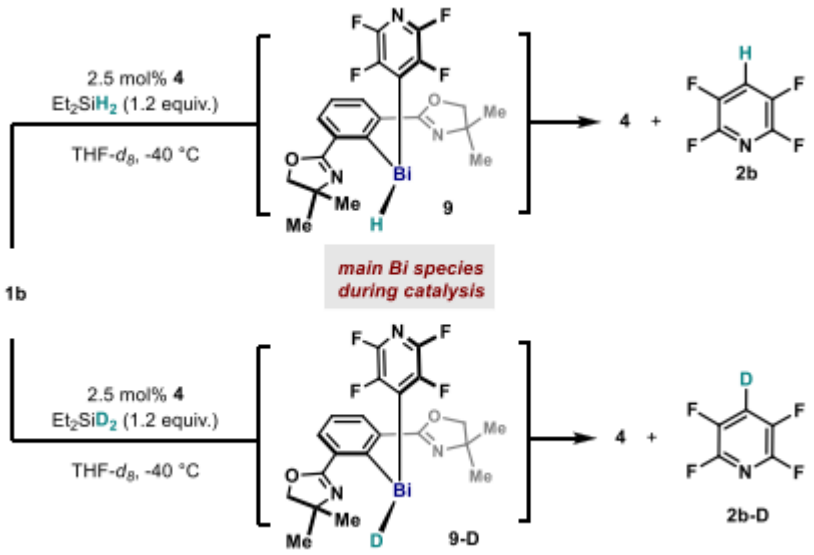



| | 3 | 4 Phebox-Bi(I) | 5 OMe-Phebox-Bi(I) |
|---|---|---|---|
| Yield of **2a** | < 1% | 40% | 74% (16% **2a'**) |
| C1-Bi1 (Å) | 2.146 | 2.193 | 2.201 |

# 二、Bi(I)/Bi(III)


A. Oxidative addition into the C(sp²)-F bond
4
(1b, 1.0 equiv.)
THF-d8, 25 °C
path a
8a
other Bi species
[¹H, ¹⁹F NMR, ROESY, ¹H-¹⁹F HOESY, etc.]
Et2SiH2
(2.0 equiv.)
25 °C
4 + 2b
>99% 77%
path b
1b (1.1 equiv.)
LiOTf (1.0 equiv.)
THF, 25 °C
87%
8b
LiAlH4
(0.5 equiv.)
THF, -40 °C
B. XRD of 8b
C4
C2
C1
C3
N1
N2
Bi1


2.5 mol% 4
Et2SiH2 (1.2 equiv.)
THF-d8, -40 °C
9
4 +
2b
1b
main Bi species
during catalysis
2.5 mol% 4
Et2SiD2 (1.2 equiv.)
THF-d8, -40 °C
9-D
4 +
2b-D

# 二、Bi(I)/Bi(III)

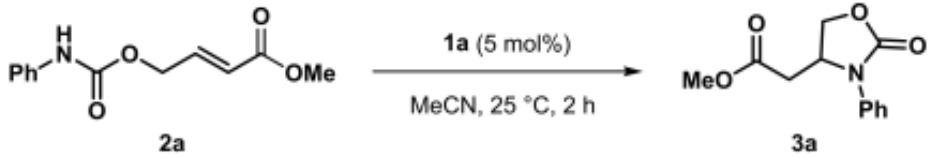
COMMUNICATIONS doi.org/10.1002/adsc.202300857 Advanced Synthesis & Catalysis

*Very Important Publication*

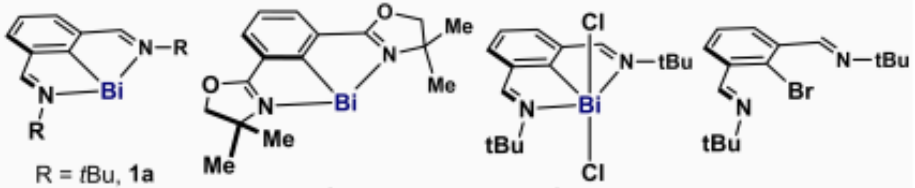
## Conjugate Aminocyclization Catalyzed by a Bismuthinidene

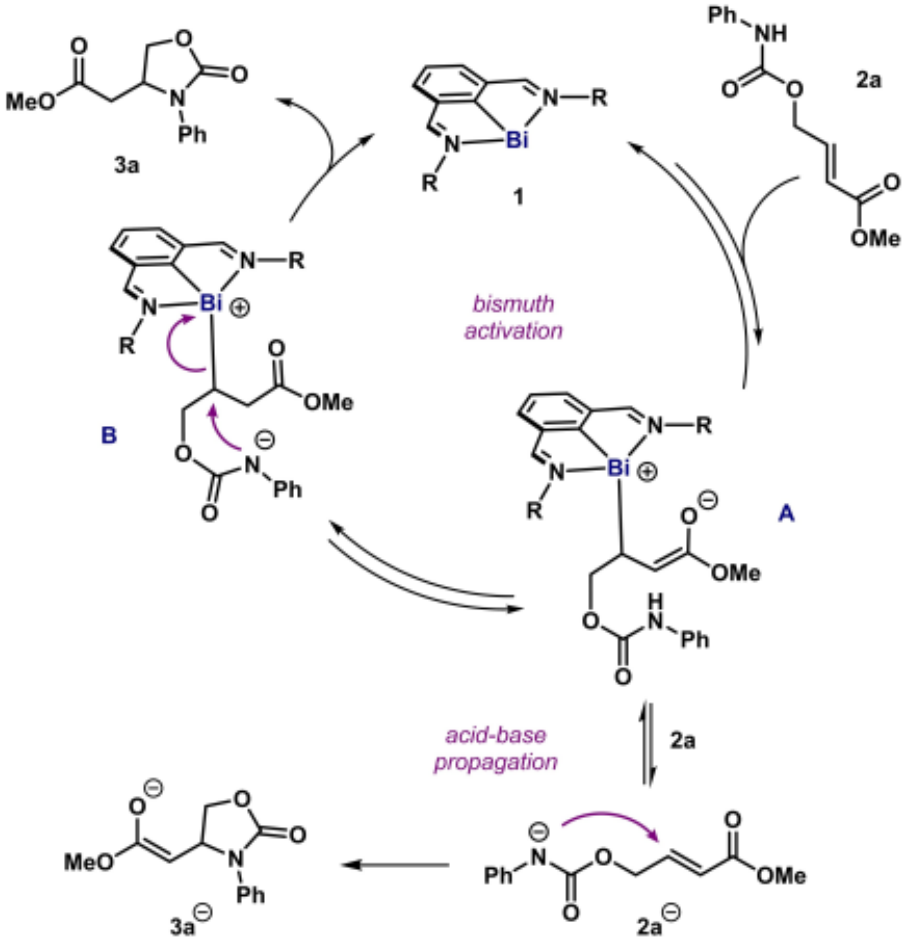
Mauro Mato,[a] Feng Wang,[a] and Josep Cornella[a,*]

# 二、Bi(I)/Bi(III)




| Entry | Deviation from standard conditions[a] | Yield of **3a** |
|---|---|---|
| 1 | none | >95% (93%) |
| 2 | **1b** (5 mol%) instead of **1a** | >95% |
| 3 | **1c** (5 mol%) instead of **1a** | 94% |
| 4 | without **1a**, 16 h | n/d |
| 5 | 1 mol% of **1a**, 15 min | >95% |
| 6 | 0.1 mol% of **1a**, 1 h | >95% |
| 7 | **4** (5 mol%) instead of **1a** | n/d |
| 8 | **5** (5 mol%) instead of **1a** | n/d |
| 9 | Weak bases (50 mol%) instead of **1a**: $NEt_3$ *or* AcONa, 16 h | n/d[b] |
| 10 | $ZnBr_2$, CuI, $InCl_3$, $FeBr_3$, $AgF_2$,16 h instead of **1a** | n/d[b] |
| 11 | Zn dust (50 mol%) instead of **1a**, 16 h | n/d |
| 12 | $PPh_3$ (20 mol%) or JohnPhos (10 mol%) instead of **1a**, 16 h | n/d |
| 13 | $PCy_3$ (20 mol%) instead of **1a** | >95% |



# 二、Bi(I)/Bi(III)

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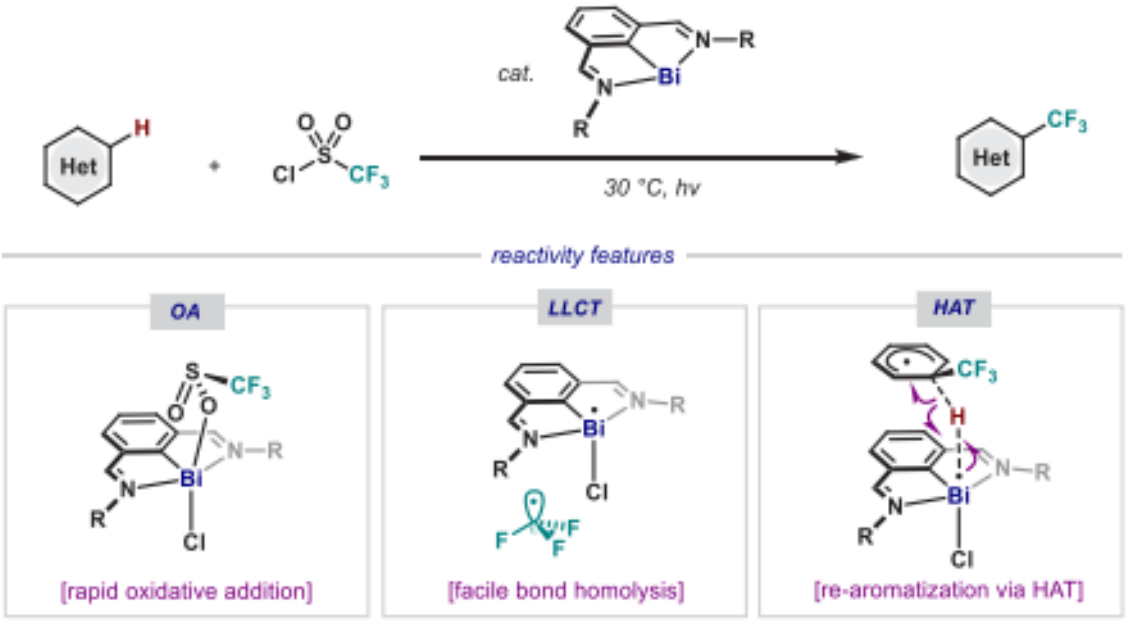
## Bi-Catalyzed Trifluoromethylation of C(sp$^2$)–H Bonds under Light

Takuya Tsuruta, Davide Spinnato, Hye Won Moon, Markus Leutzsch, and Josep Cornella*



# 二、Bi(I)/Bi(III)

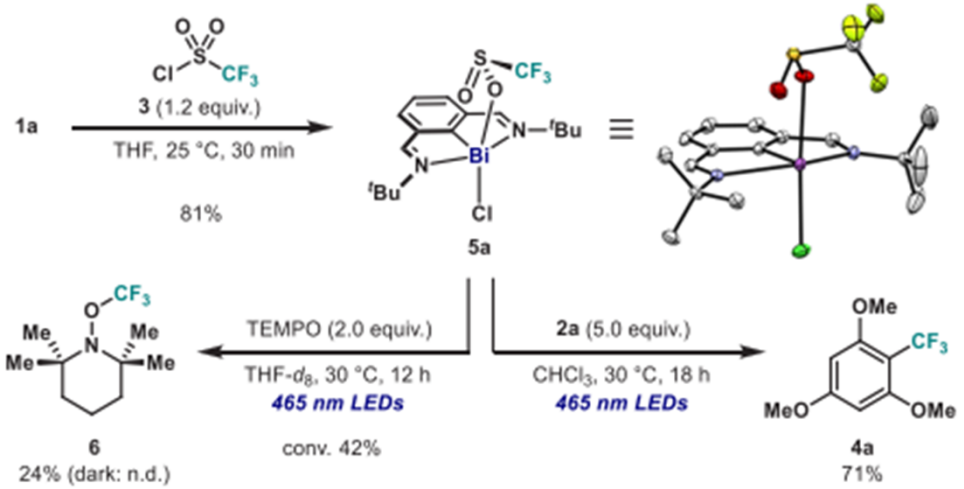
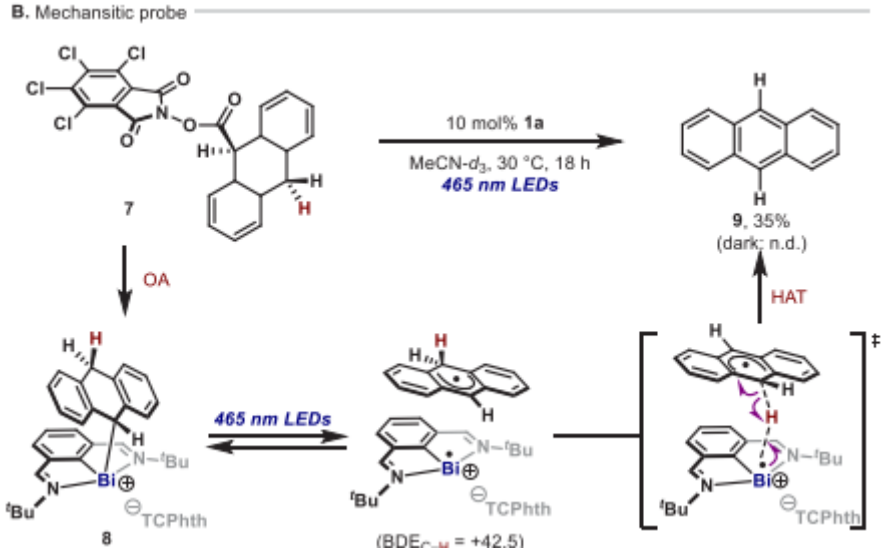
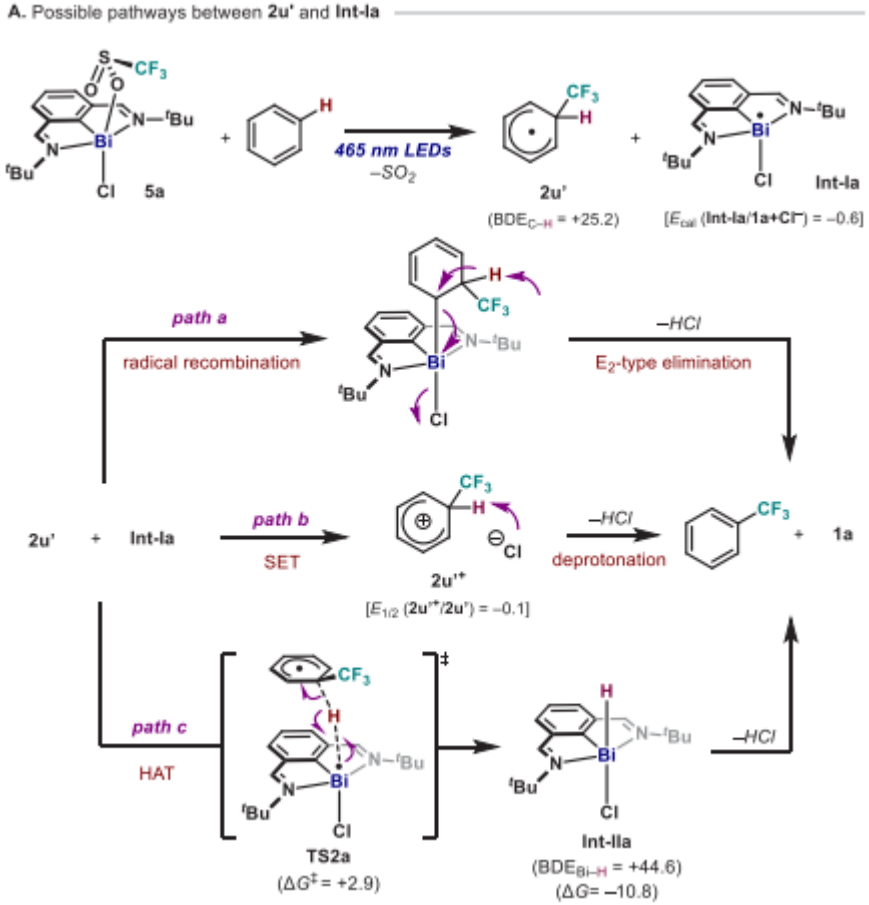



**Figure 2.** Synthesis of Bi(III) complex **5a** and SC-XRD structure (hydrogen atoms omitted for clarity) through oxidative addition of **1a** to **3**, and its reactivity toward generating the $CF_3$ radical.



# 二、Bi(I)/Bi(III)

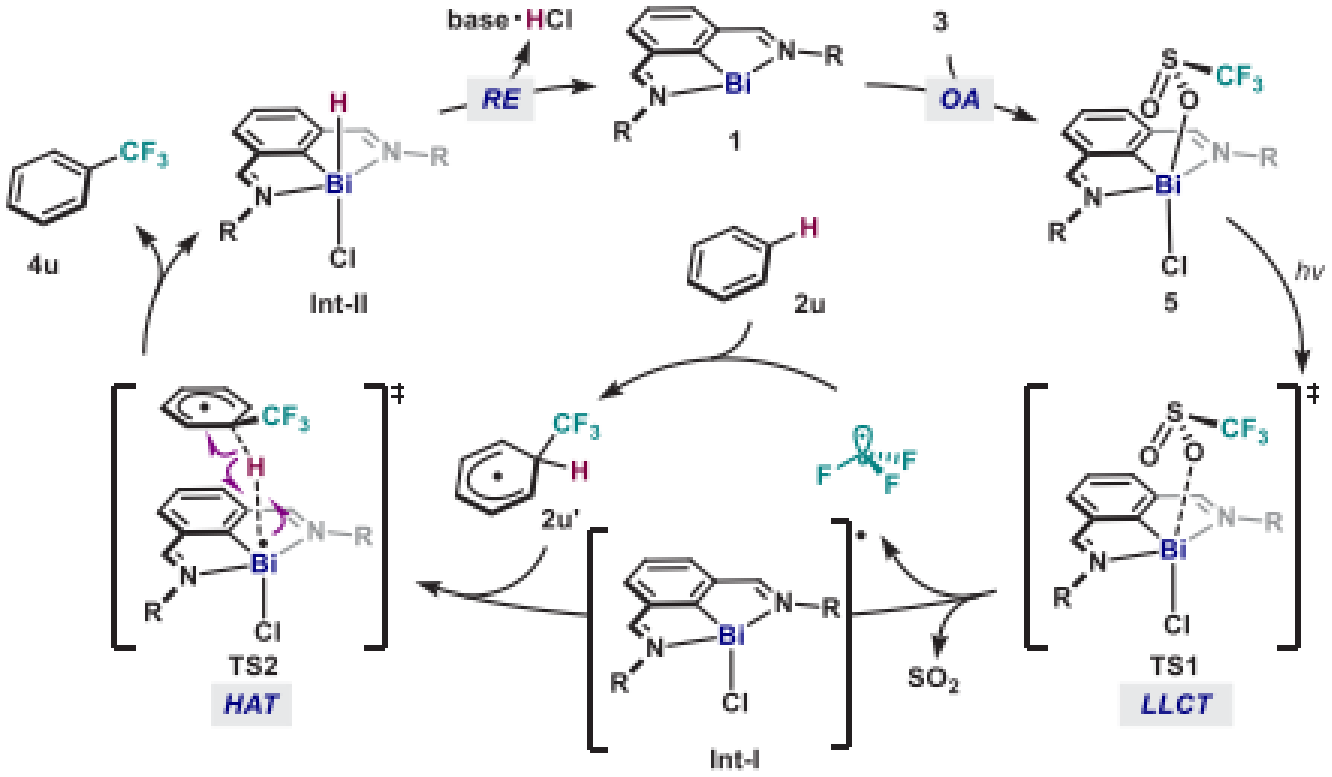



**Figure 5.** Proposed catalytic cycle of direct C–H radical trifluoromethylation of (hetero)arenes via open-shell bismuth redox cycle.

