Chalcogen Bonding Catalysis

2024/ 11/ 22 (Fri)

Mayu Urata

Contents

1. Introduction

Catalyst { Covalent Catalyst
Non-Covalent Catalyst

Examples)
- Hydrogen Bond
- Halogen Bond
- Chalcogen Bond
- Pnictogen Bond
- Ion Pairing
- π—Stacking ...

	Group V (pnictogen)	Group VI (chalcogen)	Group VII (halogen)
Row 3	**P** 25.0	**S** 19.3	**Cl** 14.3
Row 4	**As** 29.7	**Se** 25.4	**Br** 20.5
Row 5	**Sb** 43.3	**Te** 38.3	**I** 32.3

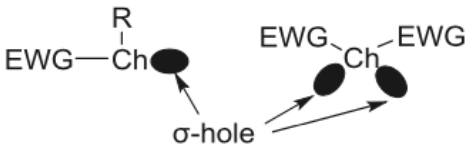
•Chalcogen (group 16 elements)

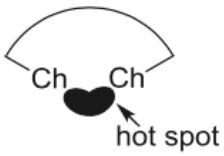
Atom:	8 **O** Oxygen	16 **S** Sulfur	34 **Se** Selenium	52 **Te** Tellurium
Polarizabilities:	4.9 a.u.	19.33 a.u.	25.4 a.u.	38.3 a.u.

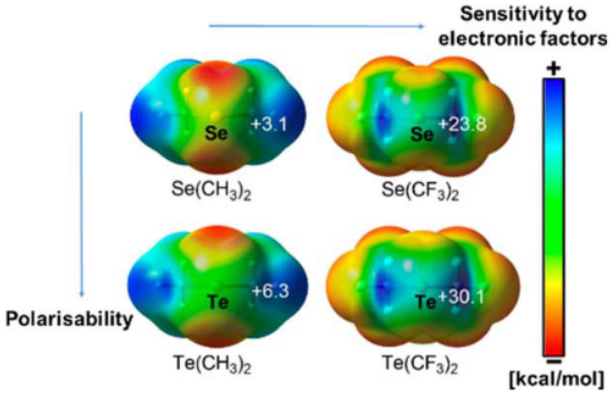
Chalcogen (石を作る元素)

•σ-hole

= Positively charged region derived from the antibonding orbital of the C-Ch bond



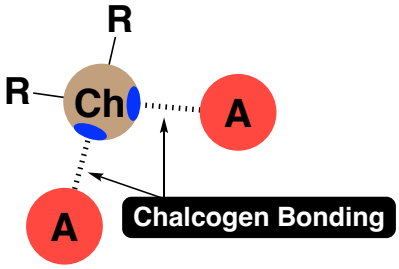




1) Pale, P.; Mamane, V. *et. al. Chem. Sci.,* **2023,** *14,* 7221
2) Bolotin, D. S. *et. al. ChemCatChem* **2024,** *16,* e202400672
3) Matile, S. *et. al. Angew. Chem. Int. Ed.* **2018,** *57,* 5408
4) Pale, P.; Mamane, V. *Chem. Eur. J.* **2023,** *29,* e202302755
5) Schmidt, B. M. *et. al. Chem. Commun.,* **2022,** *58,* 5233
6) 有機合成化学協会誌 2020, Vol.78, No. 9, 894

1. Introduction

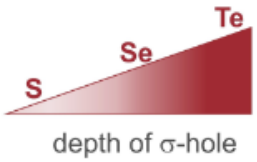
•Chalcogen Bonding

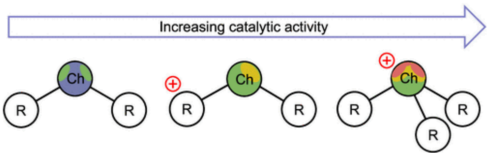


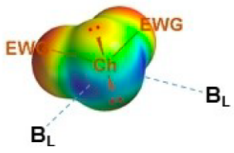
Ch : Chalcogen (S, Se, Te)
R : EWG
A : Lewis Base

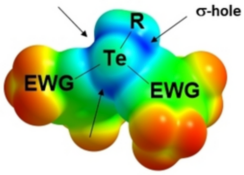
Strength of chalcogen bond depends on:

1. the Lewis Basicity of the interacting partner
2. the nature of the chalcogen atom (Te > Se > S)
3. the polarization of the chalcogen atom
4. the R—Ch···LB interaction angle (require angles close to 180°)
5. the cationic σ-hole donors exhibit a significantly higher catalitic activity

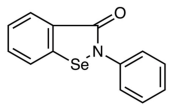




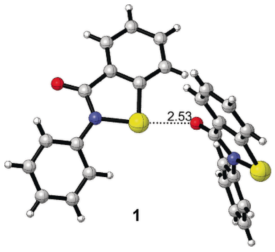




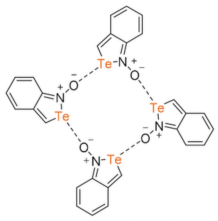
Recent development in:

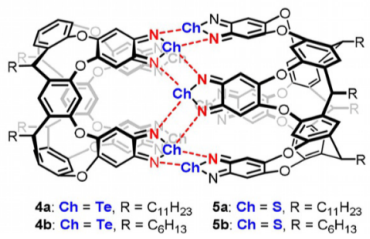


Ebselen

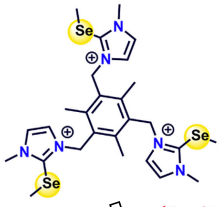


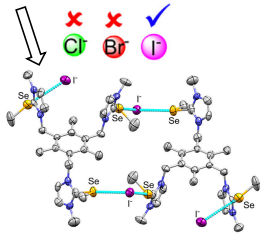
Crystal engineering



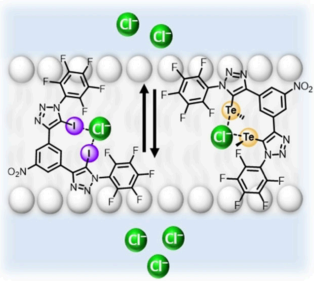


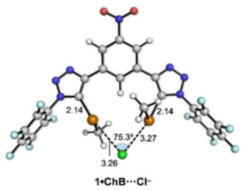
Supramolecular assemblies





Anion Recognition[4]





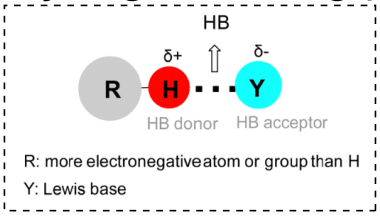
Transport tools[5]