# 二、Bi(I)/Bi(III)

GDCh Communication Angewandte International Edition Chemie
www.angewandte.org

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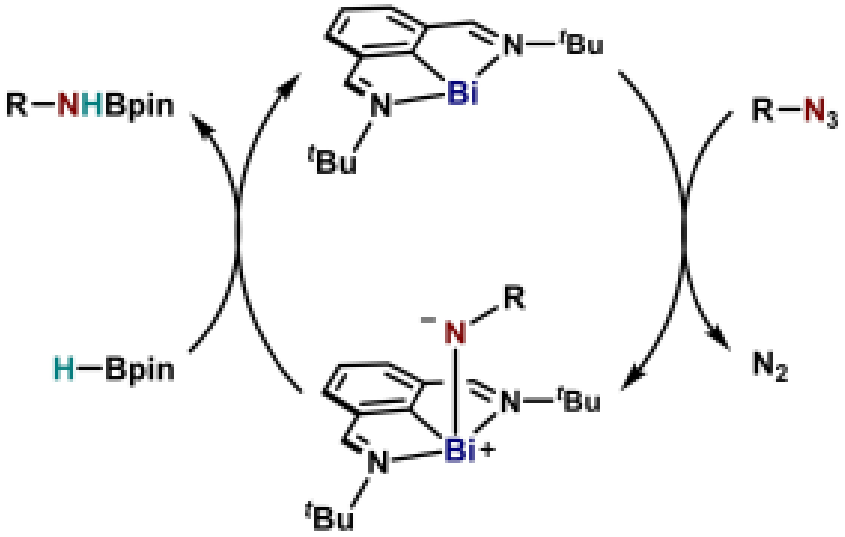
doi.org/10.1002/anie.202417864

**Main Group Catalysis**

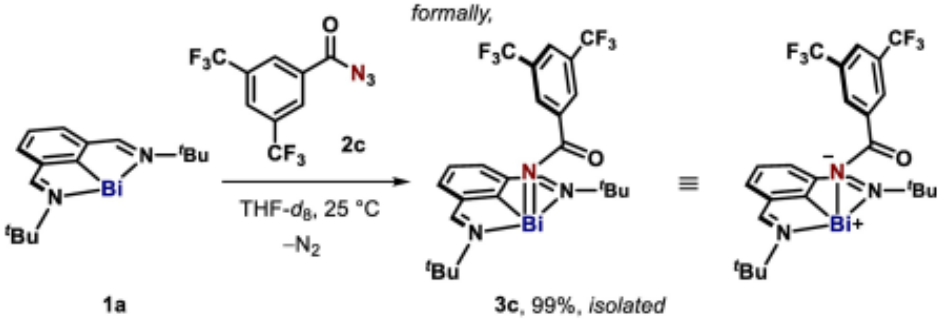
## Characterization of Iminobismuthanes and Catalytic Reduction of Organic Azides via Bi(I)/Bi(III) Redox Cycling

*Hye Won Moon, Nils Nöthling, Markus Leutzsch, Jennifer Kuziola, and Josep Cornella**

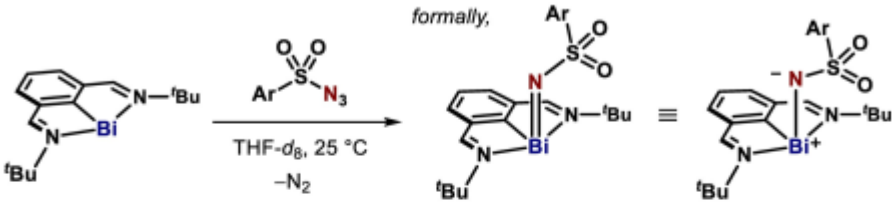


# 二、Bi(I)/Bi(III)

**A.** Preparation of iminobismuthane **3c**



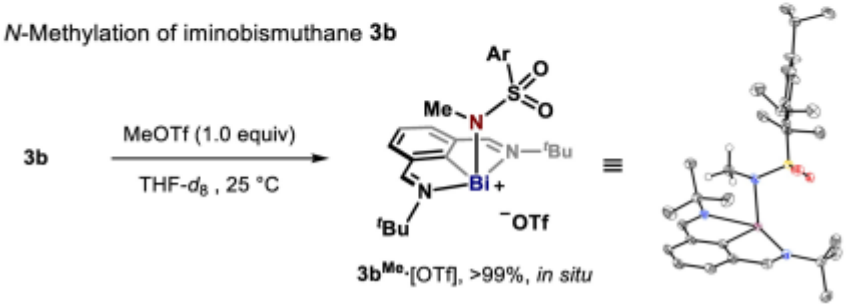

**A.** Reactivity of bismuthinidenes with arylsulfonyl azides




**1a**

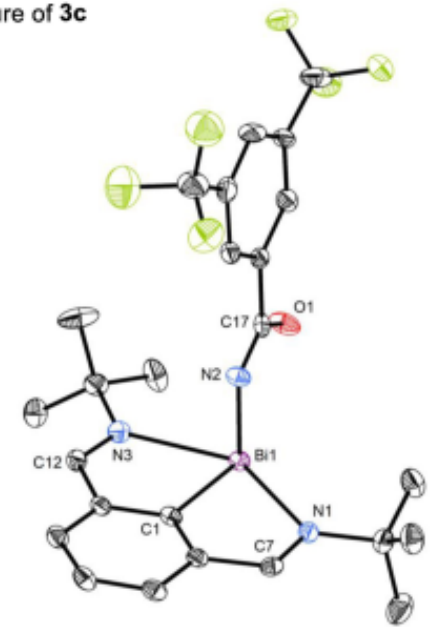
**3a**, Ar = *p*-tol, >99%, *in situ*
**3b**, Ar = 2,4,6-$^{i}$Pr$_3$-C$_6$H$_2$, >99%, *in situ*

**B.** *N*-Methylation of iminobismuthane **3b**

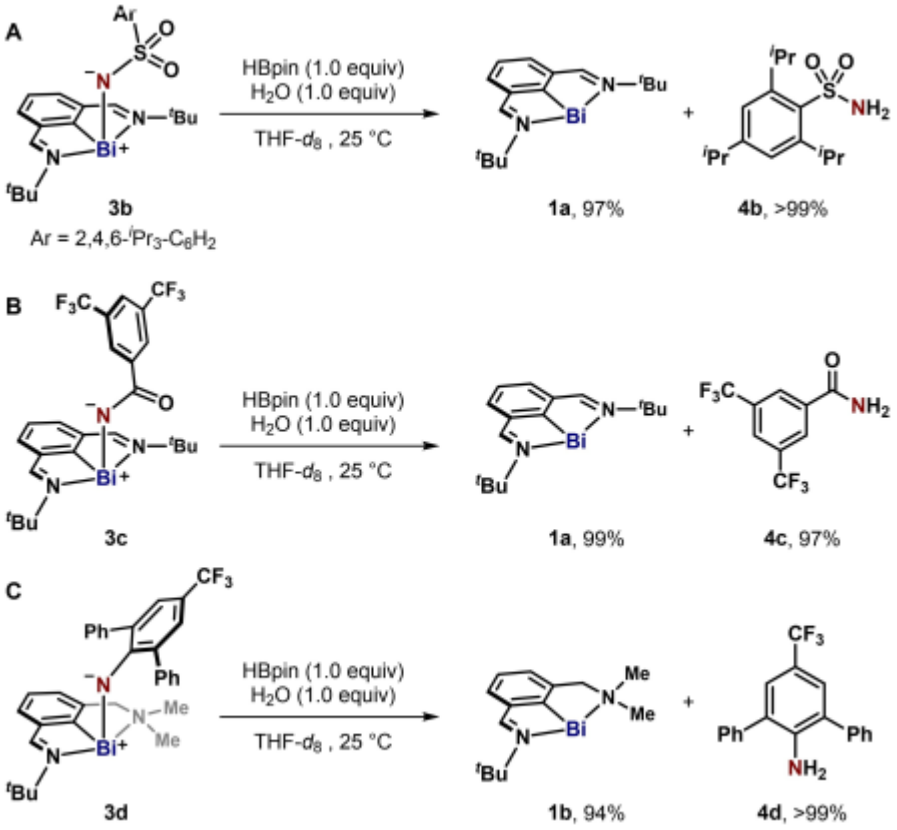


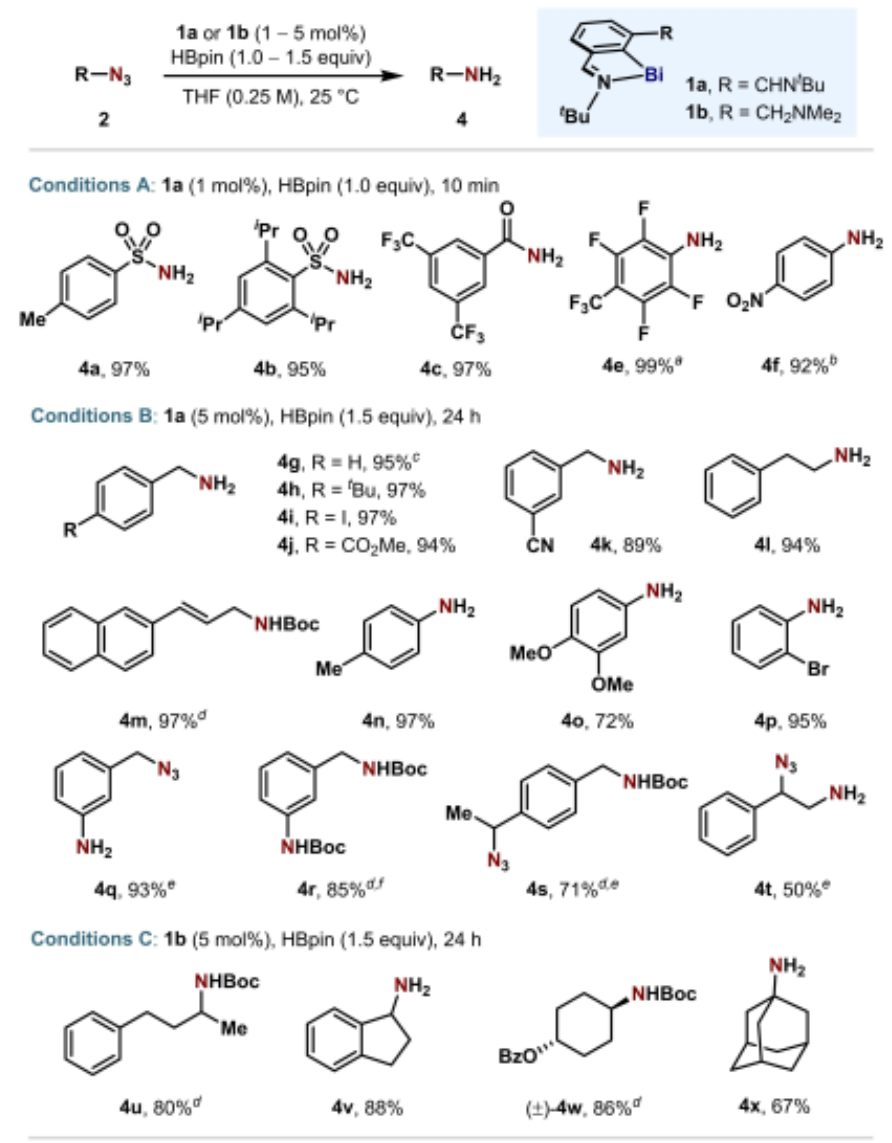

**3b$^{Me}$**-[OTf], >99%, *in situ*

**B.** Solid-state structure of **3c**

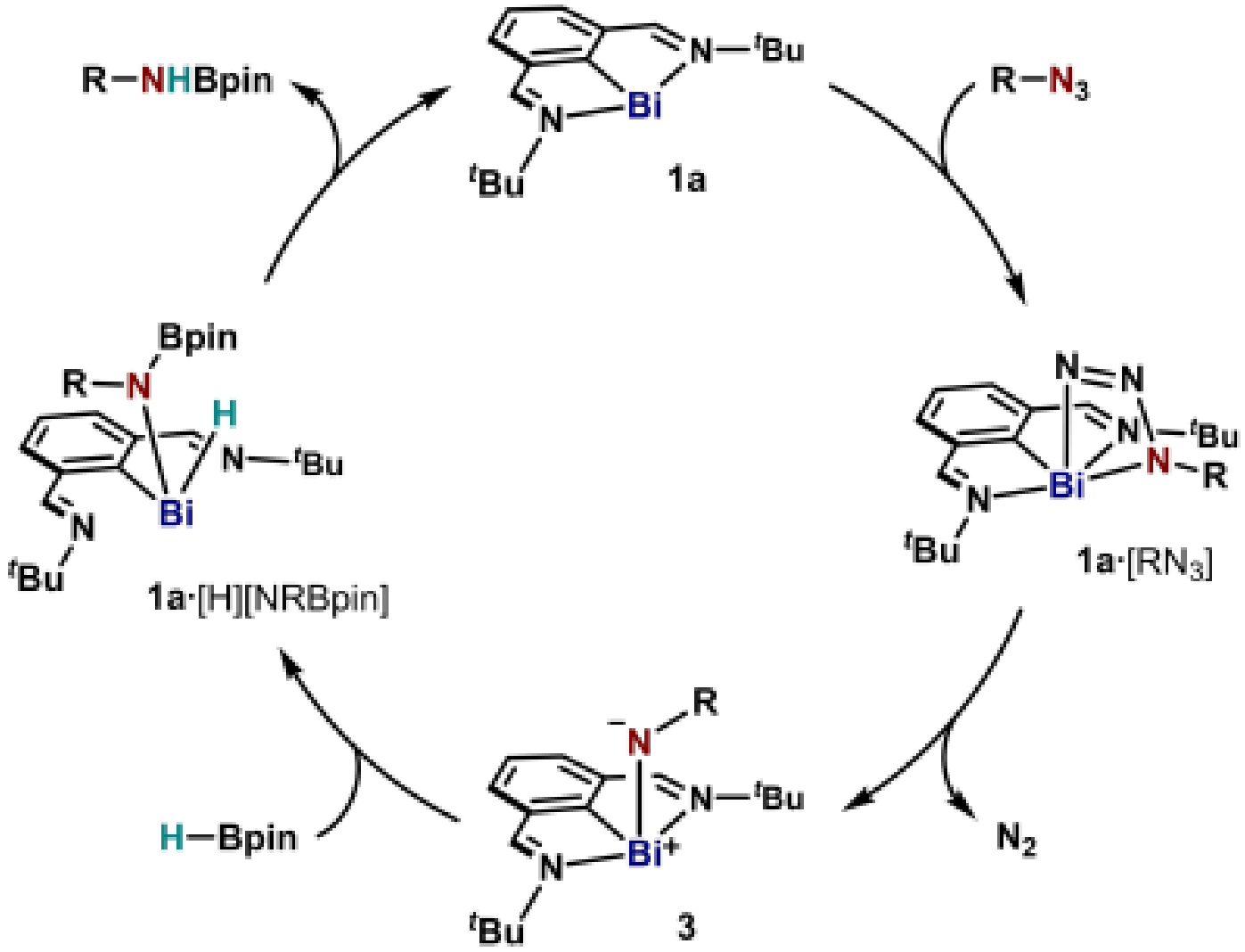


# 二、Bi(I)/Bi(III)


A
HBpin (1.0 equiv)
H2O (1.0 equiv)
THF-d8 , 25 °C
3b
Ar = 2,4,6-iPr3-C6H2
1a, 97%
4b, >99%
B
HBpin (1.0 equiv)
H2O (1.0 equiv)
THF-d8 , 25 °C
3c
1a, 99%
4c, 97%
C
HBpin (1.0 equiv)
H2O (1.0 equiv)
THF-d8 , 25 °C
3d
1b, 94%
4d, >99%


1a or 1b (1 – 5 mol%)
HBpin (1.0 – 1.5 equiv)
THF (0.25 M), 25 °C
2
4
1a, R = CHNtBu
1b, R = CH2NMe2
Conditions A: 1a (1 mol%), HBpin (1.0 equiv), 10 min
4a, 97%
4b, 95%
4c, 97%
4e, 99%a
4f, 92%b
Conditions B: 1a (5 mol%), HBpin (1.5 equiv), 24 h
4g, R = H, 95%c
4h, R = tBu, 97%
4i, R = I, 97%
4j, R = CO2Me, 94%
4k, 89%
4l, 94%
4m, 97%d
4n, 97%
4o, 72%
4p, 95%
4q, 93%e
4r, 85%d,f
4s, 71%d,e
4t, 50%e
Conditions C: 1b (5 mol%), HBpin (1.5 equiv), 24 h
4u, 80%d
4v, 88%
(±)-4w, 86%d
4x, 67%

# 二、Bi(I)/Bi(III)



# 二、Bi(I)/Bi(III)

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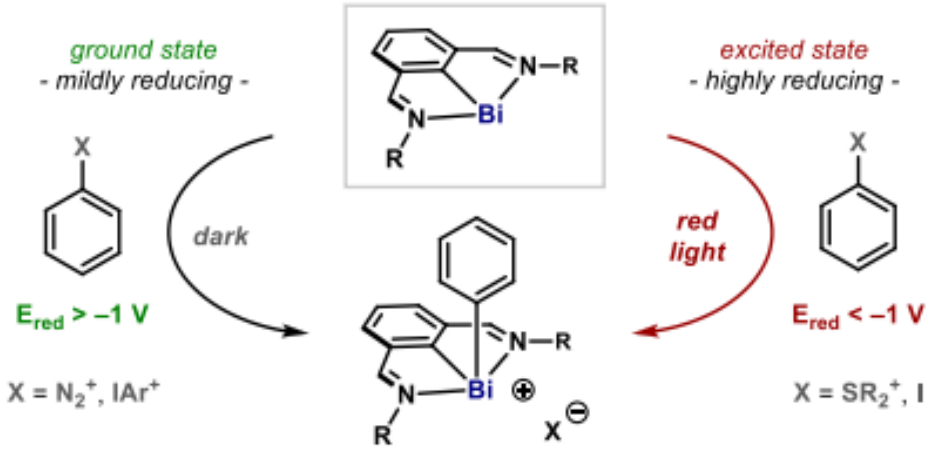
Communication

## Oxidative Addition of Aryl Electrophiles into a Red-Light-Active Bismuthinidene

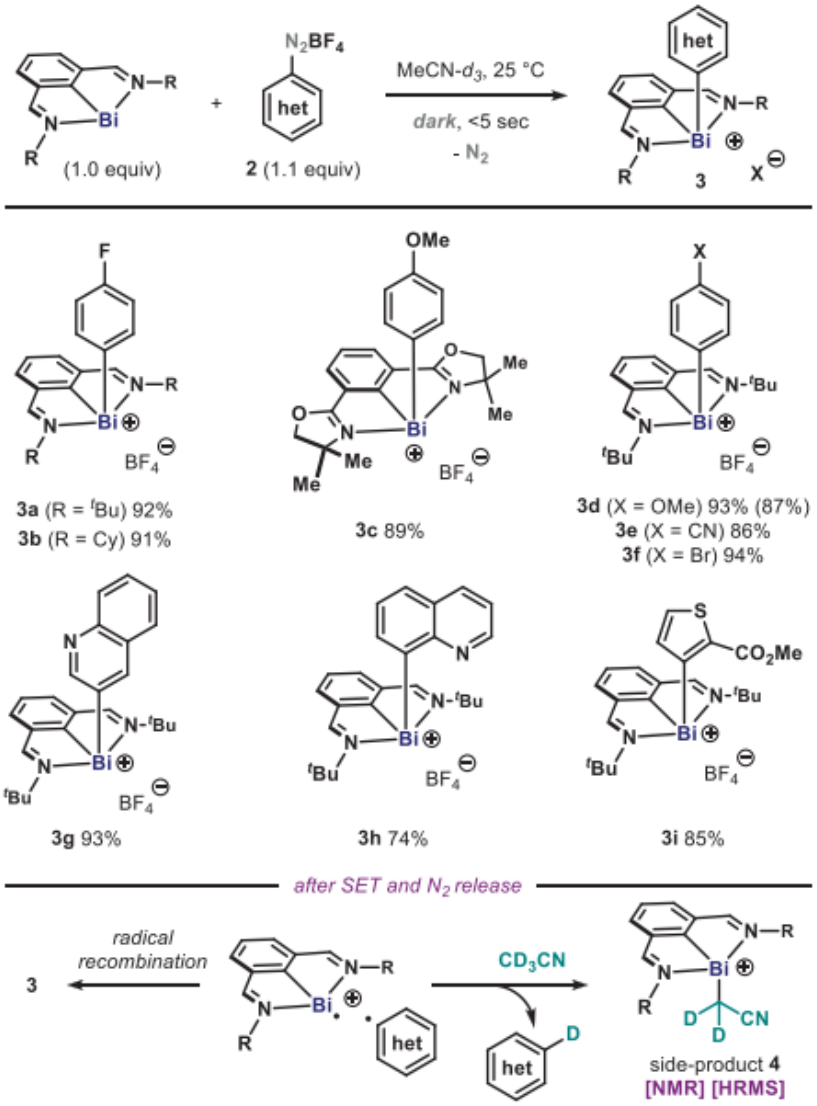
Mauro Mato, Paolo Cleto Bruzzese, Fumiya Takahashi, Markus Leutzsch, Edward J. Reijerse, Alexander Schnegg, and Josep Cornella*

**C.** A photoactive bismuthinidene to unify aryl OA into a MG complex: ***this work***



# 二、Bi(I)/Bi(III)

**Scheme 1. Scope of the Oxidative Addition of Aryl Diazonium Salts into Ground-State Bismuth(I)**[a]



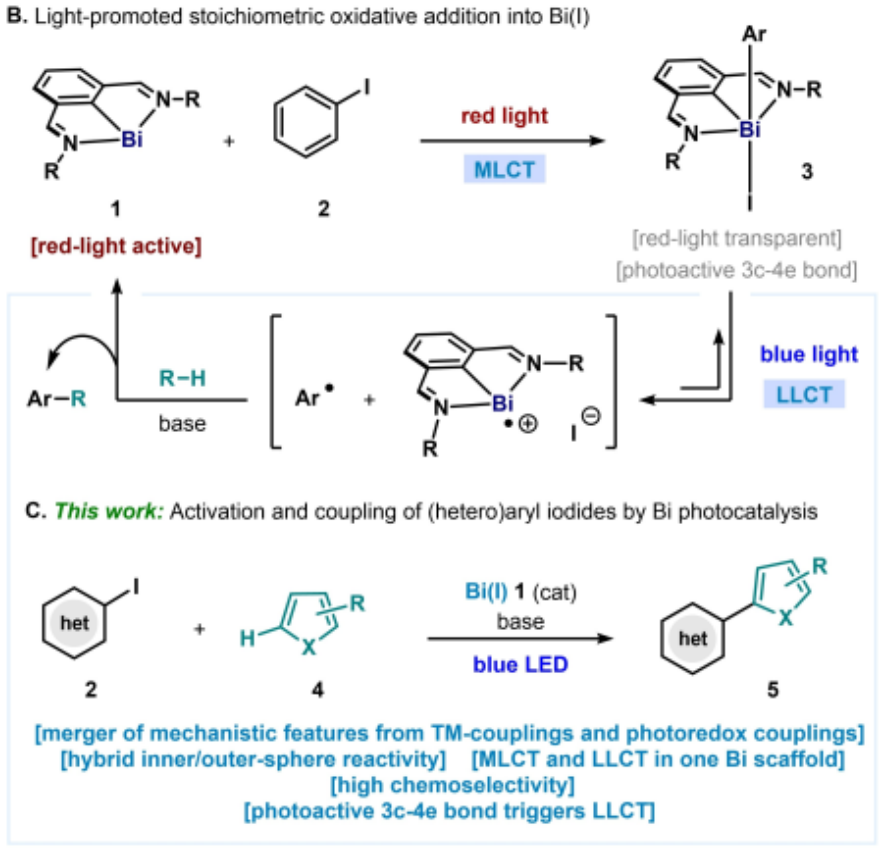
# 二、Bi(I)/Bi(III)

GDCh Communication Angewandte International Edition Chemie
www.angewandte.org

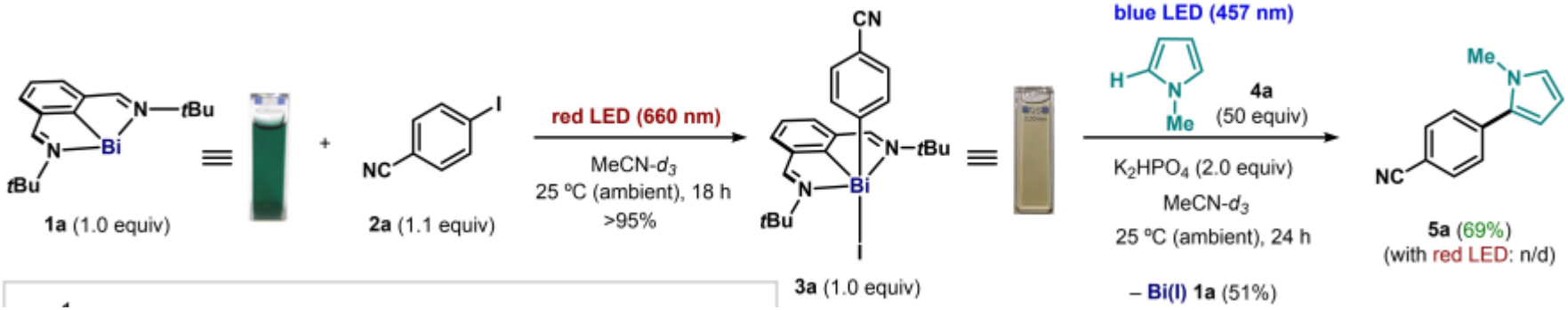
How to cite: *Angew. Chem. Int. Ed.* **2025**, *64*, e202418367
doi.org/10.1002/anie.202418367

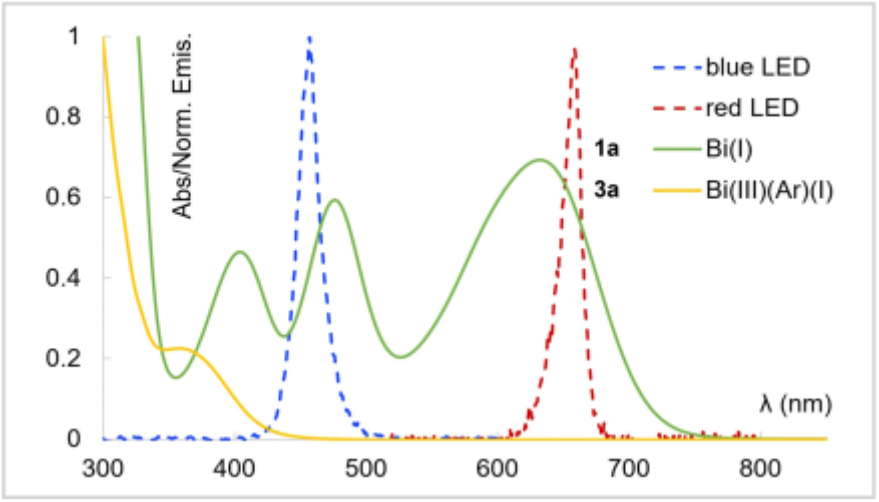
**Bismuth Catalysis** | **Hot Paper**

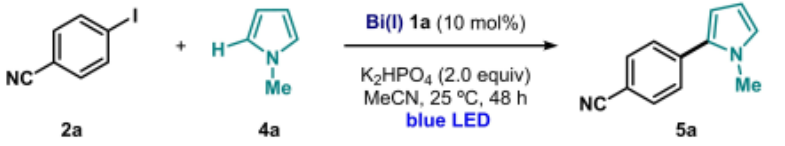
## Activation and C–C Coupling of Aryl Iodides via Bismuth Photocatalysis



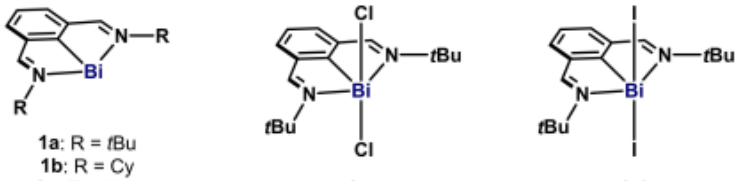
# 二、Bi(I)/Bi(III)




| Entry | Deviations from standard conditions[a] | Yield of **5a** |
|---|---|---|
| 1 | none | 58% (62%)[b] |
| 2 | 14 h instead of 48 h | 38% |
| 3 | no light, 45 °C | n/d |
| 4 | without **Bi(I)** (**blue** or **red** LED) | <1% |
| 5 | without base | 12% |
| 6 | **red LED** instead of **blue LED** | 15% |
| 7 | **1b** instead of **1a**, 60 h | 63%[b] |
| 8 | **1c** instead of **1a**, 14 h | 15% |
| 9 | $BiCl_3$ or $BiI_3$ instead of **1a** | n/d |
| 10 | **1aa** or **1ab** instead of **1a** | <2% |

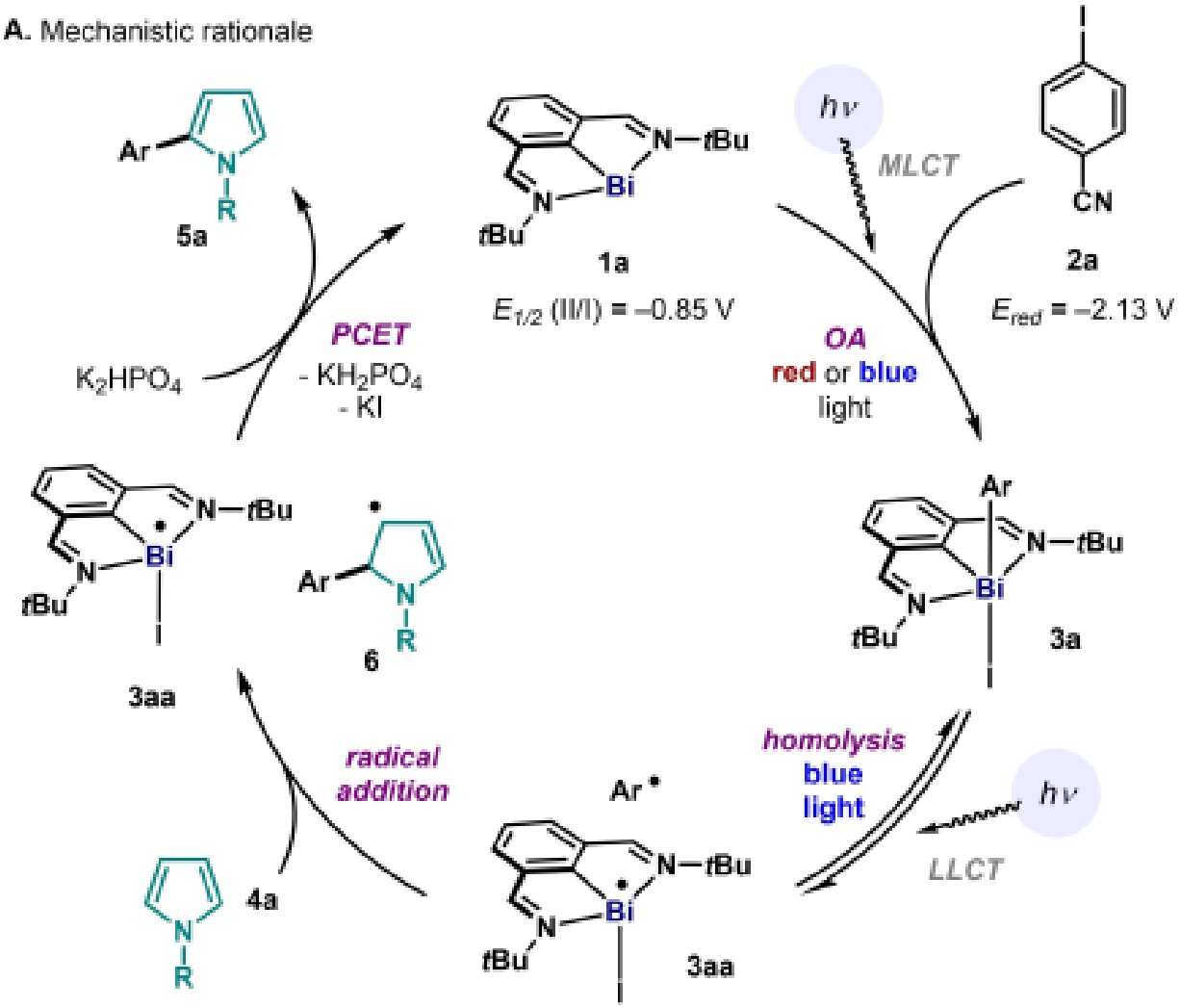


**1a**: R = *t*Bu
**1b**: R = Cy
**1c**: R = Mes

**1aa**

**1ab**

# 二、Bi(I)/Bi(III)


A. Mechanistic rationale
Ar
N
R
5a
K2HPO4
PCET
- KH2PO4
- KI
N—tBu
Bi
tBu
1a
E1/2 (II/I) = –0.85 V
hν
MLCT
CN
2a
Ered = –2.13 V
OA
red or blue
light
Ar
N—tBu
Bi
tBu
3a
homolysis
blue
light
hν
LLCT
Ar •
N—tBu
Bi
tBu
3aa
radical
addition
4a
N
R
N—tBu
Bi
tBu
3aa
Ar
N
R
6

# 二、Bi(I)/Bi(III)

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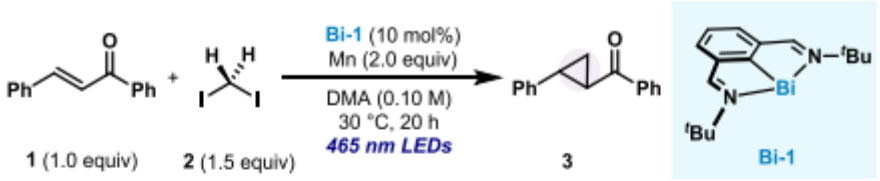
Communication

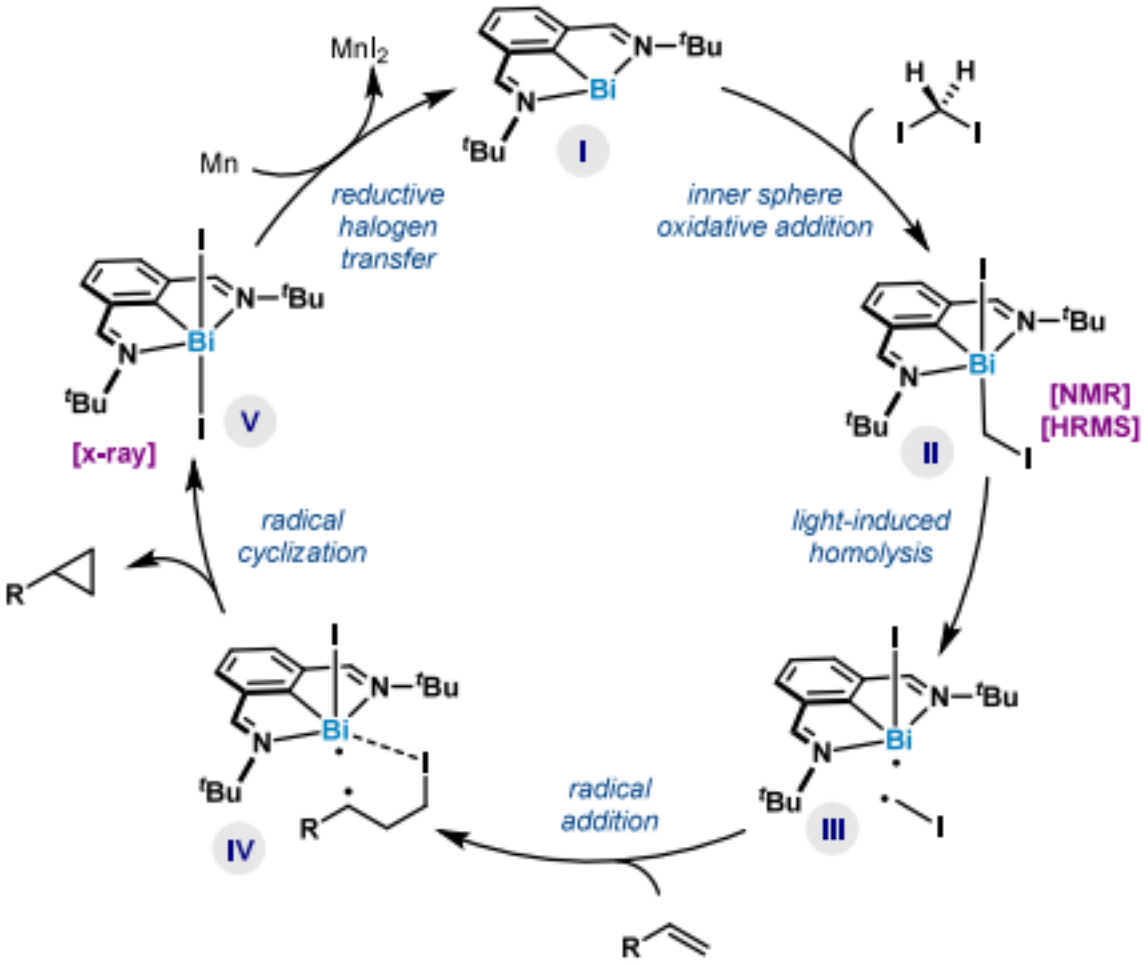
## Reductive Cyclopropanation through Bismuth Photocatalysis