Today's Topic
Development in organocatalysis

1) Huber, S. M. *et. al. Angew. Chem. Int. Ed.* **2019,** *58,* 1880 (Review)
2) Zhu, J. *et. al. Chem. Soc. Rev.,* **2024,** *53,* 586 (Review)
3) Chen, F.-E. *et. al. Green Synthesis and Catalysis* **2021,** *2,* 329 (Review)
4) Ghosh, P. *et. al. iScience* **2024,** *27, 108917*
5) Langton, M. J. *et. al. Chem. Eur. J.* **2021,** *27,* 11738
6) Haberhauer, G. *et. al. Organic Materials* **2022,** *4*, 43

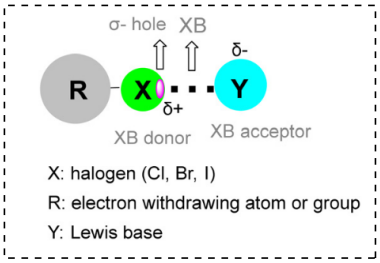
1. Introduction

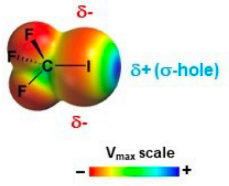
•Hydrogen Bonding (HB) *vs.* Chalcogen Bonding (ChB)

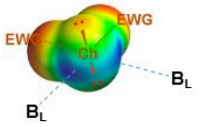


1. Hydrogen is hard→for the hard Lewis bases
   Chalcogens are "softer" Lewis acids→for the softer Lewis bases
2. ChB is more directional than HB
3. ChB is slightly weaker than HB

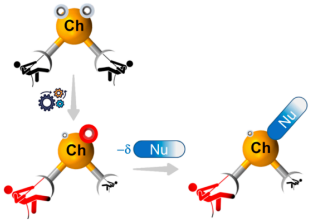
•Halogen Bonding (XB) *vs.* Chalcogen Bonding (ChB)





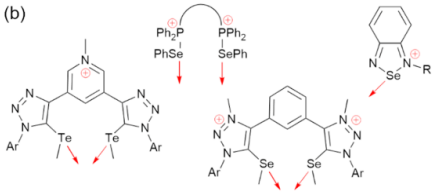


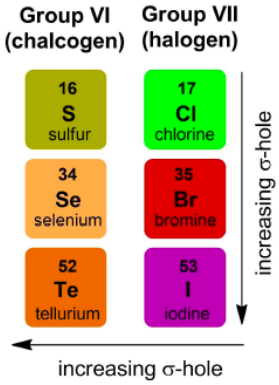
1. Existence of a second substituent on Chalcogens



2. Selective activation of ChB

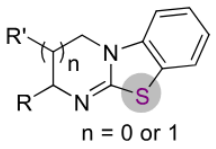
Examples)



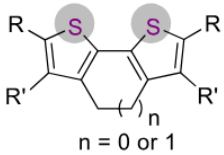


3. σ-hole of ChB is larger

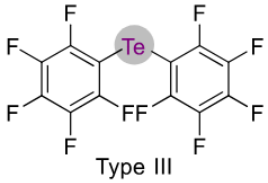
•Chalcogen Bonding in Organocatalysis (Today's Topic)



n = 0 or 1
Type I
Isothiourea-based
ChB donors
Birman & Smith *et. al.*

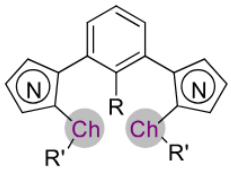


n = 0 or 1
Type II
Thiophene-based
ChB donors
Matile *et. al.*

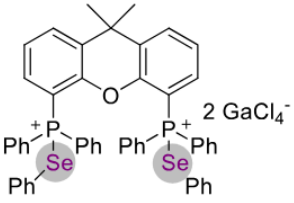


Type III
Neutral monodentate
ChB donors
Matile *et. al.*

Type IV
Hypervalent
ChB donors
Yeung *et al.*
Pale & Mamane *et al.*



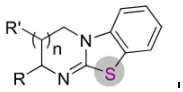
Type V
N-heterocyclic
ChB donors
Huber *et. al.*



Type VI
Phosphine-based
ChB donors
Wang *et. al.*

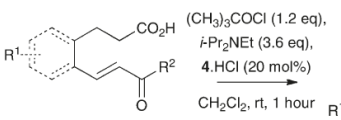
1) Fourmigue, M. *et. al. Acc. Chem. Res.* **2024,** *57,* 362
2) Mancheno, O. G. *et. al. ChemCatChem* **2019,** *11,* 5198 (Review)
3) Breugst, M. *et. al. Eur. J. Org. Chem.* **2020,** *5473* (Review)
4) Huber, S. *et. al. Angew. Chem. Int. Ed.* **2024,** *63,* e202404823
5) Wang,Y. *et. al. Acc. Chem. Res.* **2023,** *56,* 608
6) Zhu, J. *et. al. Chem. Soc. Rev.,* **2024,** *53,* 586

2. Chalcogen Bonding Catalyst

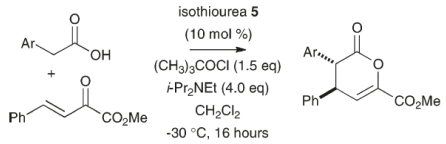


Type I
Isothiourea-based ChB donors

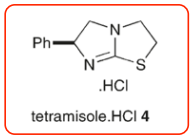
•Enantioselective Intra- and Intermolecular Michael Addition (2011, Smith)[1]

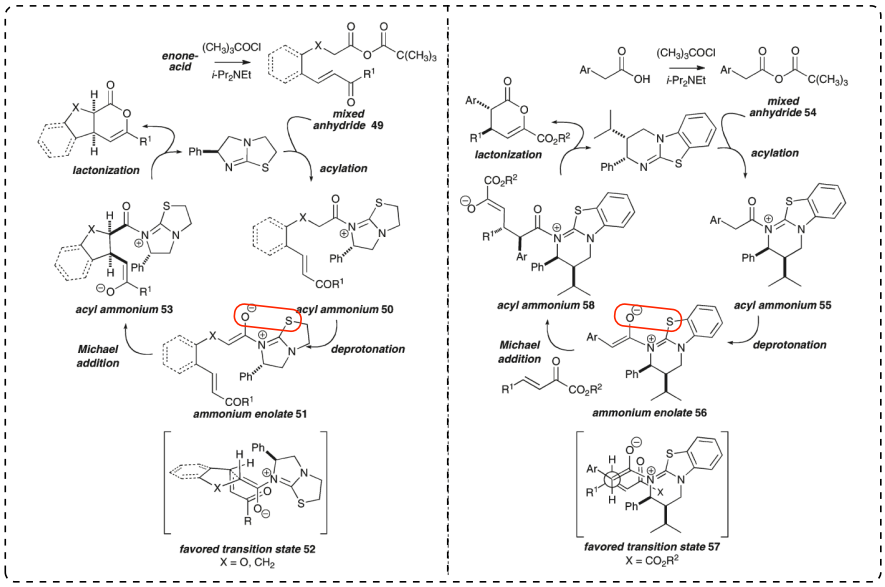


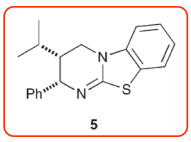
16 examples
up to 98% yield
up to 99:1 dr
up to 99% ee