Shengyang Ni, Davide Spinnato, and Josep Cornella*




| entry | deviations from above[a] | yield of 3 (%)[b] |
|---|---|---|
| 1 | none | 74 (70)[c] |
| 2 | without catalyst | trace |
| 3 | without light | trace |
| 4 | red LEDs | trace |
| 5 | MeCN instead of DMA | 51 |
| 6 | Zn instead of Mn | 30 |
| 7 | (−) Ni foam/(+) Zn; 5.0 mA, 465 nm LEDs; 12 h | 55 |
| 8 | air stable **Bi-1**·[$Cl_2$] instead of Bi-1 | 68 |
| 9 | $CH_2Br_2$/NaI instead of $CH_2I_2$ | 40 |

# 二、Bi(I)/Bi(III)

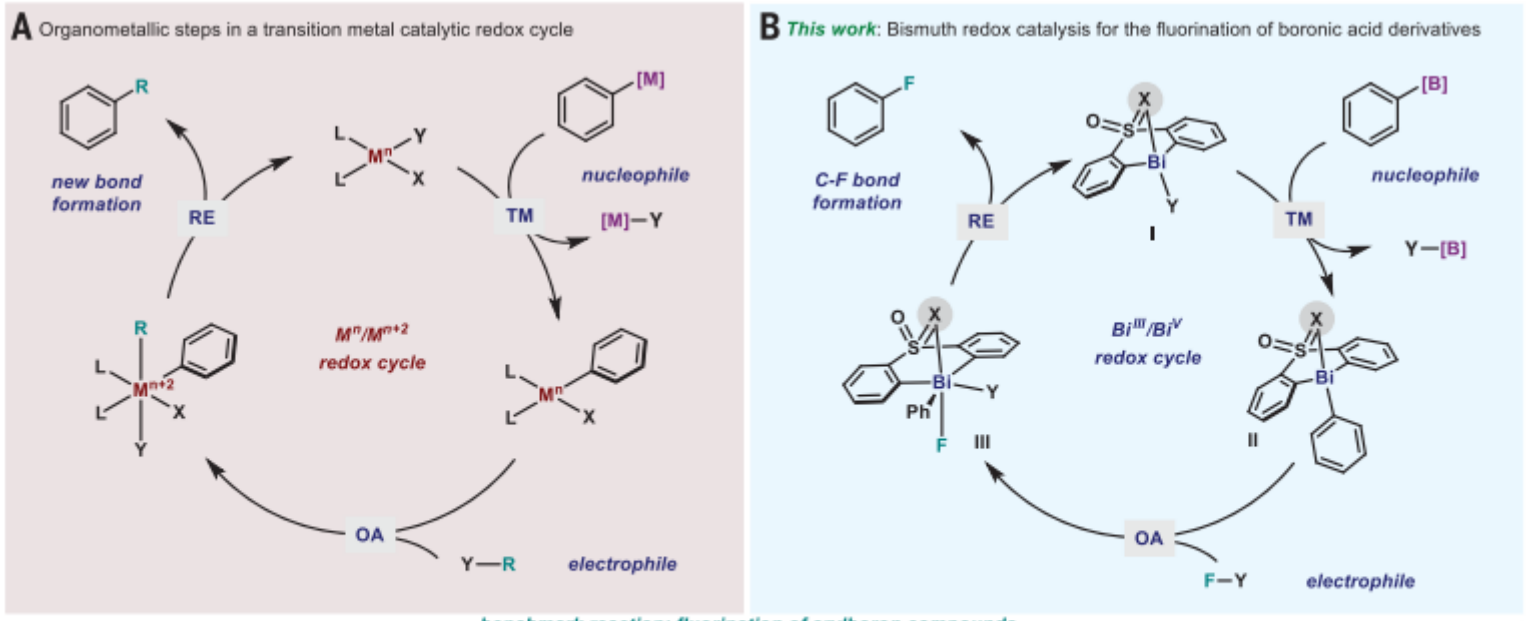

MnI2
Mn
reductive halogen transfer
inner sphere oxidative addition
[NMR]
[HRMS]
[x-ray]
radical cyclization
light-induced homolysis
radical addition
I
II
III
IV
V

# 二、Bi(III)/Bi(V)

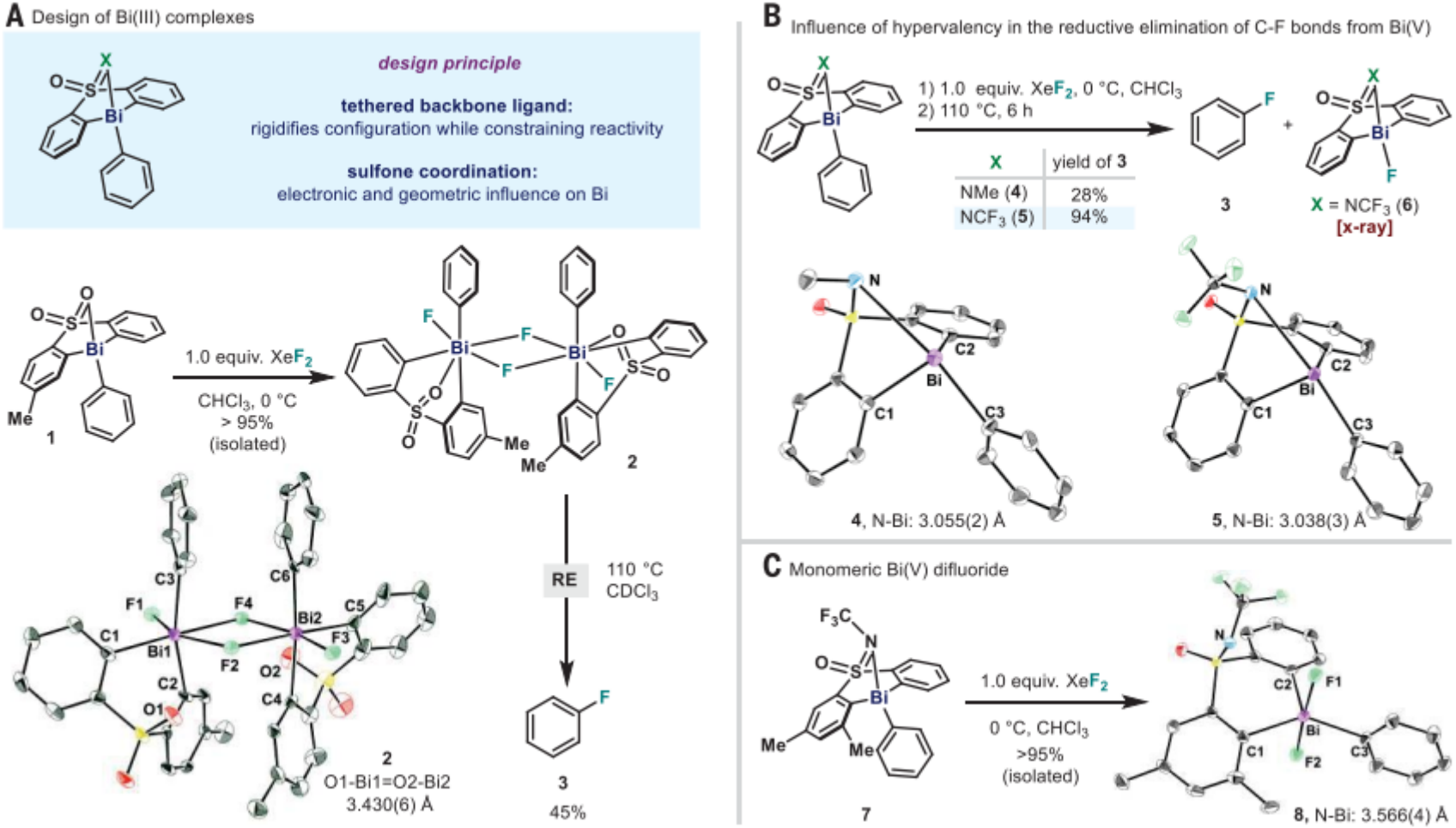
ORGANOMETALLICS

## Fluorination of arylboronic esters enabled by bismuth redox catalysis

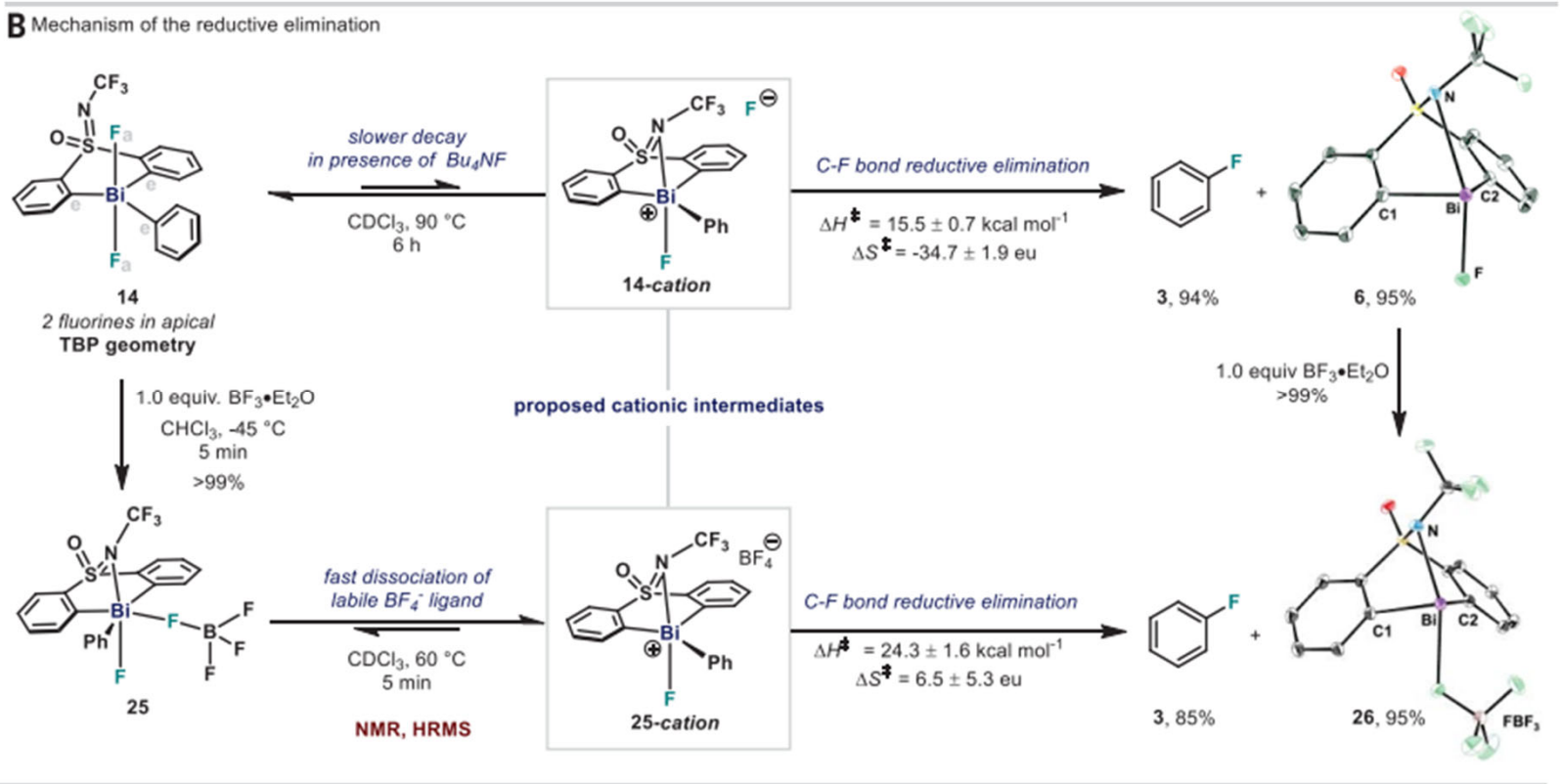
Oriol Planas*, Feng Wang*, Markus Leutzsch, Josep Cornella†



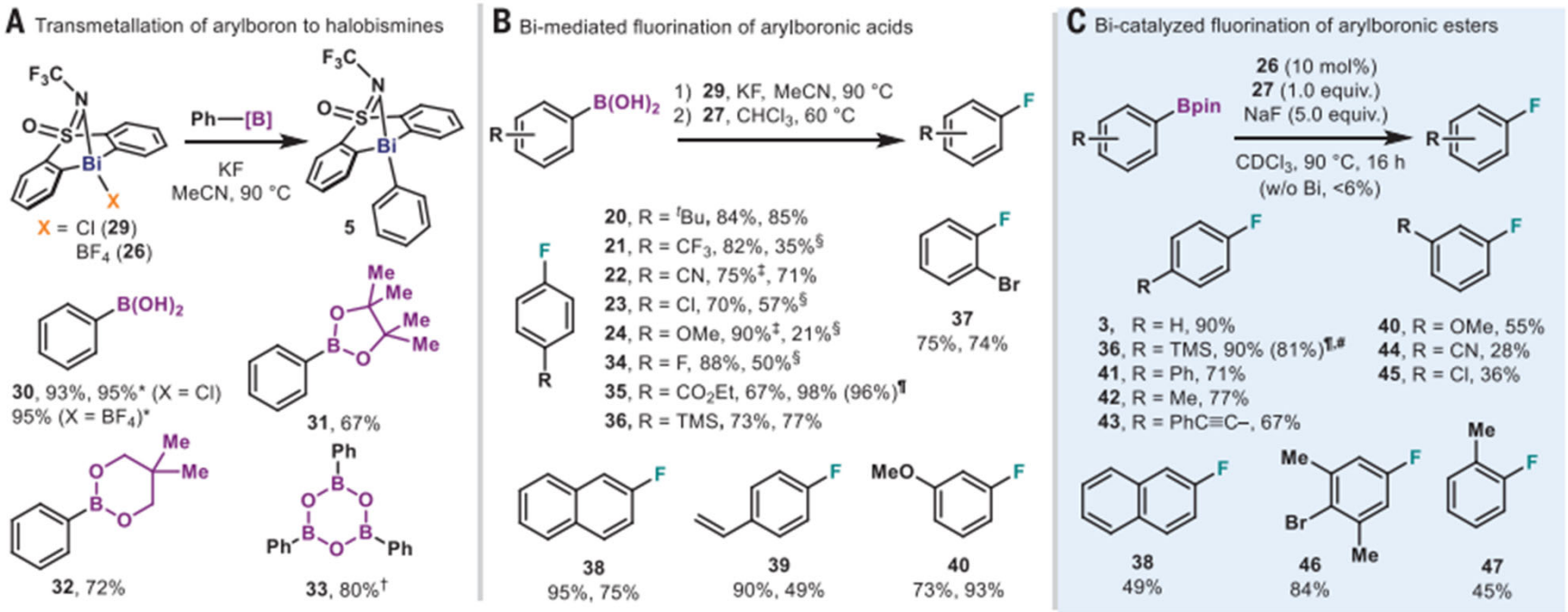
# 二、Bi(III)/Bi(V)


A Design of Bi(III) complexes
design principle
tethered backbone ligand:
rigidifies configuration while constraining reactivity
sulfone coordination:
electronic and geometric influence on Bi
1.0 equiv. XeF2
CHCl3, 0 °C
> 95%
(isolated)
RE
110 °C
CDCl3
45%
2
O1-Bi1=O2-Bi2
3.430(6) Å
B Influence of hypervalency in the reductive elimination of C-F bonds from Bi(V)
1) 1.0 equiv. XeF2, 0 °C, CHCl3
2) 110 °C, 6 h
X | yield of 3
NMe (4) 28%
NCF3 (5) 94%
X = NCF3 (6)
[x-ray]
4, N-Bi: 3.055(2) Å
5, N-Bi: 3.038(3) Å
C Monomeric Bi(V) difluoride
1.0 equiv. XeF2
0 °C, CHCl3
>95%
(isolated)
8, N-Bi: 3.566(4) Å

# 二、Bi(III)/Bi(V)


B Mechanism of the reductive elimination
14
2 fluorines in apical
TBP geometry
slower decay
in presence of Bu4NF
CDCl3, 90 °C
6 h
14-cation
C-F bond reductive elimination
ΔH‡ = 15.5 ± 0.7 kcal mol-1
ΔS‡ = -34.7 ± 1.9 eu
3, 94%
6, 95%
1.0 equiv. BF3•Et2O
CHCl3, -45 °C
5 min
>99%
proposed cationic intermediates
1.0 equiv BF3•Et2O
>99%
25
fast dissociation of
labile BF4- ligand
CDCl3, 60 °C
5 min
NMR, HRMS
25-cation
C-F bond reductive elimination
ΔH‡ = 24.3 ± 1.6 kcal mol-1
ΔS‡ = 6.5 ± 5.3 eu
3, 85%
26, 95%

# 二、Bi(III)/Bi(V)


A Transmetallation of arylboron to halobismines
X = Cl (29)
BF4 (26)
Ph—[B]
KF
MeCN, 90 °C
5
30, 93%, 95%* (X = Cl)
95% (X = BF4)*
31, 67%
32, 72%
33, 80%†
B Bi-mediated fluorination of arylboronic acids
1) 29, KF, MeCN, 90 °C
2) 27, CHCl3, 60 °C
20, R = tBu, 84%, 85%
21, R = CF3, 82%, 35%§
22, R = CN, 75%‡, 71%
23, R = Cl, 70%, 57%§
24, R = OMe, 90%‡, 21%§
34, R = F, 88%, 50%§
35, R = CO2Et, 67%, 98% (96%)¶
36, R = TMS, 73%, 77%
37
75%, 74%
38
95%, 75%
39
90%, 49%
40
73%, 93%
C Bi-catalyzed fluorination of arylboronic esters
26 (10 mol%)
27 (1.0 equiv.)
NaF (5.0 equiv.)
CDCl3, 90 °C, 16 h
(w/o Bi, <6%)
3, R = H, 90%
36, R = TMS, 90% (81%)¶,#
41, R = Ph, 71%
42, R = Me, 77%
43, R = PhC≡C–, 67%
40, R = OMe, 55%
44, R = CN, 28%
45, R = Cl, 36%
38
49%
46
84%
47
45%

# 二、Bi(III)/Bi(V)

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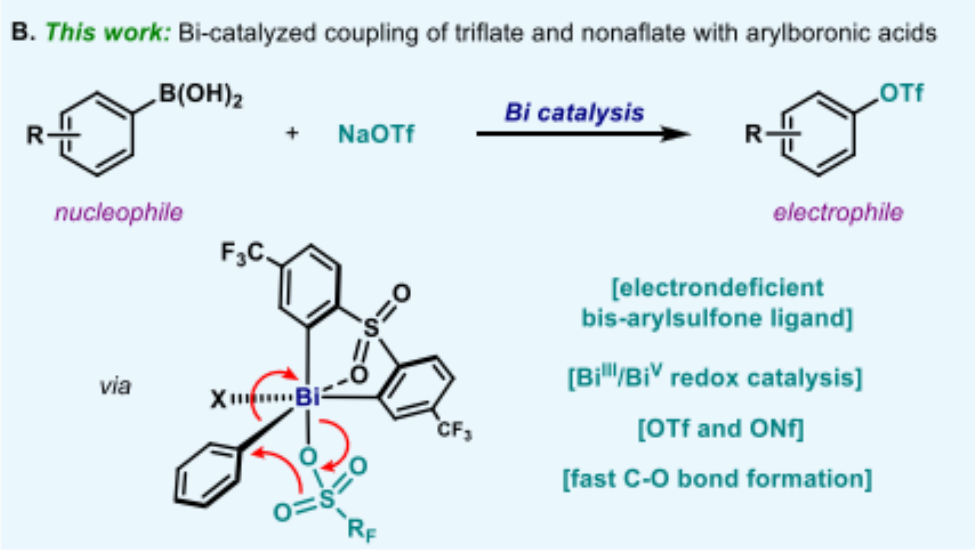
Communication

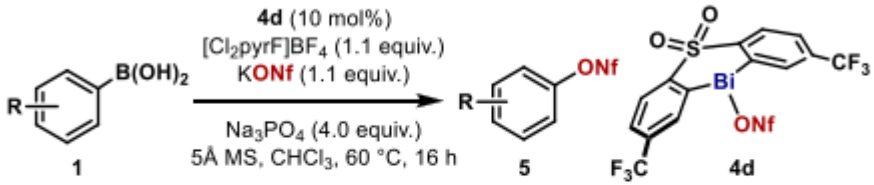
## Bismuth-Catalyzed Oxidative Coupling of Arylboronic Acids with Triflate and Nonaflate Salts

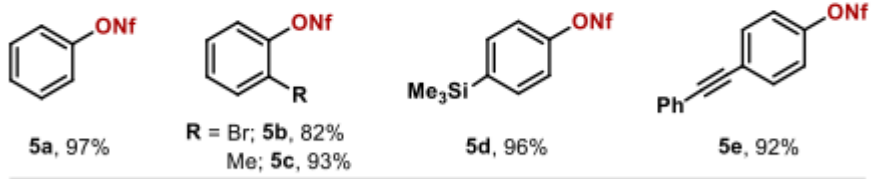
Oriol Planas, Vytautas Peciukenas, and Josep Cornella*



# 二、Bi(III)/Bi(V)

**Table 3. Scope of the Bi-Catalyzed Oxidative Coupling of Arylboronic Acids and Potassium Nonaflate**[a]

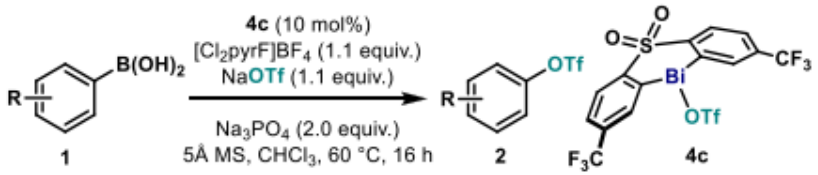


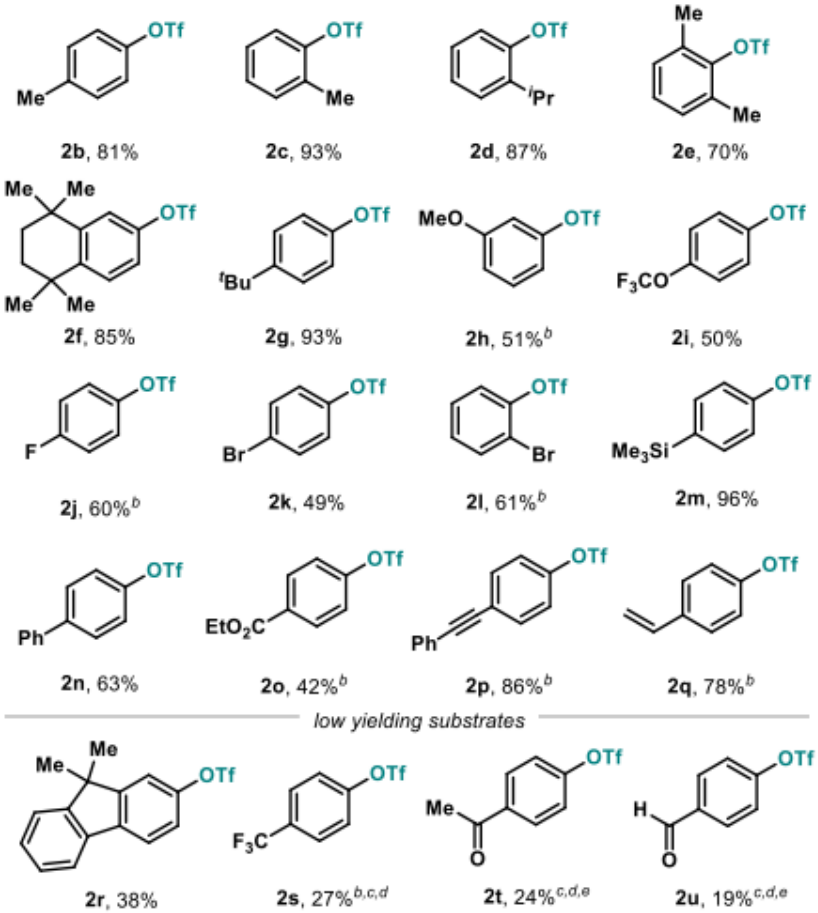




5a, 97% | R = Br; 5b, 82% Me; 5c, 93% | 5d, 96% | 5e, 92%

[a]Reaction conditions: **1** (0.3 mmol), KONf (0.33 mmol), **4d** (0.03 mmol), $[Cl_2pyrF]BF_4$ (0.33 mmol), $Na_3PO_4$ (1.2 mmol) and 5 Å MS (120 mg) in $CHCl_3$ at 60 °C for 16 h. Yields of isolated pure material.

**Table 2. Scope of the Bi-Catalyzed Oxidative Coupling of Arylboronic Acids and Sodium Triflate**[a]




2b, 81% | 2c, 93% | 2d, 87% | 2e, 70%

2f, 85% | 2g, 93% | 2h, 51%[b] | 2i, 50%

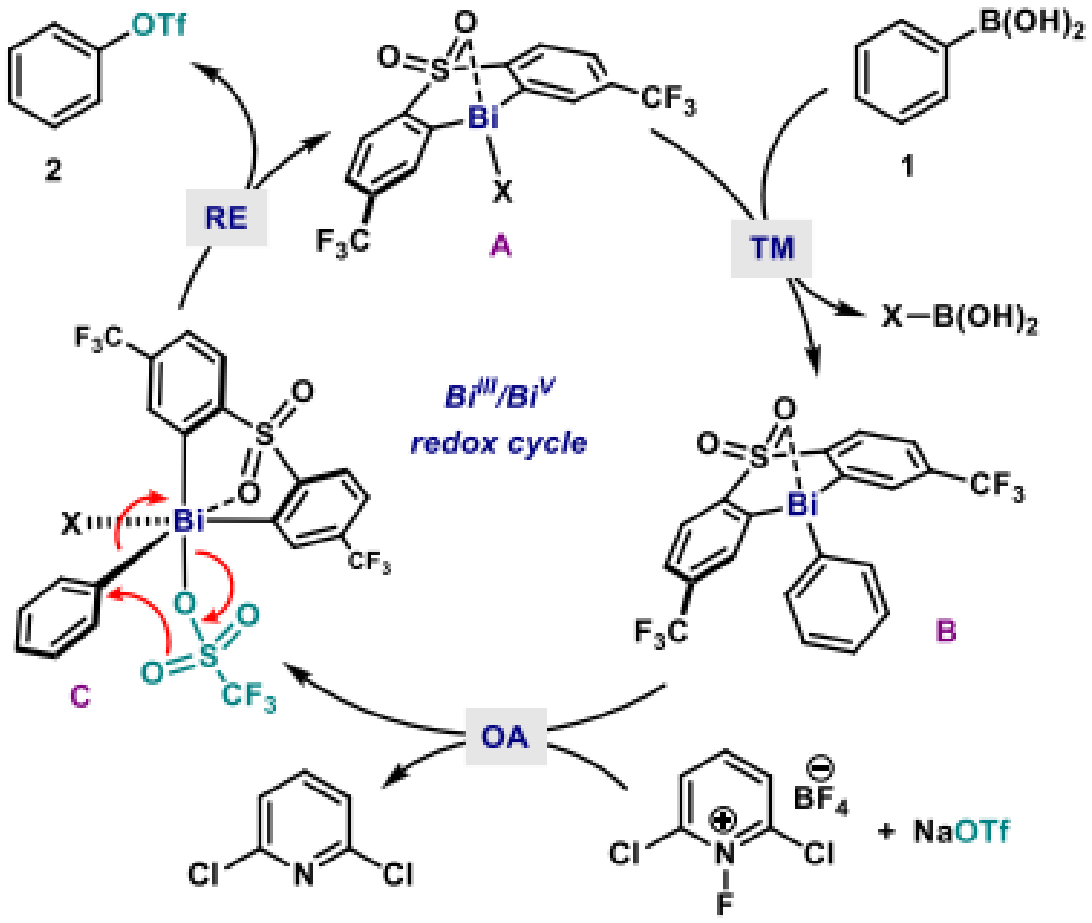
2j, 60%[b] | 2k, 49% | 2l, 61%[b] | 2m, 96%

2n, 63% | 2o, 42%[b] | 2p, 86%[b] | 2q, 78%[b]

*low yielding substrates*

2r, 38% | 2s, 27%[b,c,d] | 2t, 24%[c,d,e] | 2u, 19%[c,d,e]

# 二、Bi(III)/Bi(V)



# 二、中性催化

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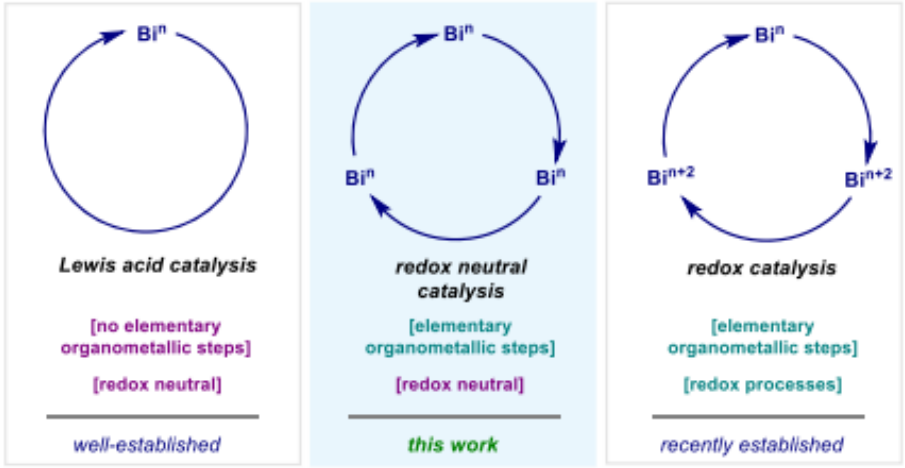
Communication

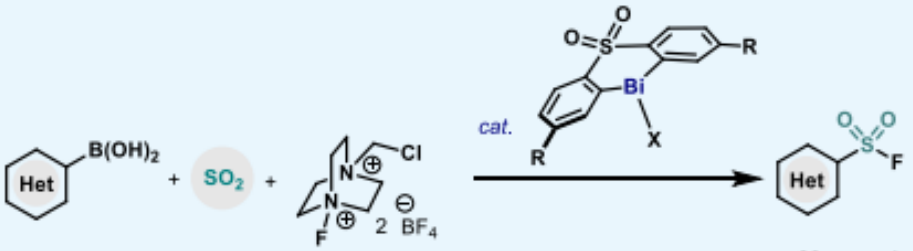
## Redox-Neutral Organometallic Elementary Steps at Bismuth: Catalytic Synthesis of Aryl Sulfonyl Fluorides

Marc Magre and Josep Cornella*

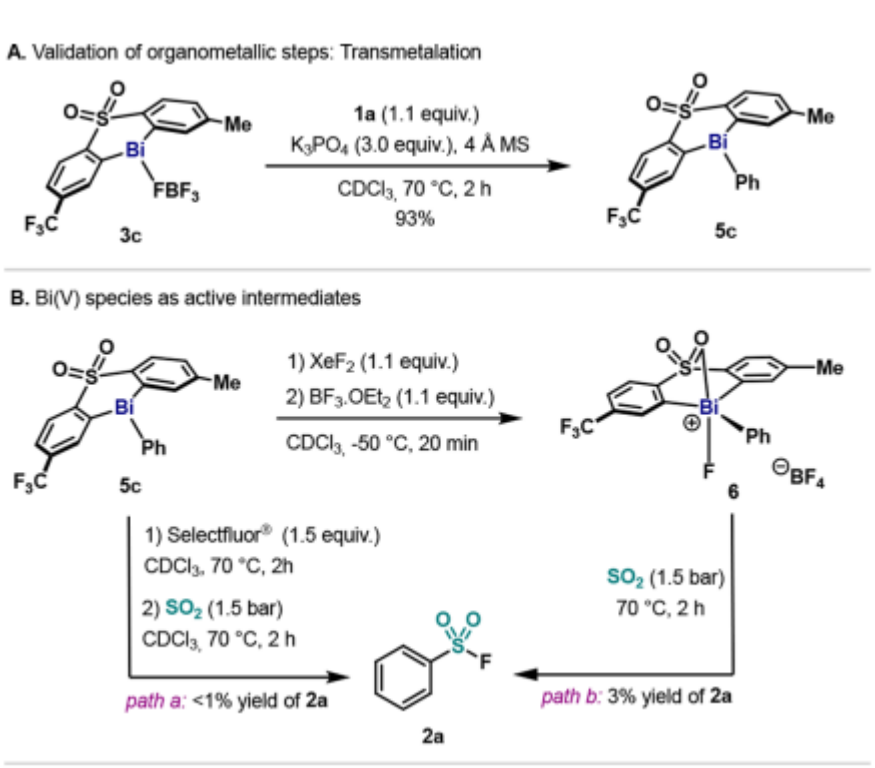
**B.** Bismuth catalysis in organic synthesis

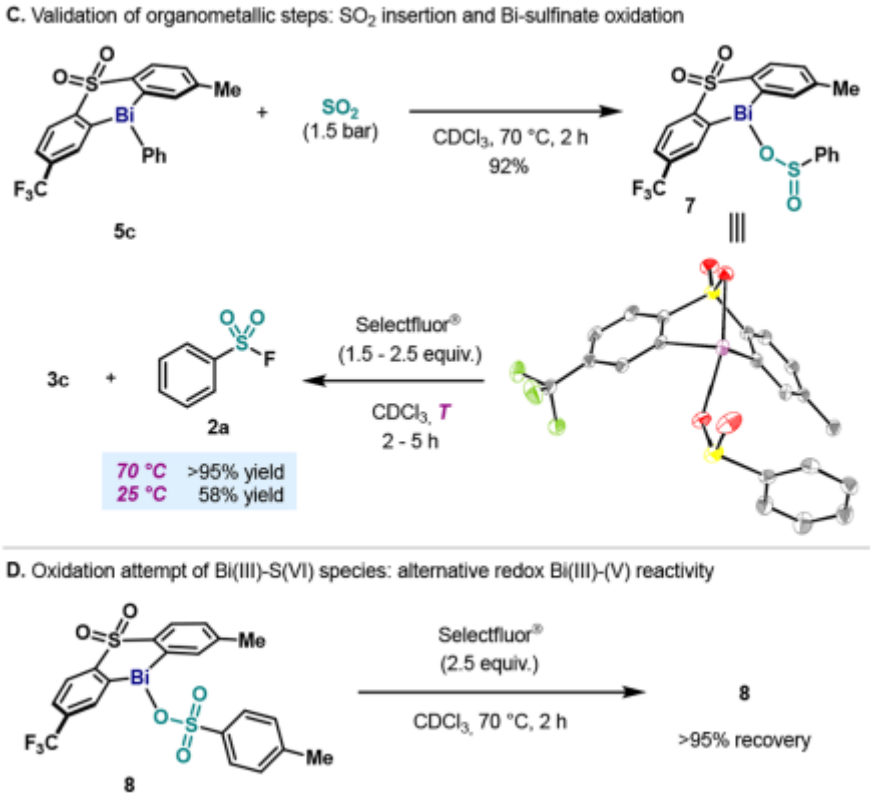



**C. This work:** bismuth redox neutral catalysis for the synthesis of sulfonyl fluorides



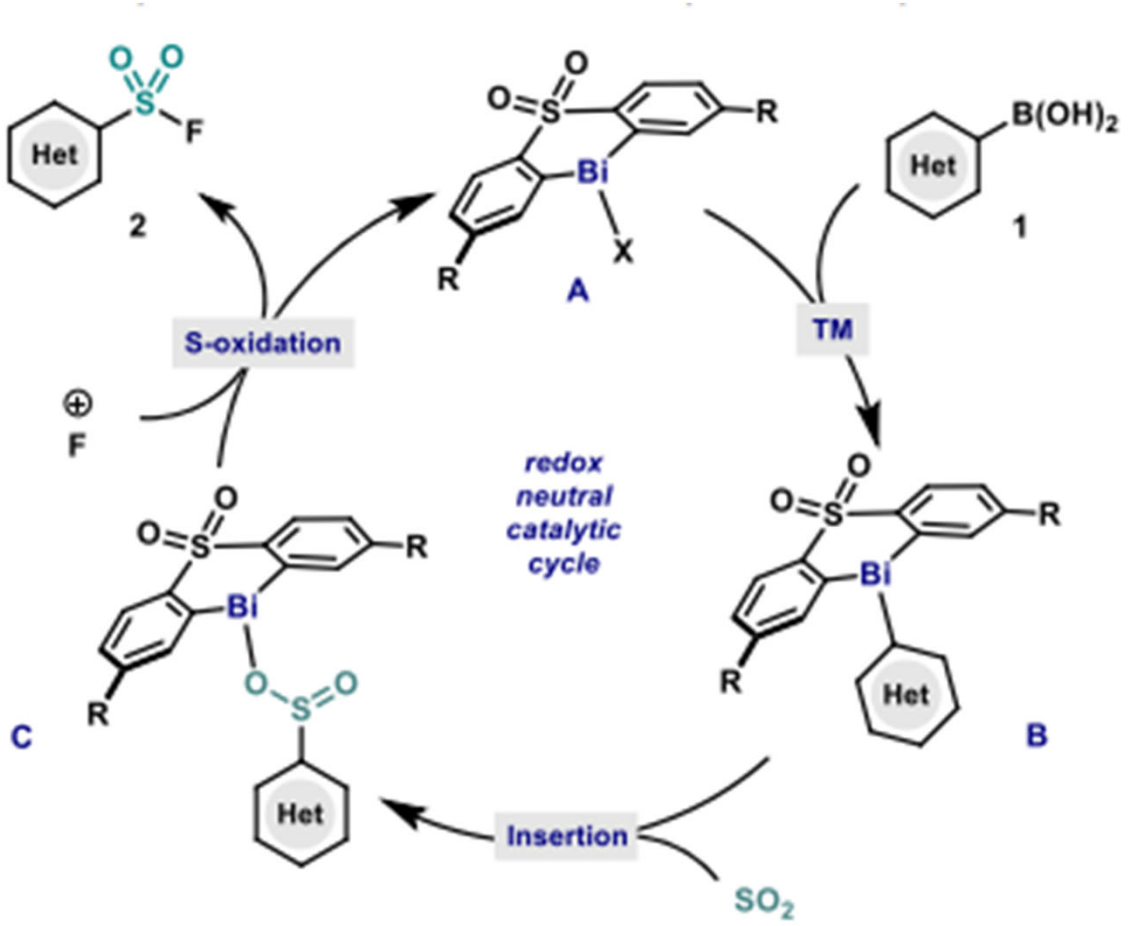
# 二、中性催化


A. Validation of organometallic steps: Transmetalation
1a (1.1 equiv.)
K3PO4 (3.0 equiv.), 4 Å MS
CDCl3, 70 °C, 2 h
93%
3c
5c
B. Bi(V) species as active intermediates
1) XeF2 (1.1 equiv.)
2) BF3.OEt2 (1.1 equiv.)
CDCl3, -50 °C, 20 min
5c
6
1) Selectfluor® (1.5 equiv.)
CDCl3, 70 °C, 2h
2) SO2 (1.5 bar)
CDCl3, 70 °C, 2 h
path a: <1% yield of 2a
SO2 (1.5 bar)
70 °C, 2 h
path b: 3% yield of 2a
2a