20 examples
up to 87% yield
up to 95:5 dr
up to 99% ee

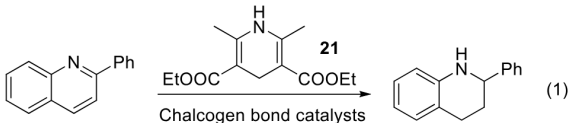




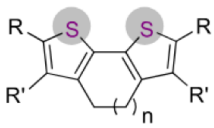


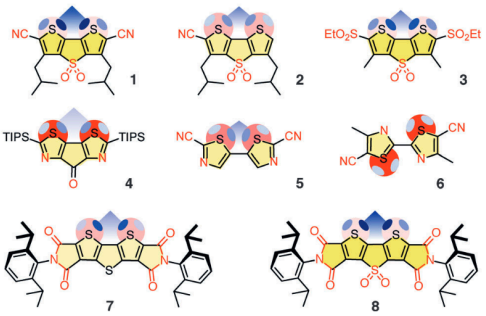
Type II
Thiophene-based ChB Donors

•Transfer Hydrogeneration (2017, Matile)[1]

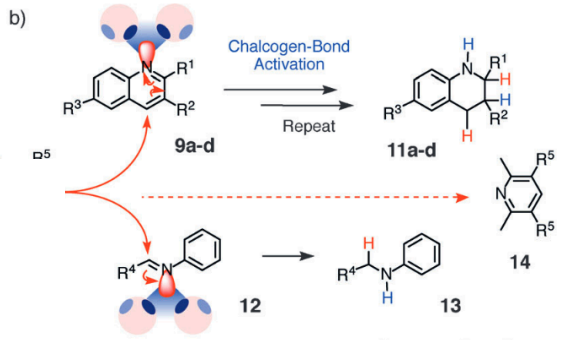


6 examples
up to 96% yield





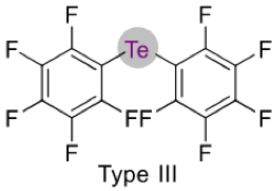
catalyst	yield (%)
1	96
2	81
3	62
4	82
5	–[h]
6	–[h]
7	78
8	94
–	–[h]



1) Smith, A. D. *et. al. J. Am. Chem. Soc.* **2011,** *133, 2714*
2) Matile, S. *et. al. Angew. Chem. Int. Ed.* **2017,** *56,* 812

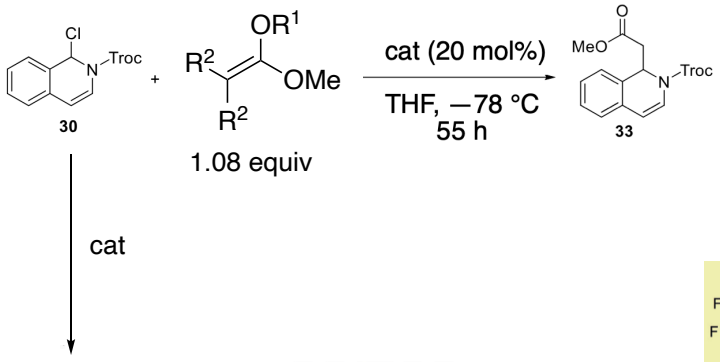
2. Chalcogen Bonding Catalyst

Type III
Neutral Monodentate ChB Donors

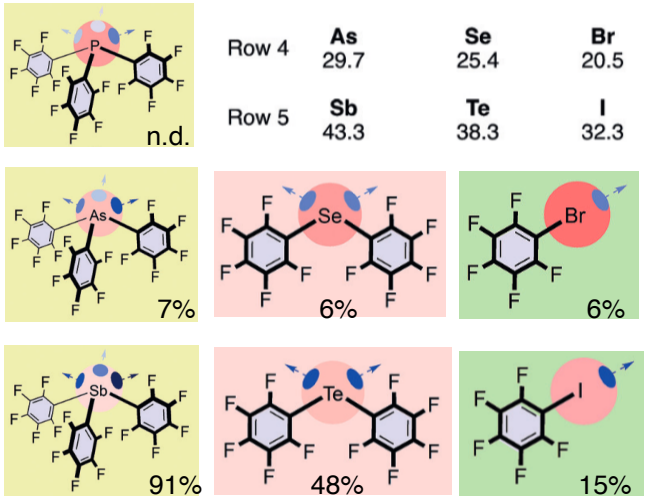


Type III
Neutral monodentate
ChB donors

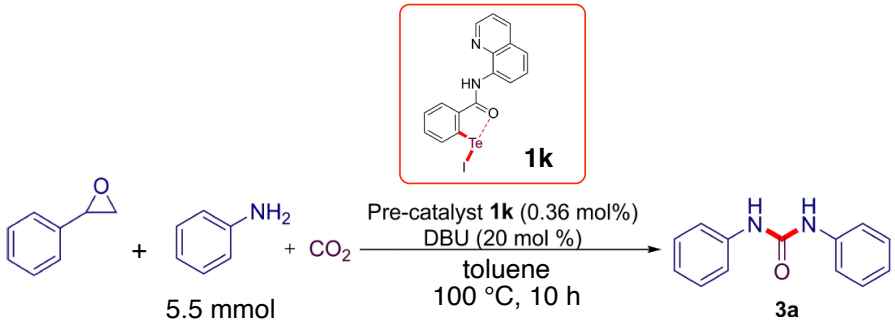
•Reissert-type Substitution (2018, Matile)[1]

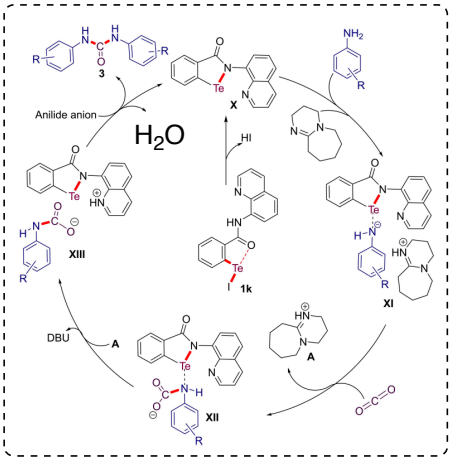


	Group V (pnictogen)	Group VI (chalcogen)	Group VII (halogen)
Row 3	**P** 25.0	**S** 19.3	**Cl** 14.3
Row 4	**As** 29.7	**Se** 25.4	**Br** 20.5
Row 5	**Sb** 43.3	**Te** 38.3	**I** 32.3



•CO_2 Mitigation (2023, Kumar)[2]





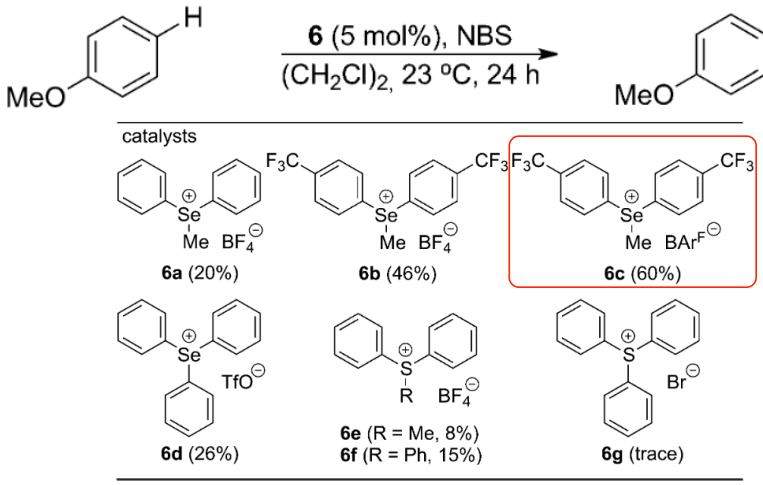
1) Matile, S. *et. al. Angew. Chem. Int. Ed.* **2018,** *57,* 5408
2) Kumar, S. *et. al. Chem. Eur. J.* **2023,** *29,* e202301502

2. Chalcogen Bonding Catalyst

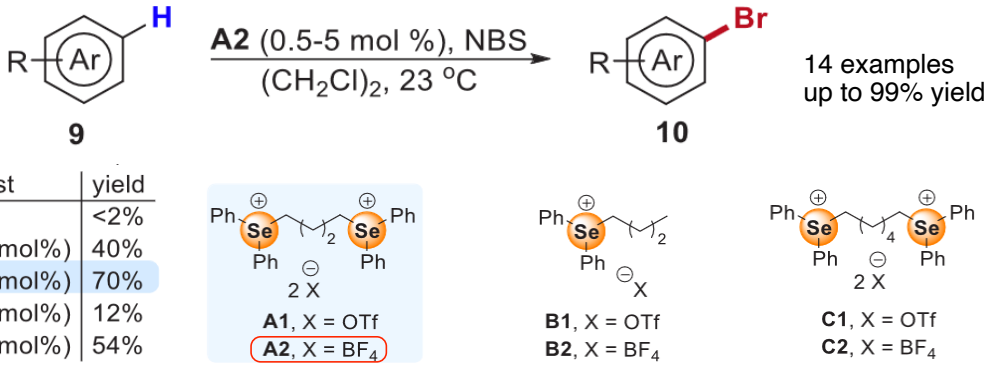
Type IV
Hypervalent
ChB donors

Type IV
Hypervalent ChB Donors

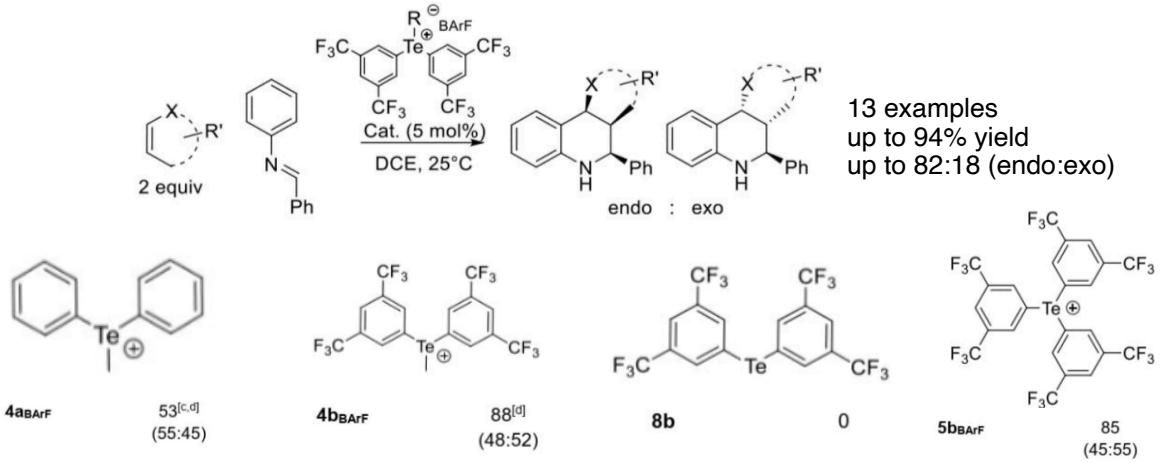
•Selenonium Cations as Monodentate Chalcogen Bond Donor (2018, Yeung)[1]



•Selenonium Cations as Bidentate Chalcogen Bond Donors (2021, Yeung)[2]



•Telluronium-Catalyzed [4+2] Cyclocondensation (2021, Yeung)[3]



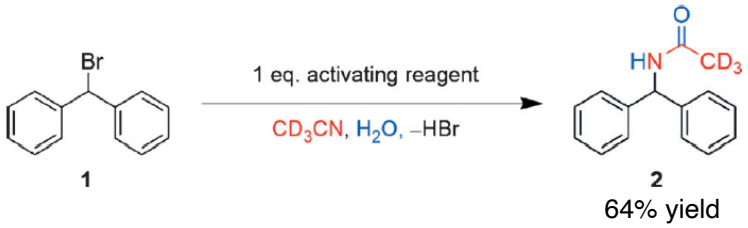
1) Yeung, Y. Y. *et. al. Angew. Chem. Int. Ed.* **2018,** *57,* 12869
2) Yeung, Y. Y. *et. al. ACS Catal.* **2021,** *11,* 12632
3) Pale, P.; Mamane, V. *et. al. Chem. Eur. J.* **2023**, *29,* e202203372