C. Validation of organometallic steps: SO2 insertion and Bi-sulfinate oxidation
5c
SO2
(1.5 bar)
CDCl3, 70 °C, 2 h
92%
7
3c
2a
Selectfluor®
(1.5 - 2.5 equiv.)
CDCl3, T
2 - 5 h
70 °C >95% yield
25 °C 58% yield


D. Oxidation attempt of Bi(III)-S(VI) species: alternative redox Bi(III)-(V) reactivity
8
Selectfluor®
(2.5 equiv.)
CDCl3, 70 °C, 2 h
8
>95% recovery

# 二、中性催化


Het
F
2
S-oxidation
A
TM
Het
B(OH)2
1
redox
neutral
catalytic
cycle
B
Het
Insertion
SO2
C
Het
F

# 二、中性催化

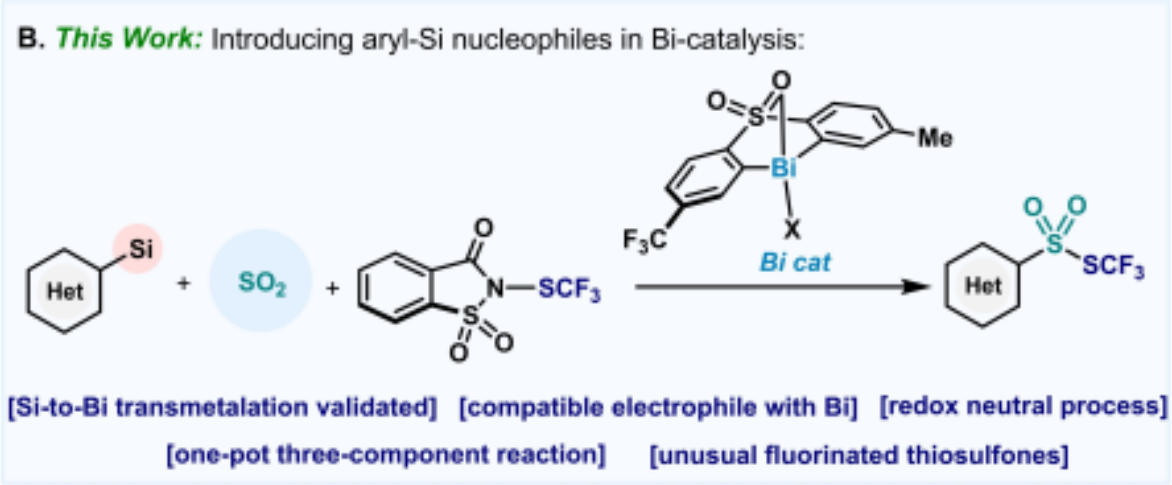
GDCh Communication Angewandte International Edition Chemie
www.angewandte.org

How to cite: *Angew. Chem. Int. Ed.* **2025**, *64*, e202424698
doi.org/10.1002/anie.202424698

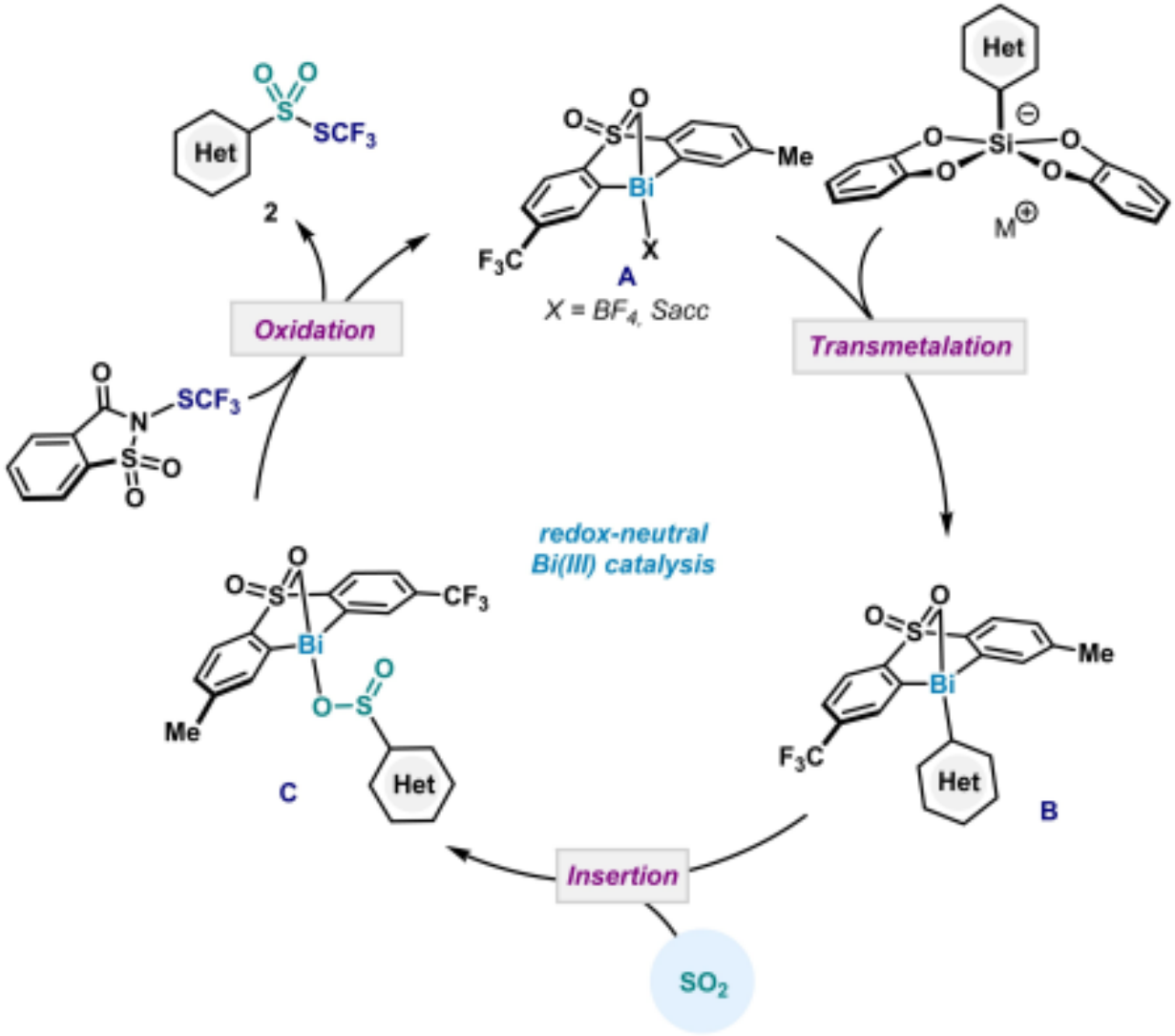
***Thiosulfonylation***

## Aryl Silicon Nucleophiles in Bismuth Catalysis

*Teresa Faber, Sophia Engelhardt, and Josep Cornella**



# 二、中性催化


Het
SCF3
2
Oxidation
Me
Bi
F3C
X
A
X = BF4, Sacc
Transmetalation
Het
Si
M
redox-neutral
Bi(III) catalysis
SCF3
CF3
Me
Bi
Me
C
Het
Me
Bi
F3C
Het
B
Insertion
SO2

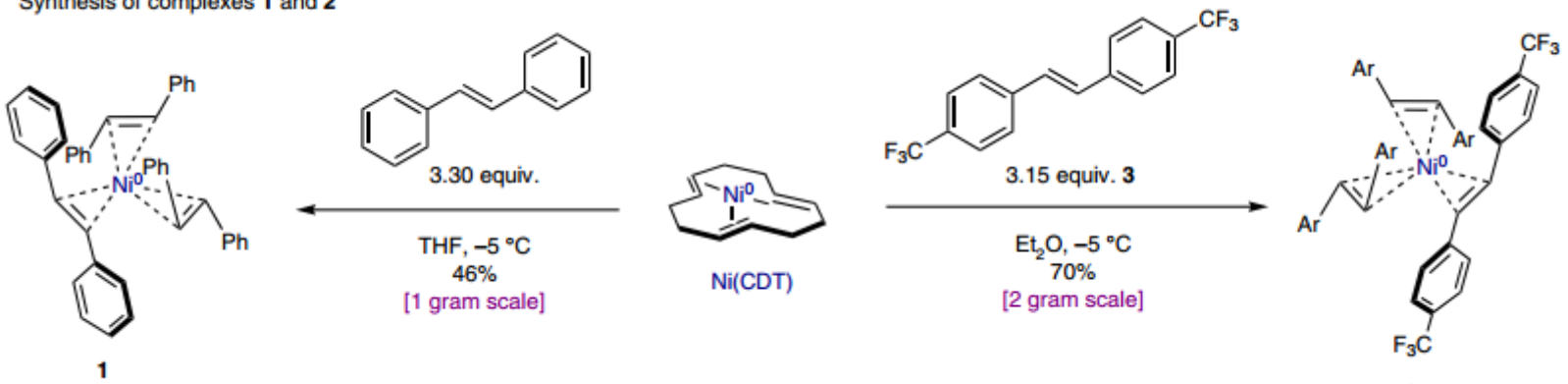
# 三、Naked Nickel

ARTICLES
https://doi.org/10.1038/s41929-019-0392-6
nature catalysis

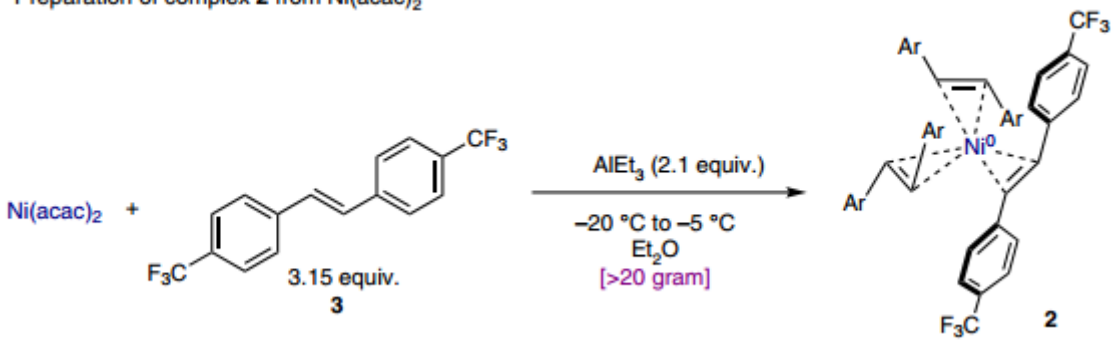
## An air-stable binary Ni(0)–olefin catalyst

Lukas Nattmann, Rakan Saeb, Nils Nöthling and Josep Cornella*

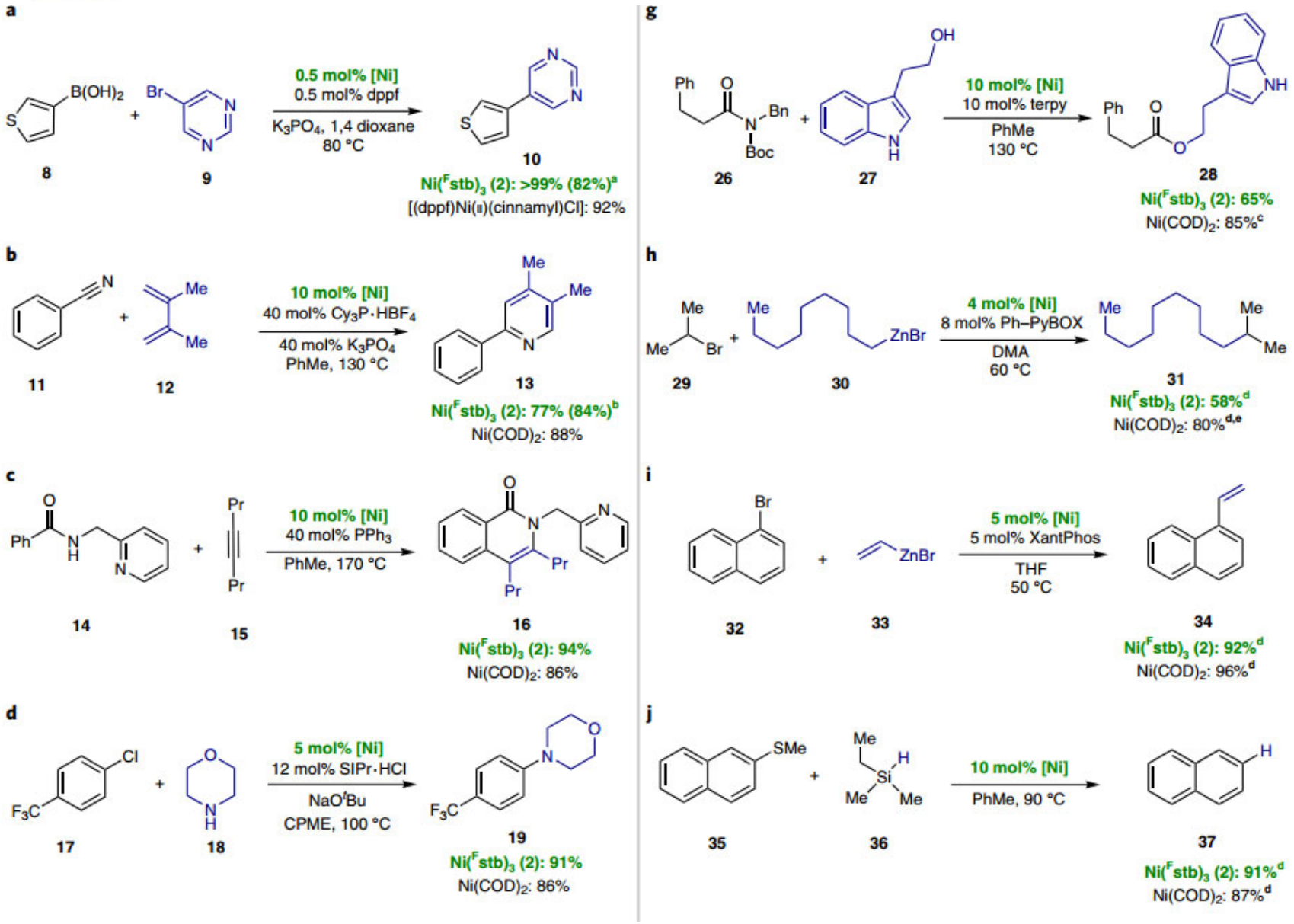
**a** Synthesis of complexes **1** and **2**




**c** Preparation of complex **2** from $Ni(acac)_2$



# 三、Naked Nickel



# 三、Naked Nickel

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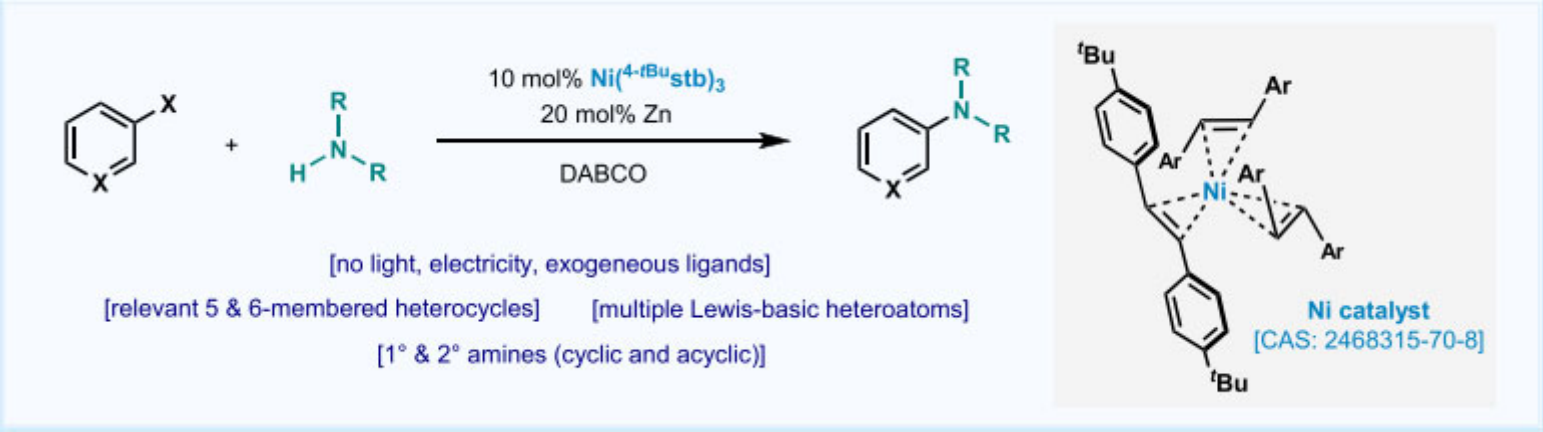
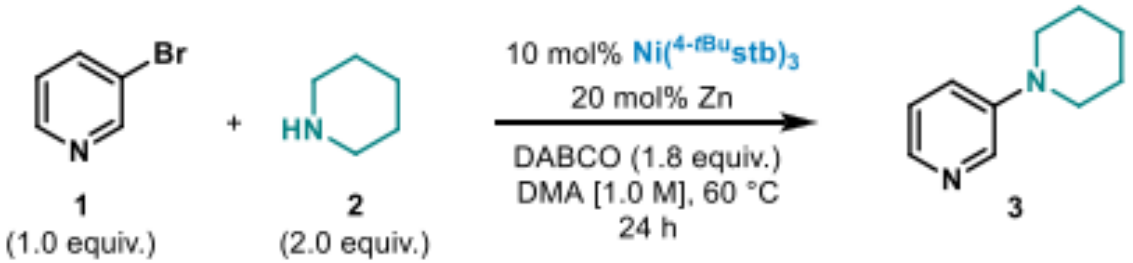
Letter

## "Naked Nickel"-Catalyzed Amination of Heteroaryl Bromides

Rakan Saeb, Bryan Boulenger, and Josep Cornella*



# 三、Naked Nickel




**1** (1.0 equiv.) + **2** (2.0 equiv.) → **3**

| entry | deviations from above | yield[a] in % of **3** | entry | deviations from above | yield[a] in % of **3** |
|---|---|---|---|---|---|
| 1 | none | 76, (76)[b] | 7 | $Ni(COD)_2$ (glovebox) | 73 |
| 2 | 40 °C | 62 | 8 | $Ni(^{4\text{-}CF3}stb)_3$ | 76 |
| 3 | 25 °C | <5 | 9 | Ni(COD)(DQ) | <1 |
| 4 | old batch of $Ni(^{4\text{-}tBu}stb)_3$[c] | 76 | 10 | DMA stored on benchtop | 77 |
| 5 | $NiBr_2$(dme) (glovebox) | 84 | 11 | No [Ni] | <1 |
| 6 | $NiBr_2(bipy)_3$ | <1 | 12 | No Zn | 17 |