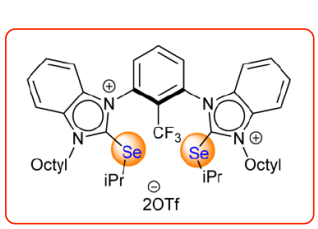
2. Chalcogen Bonding Catalyst

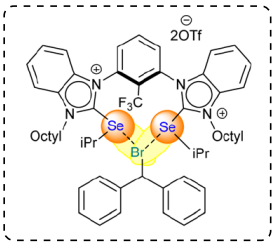
Type V
N-heterocyclic
ChB donors

Type V
N-heterocyclic ChB donors

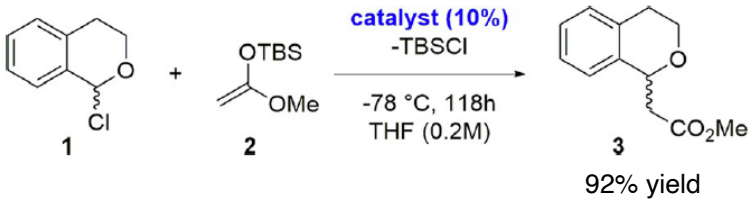
•Carbon—Bromine Bond Activation (2017, Huber)[1]

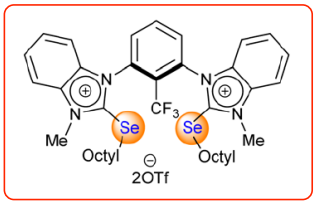


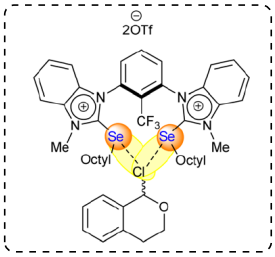




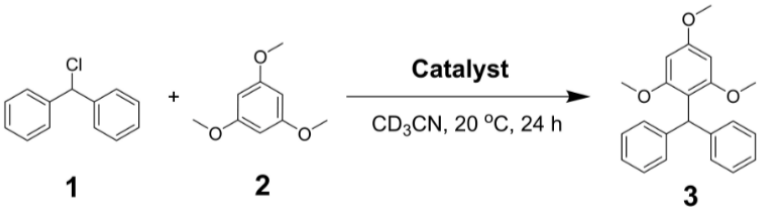
•Carbon—Chlorine Bond Activation (2017, Huber)[2]

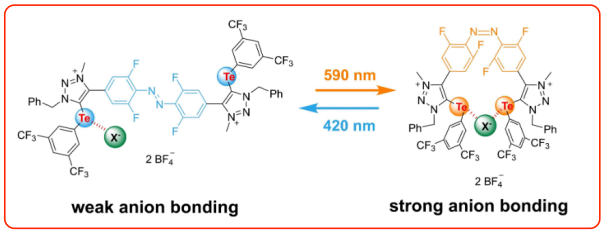




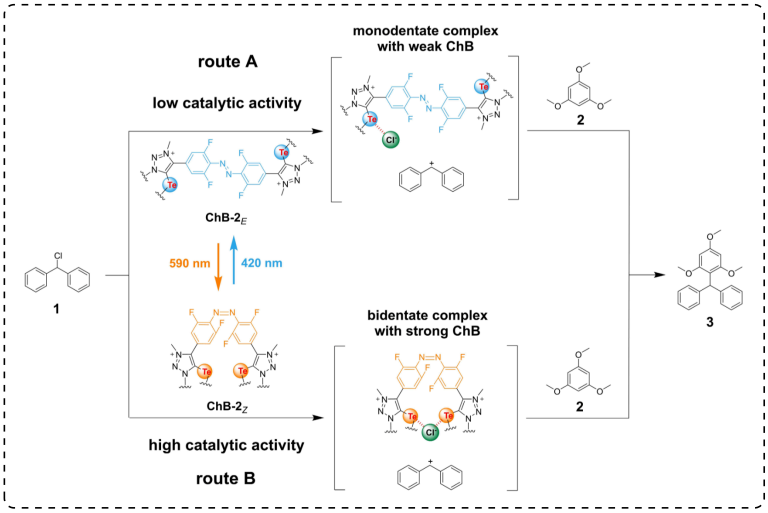


•Visible-Light-Swichable Tellurium-Based Chalcogen Bonding (2023, Zhang)[3]



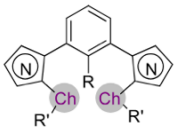


Entry	2/1 Ratios	Catalyst	Conditions	Yield [%][d]
1[a]	1	none	in dark	<1
2[a]	1	**ChB-2**$_E$	in dark	9
3[a]	1	**ChB-2** (Z/E)[c] = 92/8	in dark	34
4[b]	1	**ChB-2** (Z/E)[c] = 92/8	590 nm	58



1) Huber, S. M. *et. al. Angew. Chem. Int. Ed.* **2017,** *56,* 12009
2) Huber. S. M. *et. al. Chem. Eur. J.* **2017,** *23,* 16972
3) Zhang, K.-D. *et. al. Angew. Chem. Int. Ed.* **2023,** *62, e202212707*

2. Chalcogen Bonding Catalyst

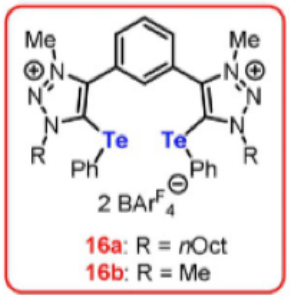


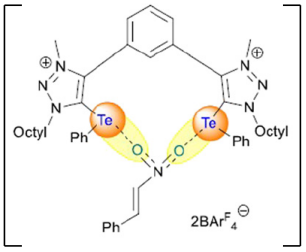
Type V
N-heterocyclic
ChB donors

Type V
N-heterocyclic ChB donors

•Nitro-Michael Reaction (2019, Huber)[1]

81% yield





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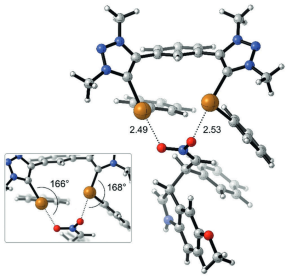
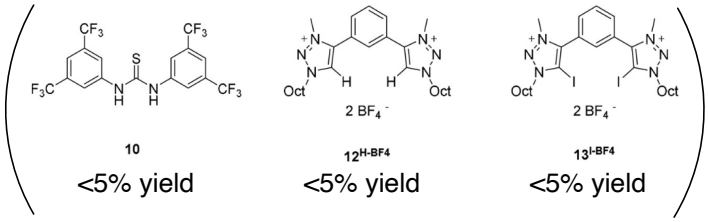
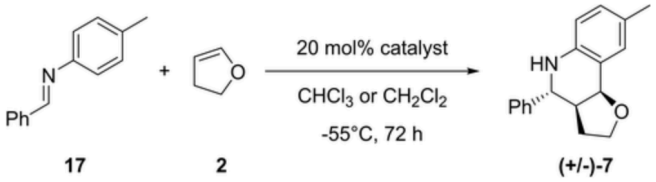
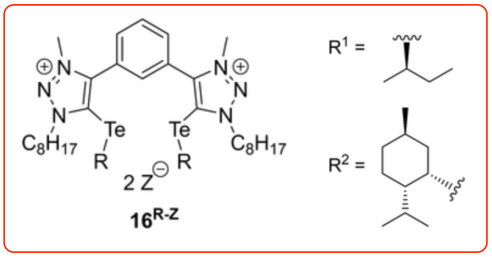




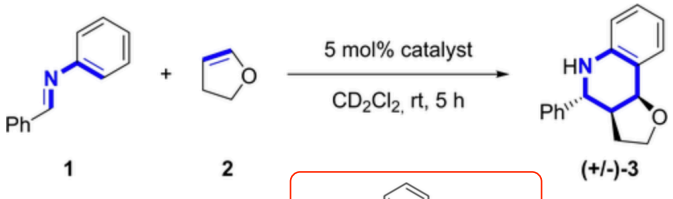
•Povarov [4+2] Cycloaddition (2022, Huber)[2]

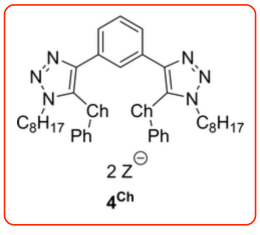


6 examples
up to 85% yield
up to 94:6 (endo:exo)
0% ee



Initial Screening in Achiral Reaction

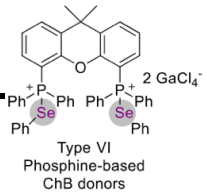




Entry	Catalyst	Mol %[a]	Yield of (+/−)-**3** [%][b]	*endo:exo*[b]
1	$4^{Te-BArF4}$	5	82	47:53
2	4^{Te-BF4}	5	81	68:32
3	4^{Te-OTf}	5	64	70:30
5	$4^{Se-BArF4}$	5	26	56:44
6	4^{Se-BF4}	5	25	72:28
7	4^{Se-OTf}	5	67	72:28
8	$4^{S-BArF4}$	5	<5	–
9	4^{S-BF4}	5	<5	–
10	4^{S-OTf}	5	74	74:26

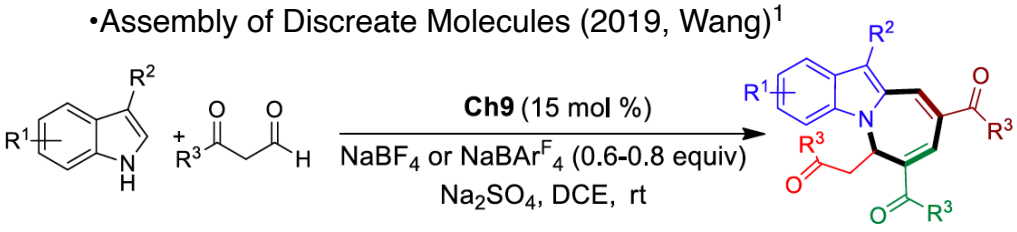
1) Huber, S. M. *et. al. Angew. Chem. Int. Ed.* **2019,** *58,* 16923
2) Huber, S. M. *et. al. Chem. Eur. J.* **2022,** *28,* e202200917

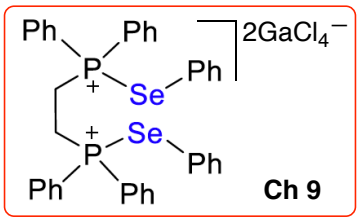
2. Chalcogen Bonding Catalyst

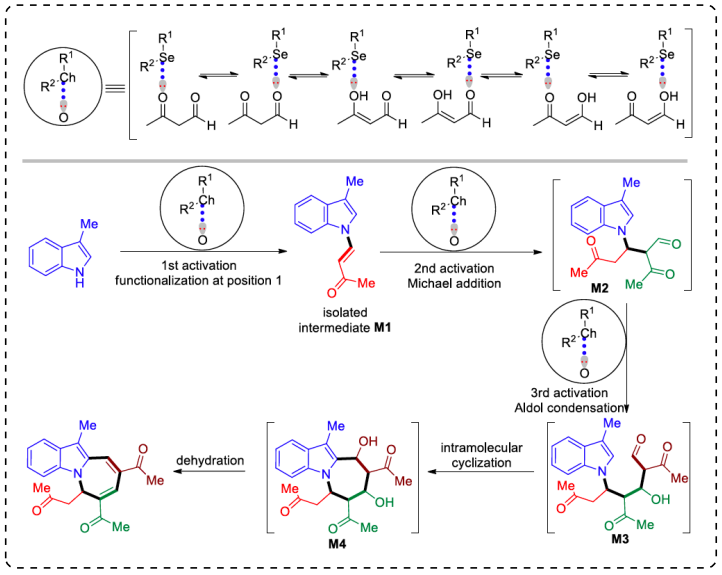


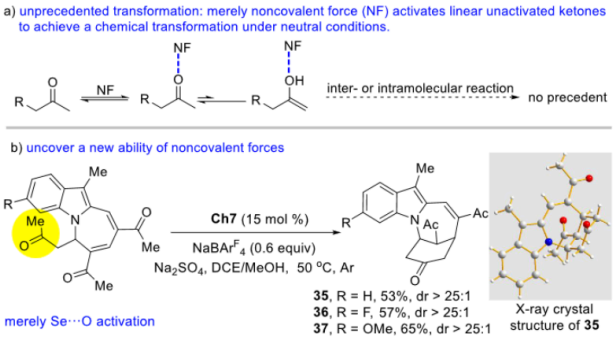
Type VI
Phosphine-based ChB donors

•Assembly of Discreate Molecules (2019, Wang)[1]