[a] $^1$H NMR yield as determined by using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield (0.3 mmol scale), [c] 6 months old batch stored at –18 °C under air. $^{4\text{-}tBu}$stb = (*E*)-1,2-bis(4-(*tert*-butyl)phenyl)ethene, dme = dimethoxyethane, bipy = 2,2'-bipyridine, COD = 1,5-cyclooctadiene, $^{4\text{-}CF3}$stb = (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)ethene, DQ = duroquinone,

# 三、Naked Nickel

GDCh **Communication** Angewandte International Edition Chemie www.angewandte.org

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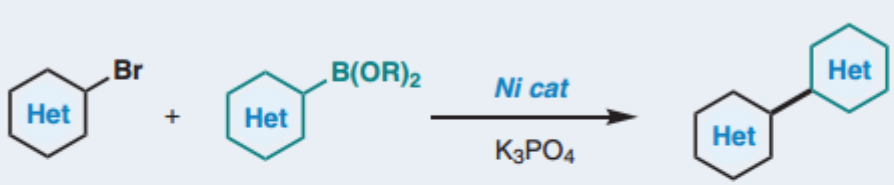
doi.org/10.1002/anie.202424051

**Cross-Coupling**

## "Naked Nickel"-Catalyzed Heteroaryl–Heteroaryl Suzuki–Miyaura Coupling

*Rakan Saeb, Byeongdo Roh, and Josep Cornella**

**b)** ***This work:*** exogenous ligand-free naked nickel Suzuki–Miyaura Coupling



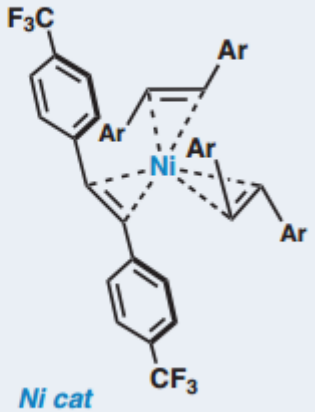

[relevant 5 & 6-membered heterocycles]

[multiple Lewis basic heteroatoms]

[no exogenous ligands]

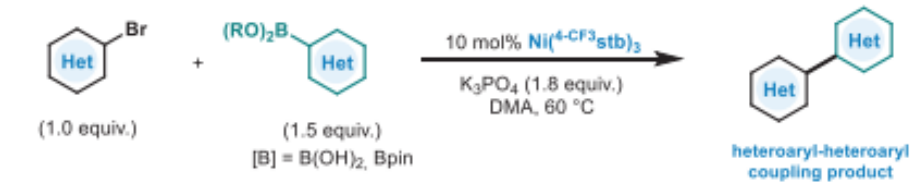
[rapid and simple setup]

[air-stable and commercially available catalyst]

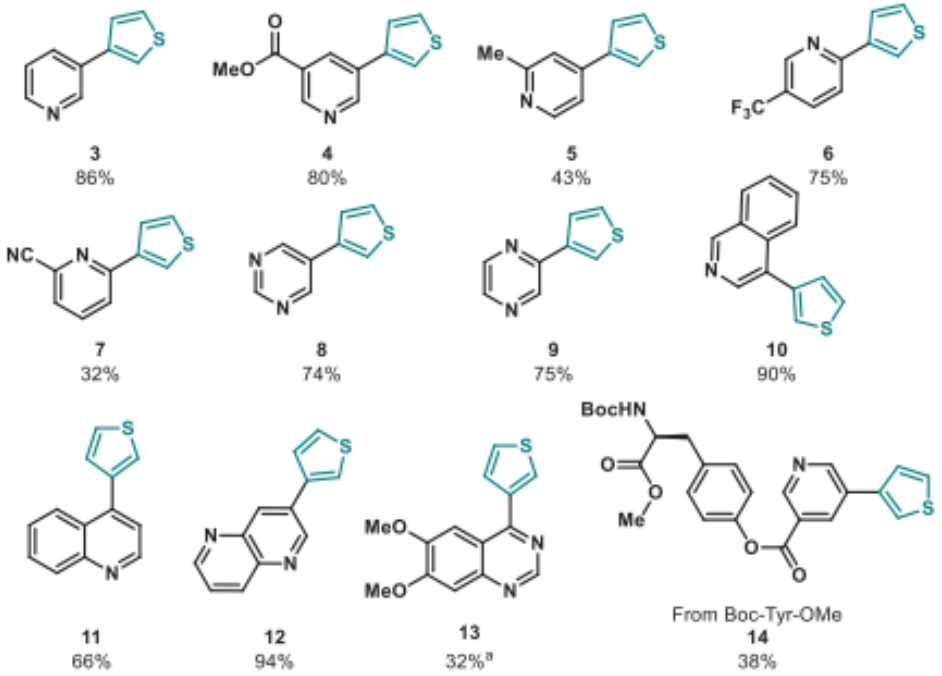



*Ni cat*
[CAS: 2413906-36-0]

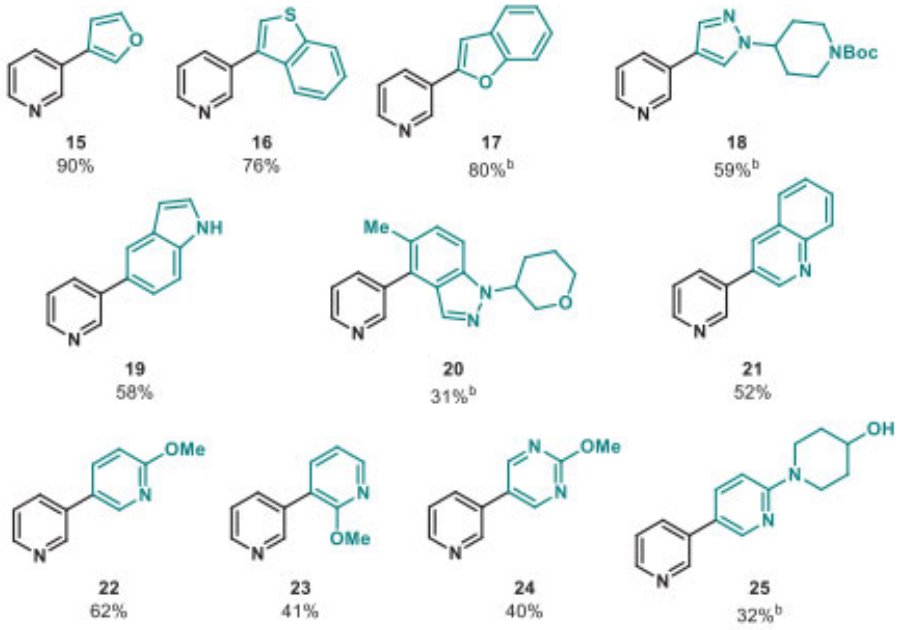
# 三、Naked Nickel



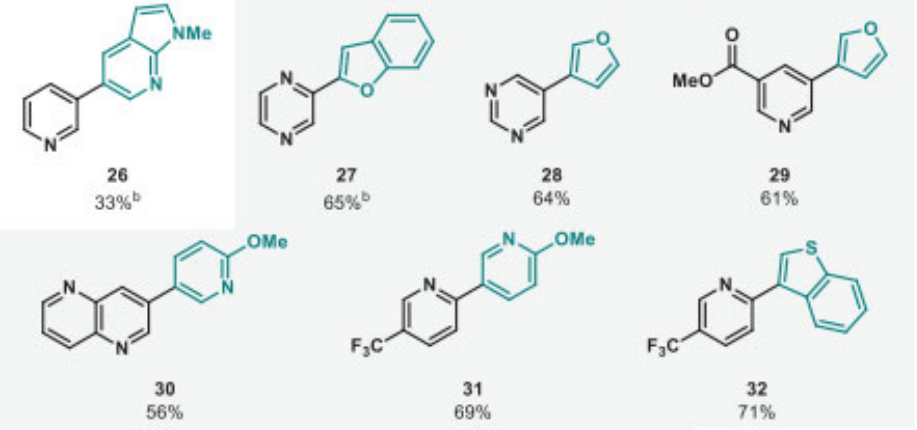

*Scope of heteroaryl bromides*




*Scope of B-based nucleophiles*




*Mixed Electrophiles & Nucleophiles*



# 四、四氟硼酸吡喃鎓盐

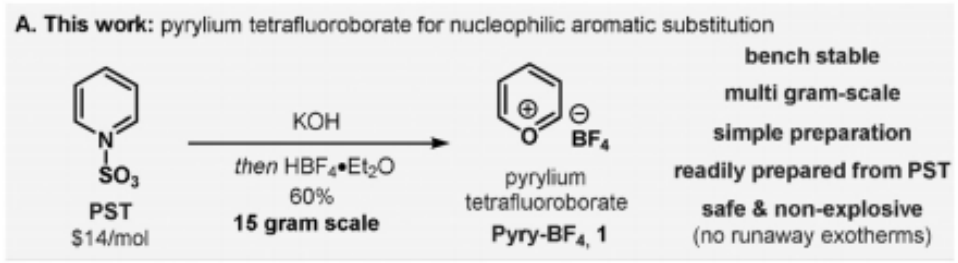
GDCh Communications Angewandte International Edition Chemie

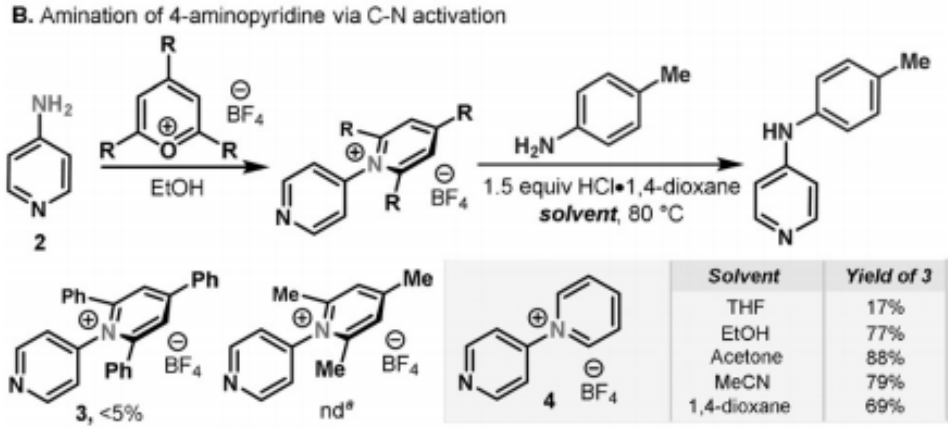
C–N Activation

International Edition: DOI: 10.1002/anie.201806271
German Edition: DOI: 10.1002/ange.201806271

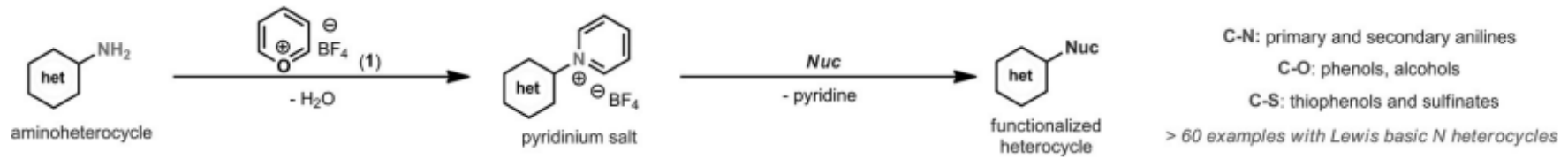
## Selective Functionalization of Aminoheterocycles by a Pyrylium Salt

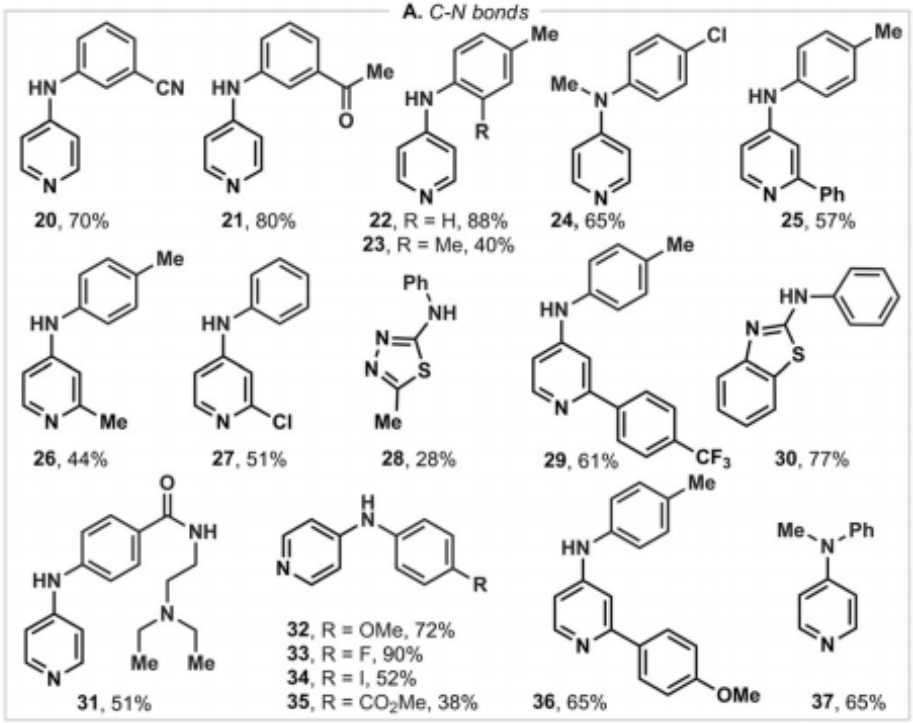
*Daniel Moser[+], Yaya Duan[+], Feng Wang, Yuanhong Ma, Matthew J. O'Neill, and Josep Cornella**

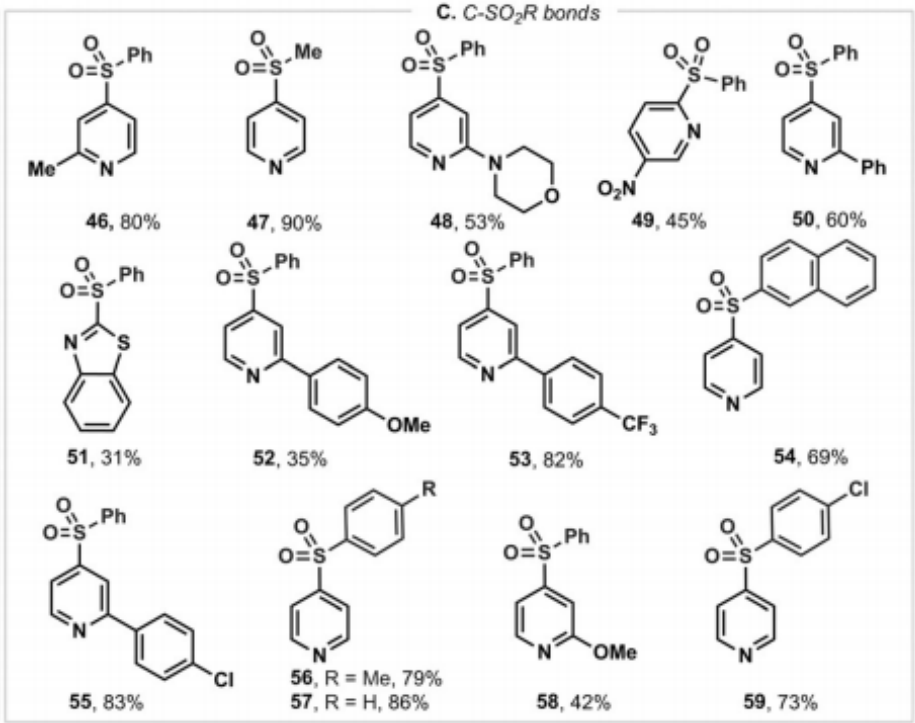


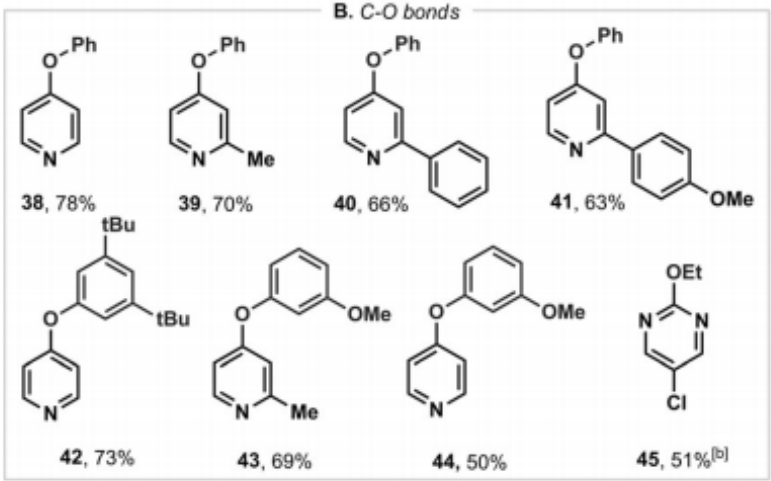



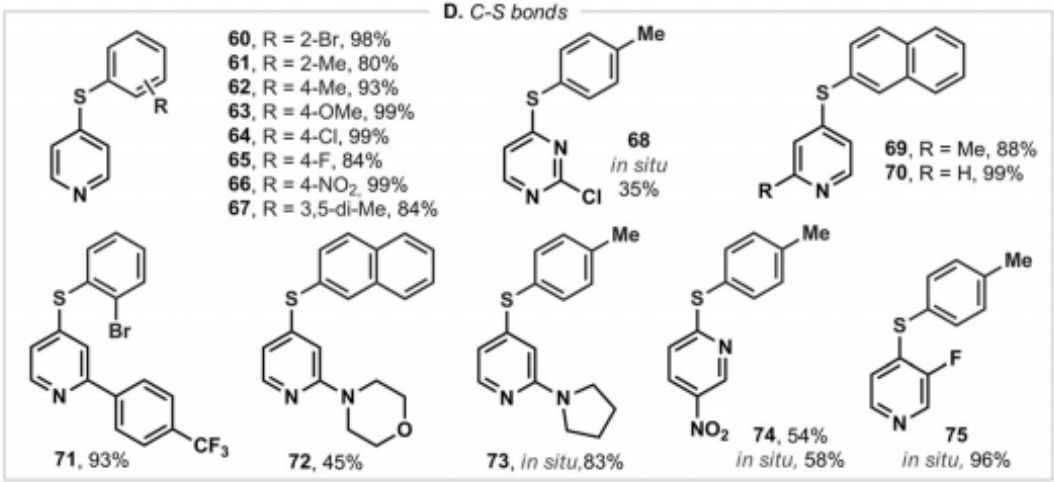

| Solvent | Yield of 3 |
|---|---|
| THF | 17% |
| EtOH | 77% |
| Acetone | 88% |
| MeCN | 79% |
| 1,4-dioxane | 69% |


het
NH2
aminoheterocycle
BF4
(1)
- H2O
pyridinium salt
Nuc
- pyridine
functionalized heterocycle
C-N: primary and secondary anilines
C-O: phenols, alcohols
C-S: thiophenols and sulfinates
> 60 examples with Lewis basic N heterocycles


A. C-N bonds
20, 70%
21, 80%
22, R = H, 88%
23, R = Me, 40%
24, 65%
25, 57%
26, 44%
27, 51%
28, 28%
29, 61%
30, 77%
31, 51%
32, R = OMe, 72%
33, R = F, 90%
34, R = I, 52%
35, R = CO2Me, 38%
36, 65%
37, 65%