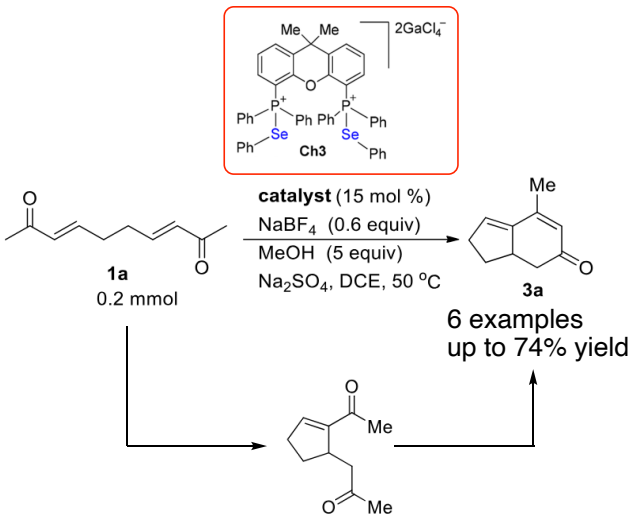


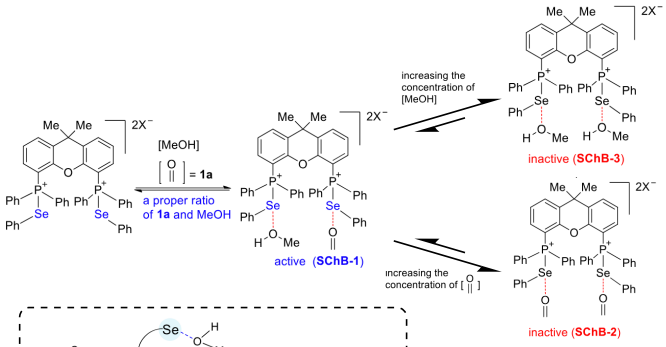


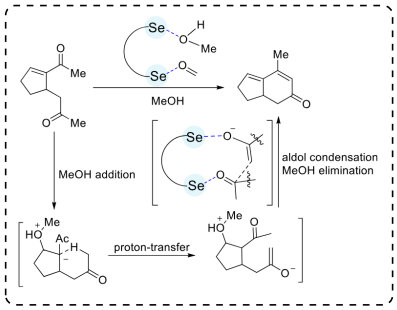




•Cyclization of Enone (2020, Wang)[2]

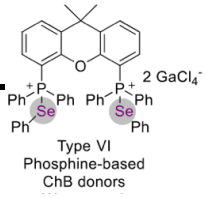






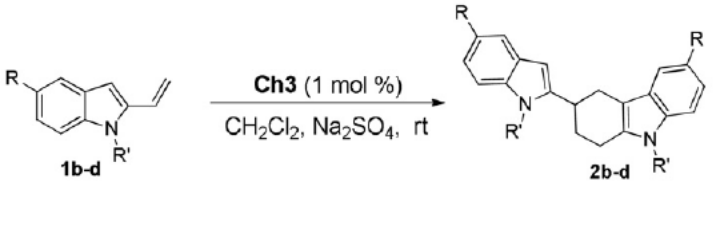
1) Wang, Y. *et. al. J. Am. Chem. Soc.* **2019,** *141,* 9175
2) Wang, Y. *et. al. J. Am. Chem. Soc.* **2020,** *142,* 3117

2. Chalcogen Bonding Catalyst

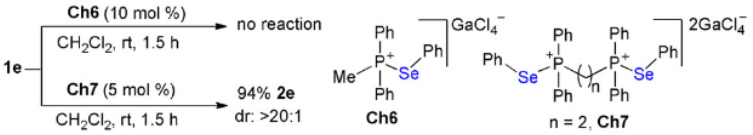


Type VI
Phosphine-based ChB donors

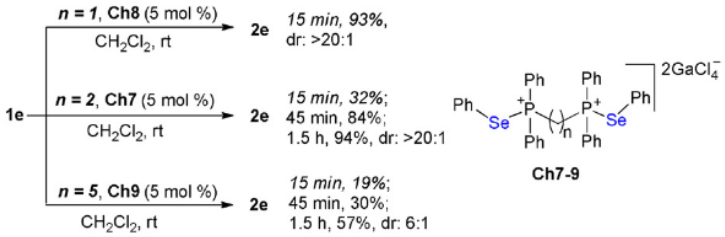
•Diels—Alder Reaction (2021, Wang)[1]



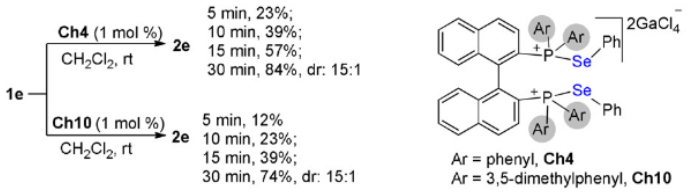
a) different catalytic activities between bidentate catalysts and monodentate catalysts

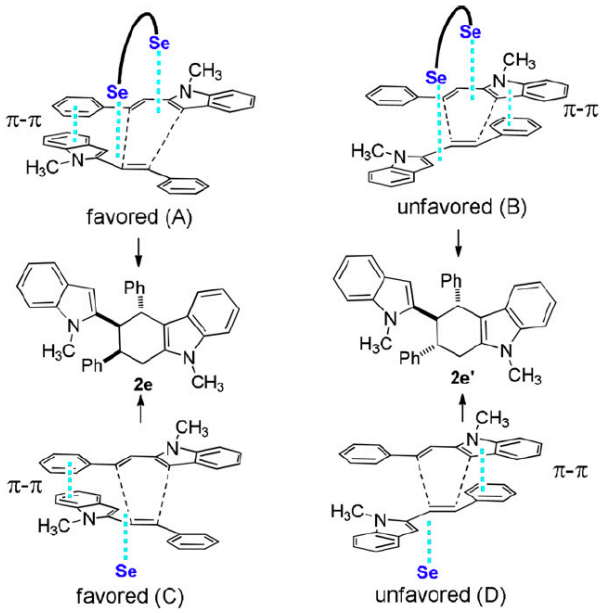


b) the effect of the distance between the two binding sites of bidentate catalysts



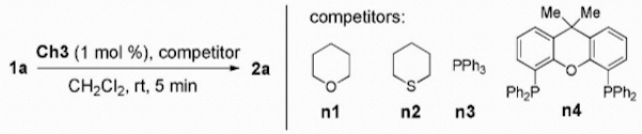
c) steric effect





Proposed Se···π bonding catalysis mode.