C. C-SO2R bonds
46, 80%
47, 90%
48, 53%
49, 45%
50, 60%
51, 31%
52, 35%
53, 82%
54, 69%
55, 83%
56, R = Me, 79%
57, R = H, 86%
58, 42%
59, 73%


B. C-O bonds
38, 78%
39, 70%
40, 66%
41, 63%
42, 73%
43, 69%
44, 50%
45, 51%[b]


D. C-S bonds
60, R = 2-Br, 98%
61, R = 2-Me, 80%
62, R = 4-Me, 93%
63, R = 4-OMe, 99%
64, R = 4-Cl, 99%
65, R = 4-F, 84%
66, R = 4-NO2, 99%
67, R = 3,5-di-Me, 84%
68
in situ
35%
69, R = Me, 88%
70, R = H, 99%
71, 93%
72, 45%
73, in situ,83%
74, 54%
in situ, 58%
75
in situ, 96%

# 四、四氟硼酸吡喃鎓盐

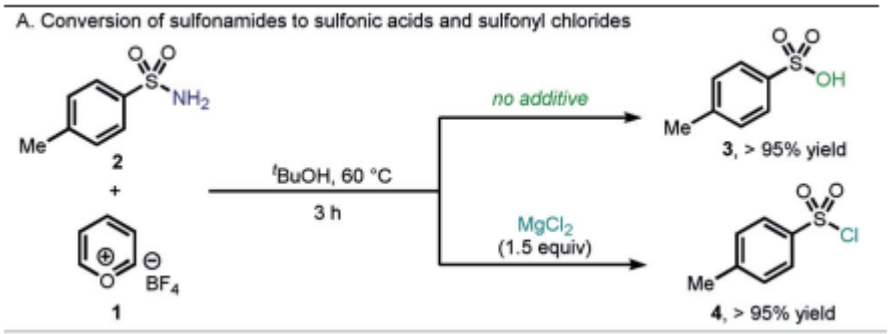
GDCh **Communications** Angewandte International Edition Chemie

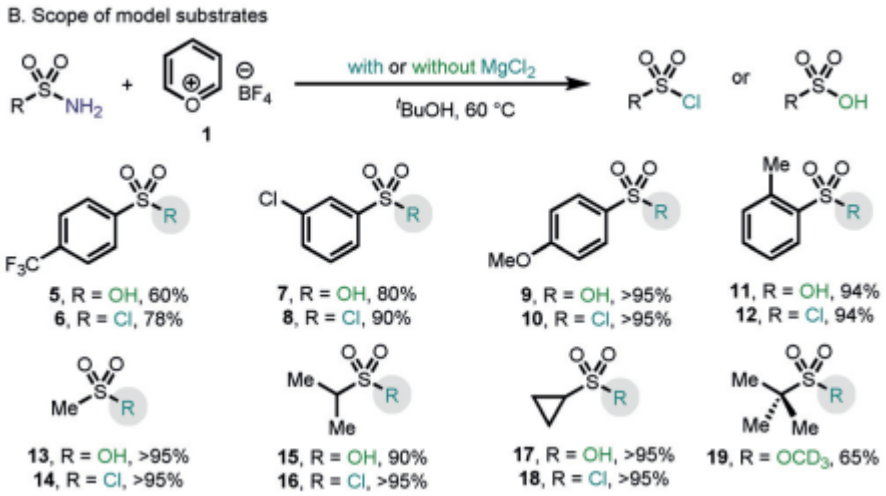
**Sulfonamides**

International Edition: DOI: 10.1002/anie.201910895
German Edition: DOI: 10.1002/ange.201910895

## Selective Late-Stage Sulfonyl Chloride Formation from Sulfonamides Enabled by Pyry-$BF_4$

*Alejandro Gómez-Palomino and Josep Cornella**



# 四、四氟硼酸吡喃鎓盐

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European Journal of Organic Chemistry
Communication
doi.org/10.1002/ejoc.202000022
Chemistry Europe
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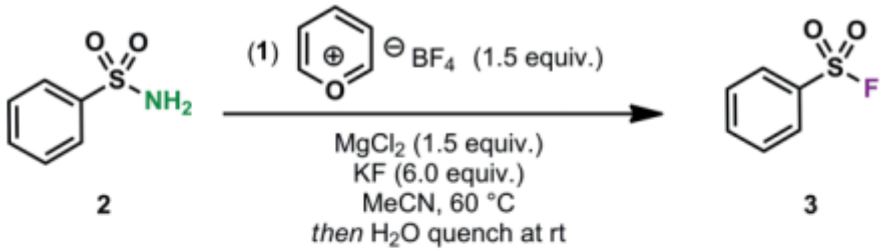
## Synthesis of Sulfonyl Fluorides from Sulfonamides

Marina Pérez-Palau[a] and Josep Cornella*[a]




2 3

| Entry | Deviation from above | Yield of **3** (%)[a] |
|---|---|---|
| 1 | none | ***97% (76%)***[b] |
| 2 | w/o $MgCl_2$ | 18% |
| 3 | w/o KF | < 5% |
| 4 | w/o **1** | < 5% |
| 5 | w/o $H_2O$ quench | < 5% |
| 6 | 4 equiv. KF | 50% |
| 7 | 5 equiv. KF | 67% |
| 8 | 6 equiv. $KHF_2$ instead of KF | 93% |

[a] Yield determined by $^1H$ and $^{19}F$ NMR using 4-fluoroanisole as internal standard. [b] Yield of isolated pure material.

# 四、四氟硼酸吡喃鎓盐

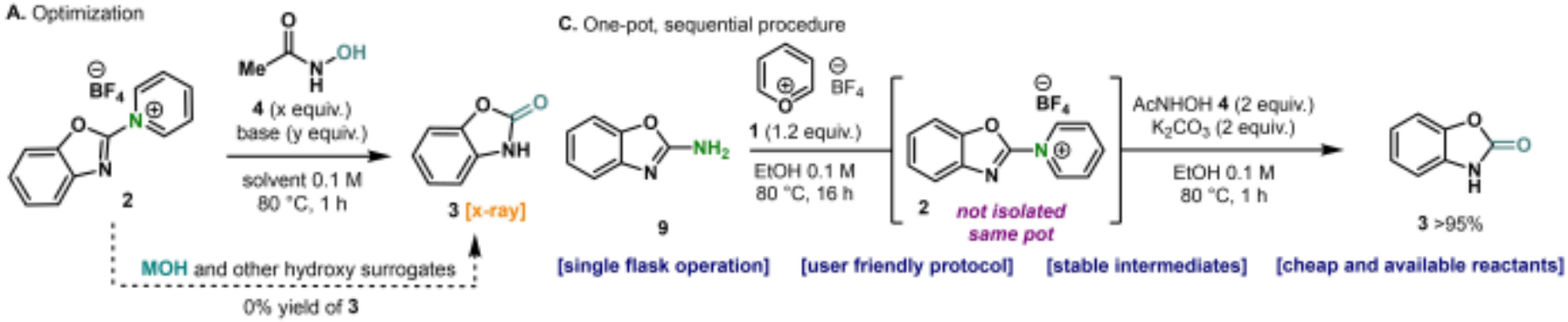
GDCh Communications Angewandte International Edition Chemie www.angewandte.org

How to cite: *Angew. Chem. Int. Ed.* **2023,** *62,* e202212219
International Edition: doi.org/10.1002/anie.202212219
German Edition: doi.org/10.1002/ange.202212219

**Heterocycles**

## Bio-Inspired Deaminative Hydroxylation of Aminoheterocycles and Electron-Deficient Anilines

*Clément Ghiazza, Lucas Wagner, Sergio Fernández, Markus Leutzsch, and Josep Cornella**



# 四、四氟硼酸吡喃鎓盐

ARTICLES
https://doi.org/10.1038/s41557-021-00812-0
nature chemistry

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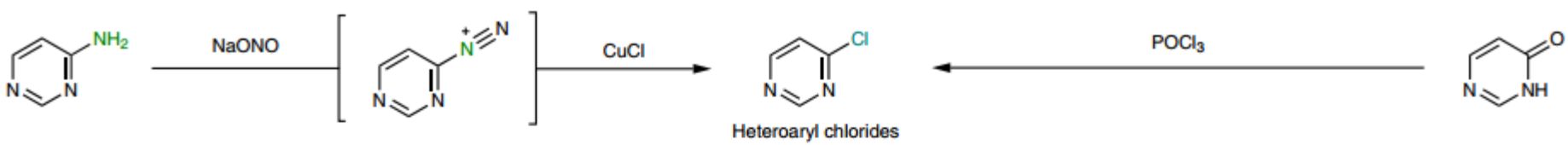
OPEN

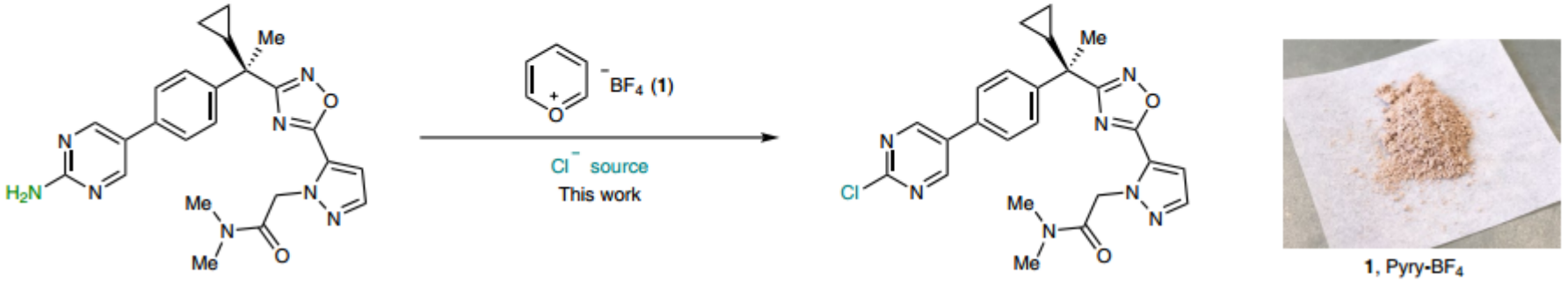
## Deaminative chlorination of aminoheterocycles

Clément Ghiazza, Teresa Faber, Alejandro Gómez-Palomino and Josep Cornella ✉

c




d



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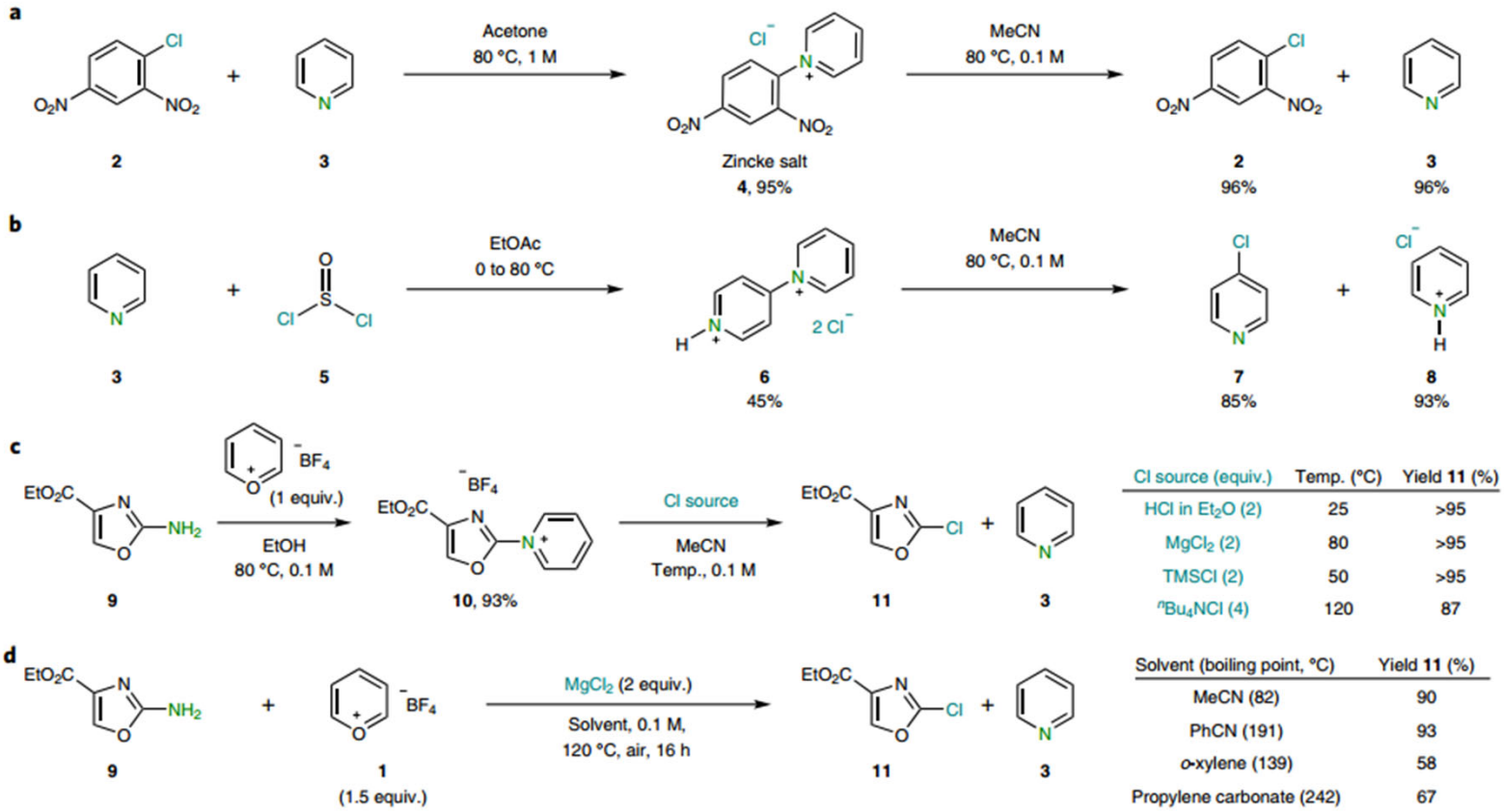
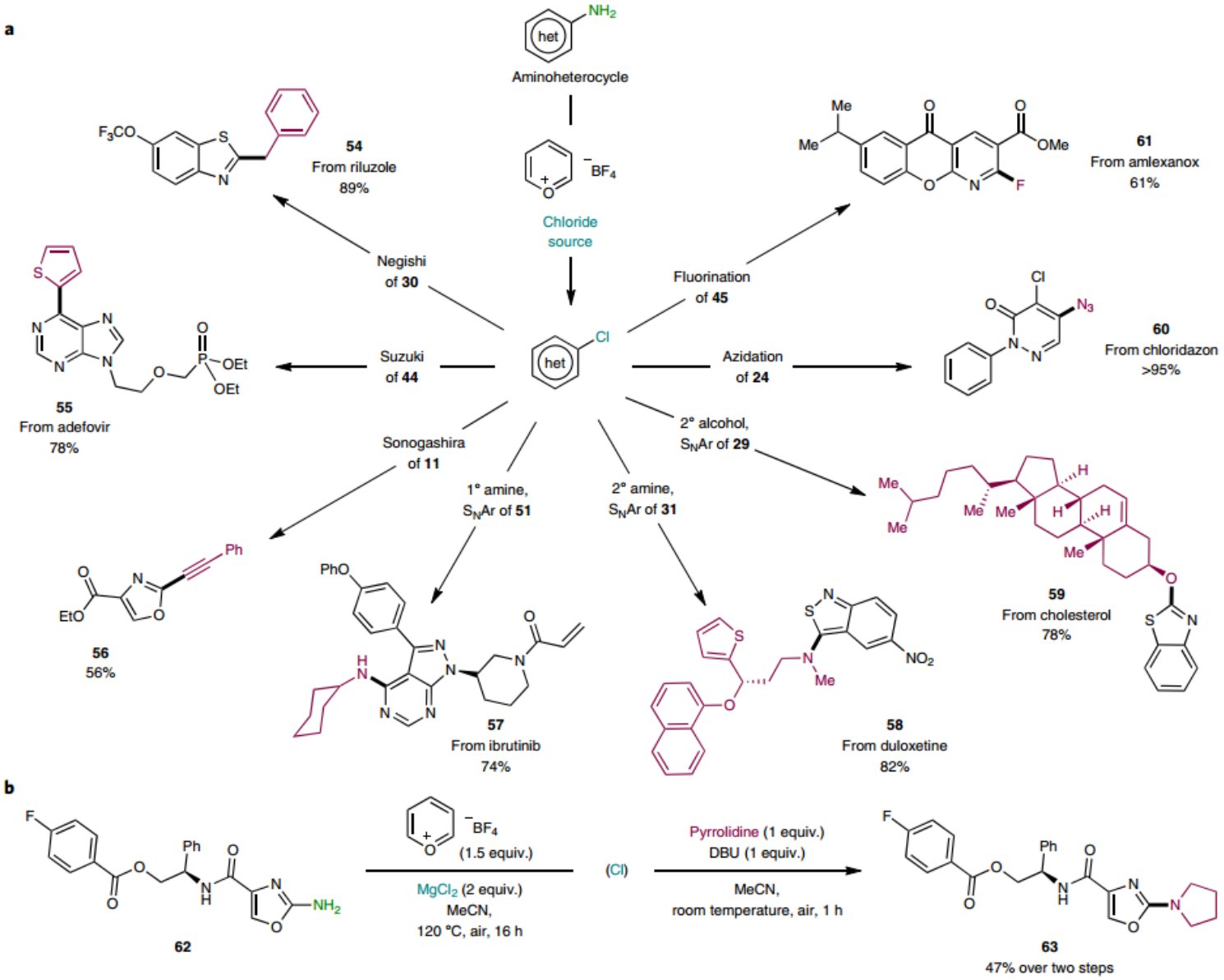



| Cl source (equiv.) | Temp. (°C) | Yield **11** (%) |
|---|---|---|
| HCl in $Et_2O$ (2) | 25 | >95 |
| $MgCl_2$ (2) | 80 | >95 |
| TMSCl (2) | 50 | >95 |
| $^nBu_4NCl$ (4) | 120 | 87 |

| Solvent (boiling point, °C) | Yield **11** (%) |
|---|---|
| MeCN (82) | 90 |
| PhCN (191) | 93 |
| *o*-xylene (139) | 58 |
| Propylene carbonate (242) | 67 |

# 四、四氟硼酸吡喃鎓盐


a
Aminoheterocycle
Chloride source
Negishi of 30
Suzuki of 44
Fluorination of 45
Azidation of 24
Sonogashira of 11
1° amine, SNAr of 51
2° amine, SNAr of 31
2° alcohol, SNAr of 29
54 From riluzole 89%
55 From adefovir 78%
56 56%
57 From ibrutinib 74%
58 From duloxetine 82%
59 From cholesterol 78%
60 From chloridazon >95%
61 From amlexanox 61%
b
62
(1.5 equiv.)
MgCl2 (2 equiv.)
MeCN,
120 °C, air, 16 h
(Cl)
Pyrrolidine (1 equiv.)
DBU (1 equiv.)
MeCN,
room temperature, air, 1 h
63
47% over two steps

The Yang Research Group
Precise Synthesis Lab at Tongji University

# 谢谢大家

## 请老师和各位同学批评指正