Table 2: Competition between Se···n and Se···π bonding interaction.[a]

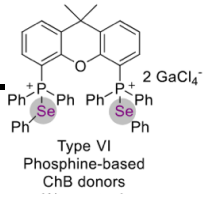


Entry	Competitor	Competitive bonding	Yield [%]
1	no	no	92
2	**n1** (1.0 equiv)	Se···O	84
3	**n1** (5.0 equiv)	Se···O	68
4	**n2** (1.0 equiv)	Se···S	92
5	**n2** (2.0 equiv)	Se···S	< 5
6	**n3** (2.0 mol %)	Se···P	< 5
7	**n4** (2.0 mol %)	Se···P	< 5

← 後の研究のきっかけ

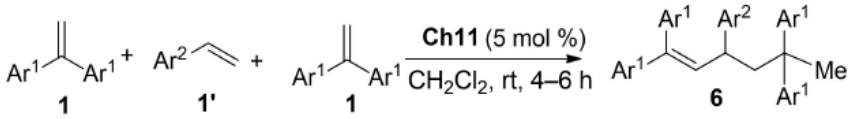
1) Wang, Y. *et. al. Angew. Chem. Int. Ed.* **2021,** *60,* 9395

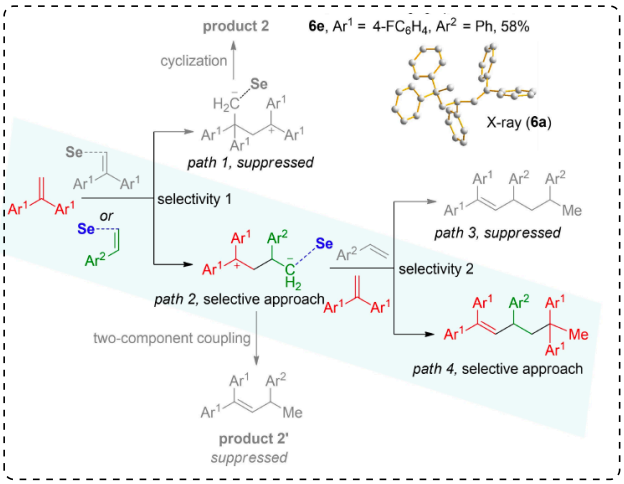
2. Chalcogen Bonding Catalyst

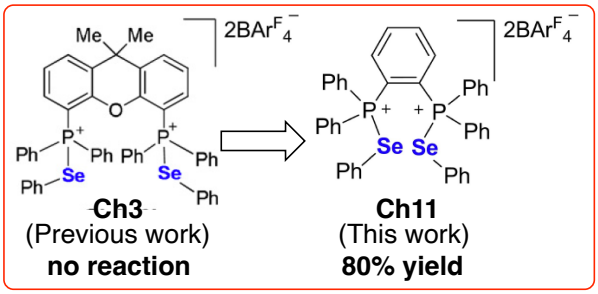


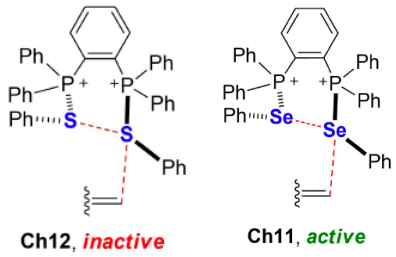
Type VI
Phosphine-based ChB donors

•Cross Coupling of Triple Alkenes (2022, Wang)[1]

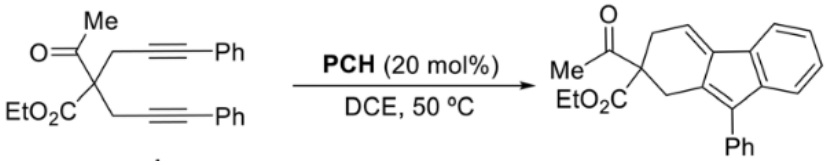




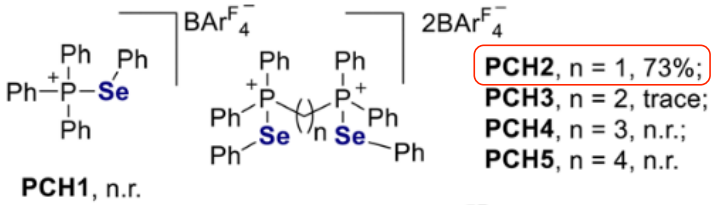


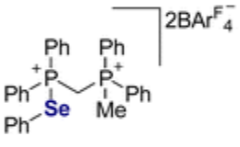


•Intramolecular Cyclization of 1,6-diynes (2023, Wang)[1]



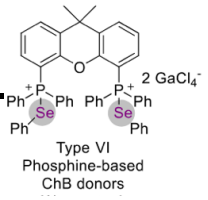
9 examples
up to 73% yield



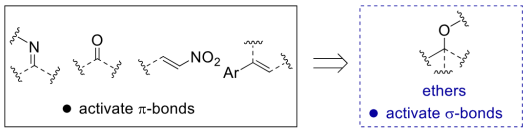


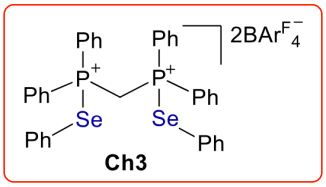
1) Wang, Y. *et. al. Angew. Chem. Int. Ed.* **2022,** *61,* e202203671
2) Wang, Y. *et. al. Chem. Commun.,* **2023,** *59,* 12278

2. Chalcogen Bonding Catalyst



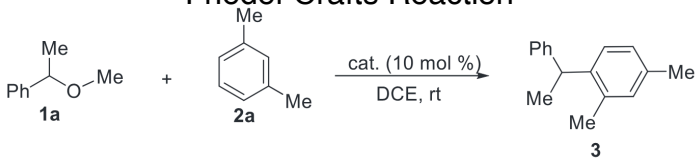
Type VI
Phosphine-based ChB donors



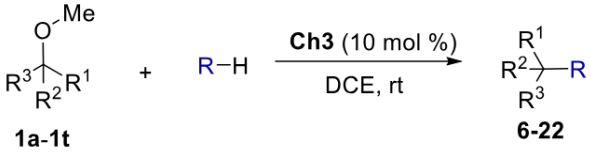


•Supramolecular Catalysis with Ether (2023, Wang)[1]

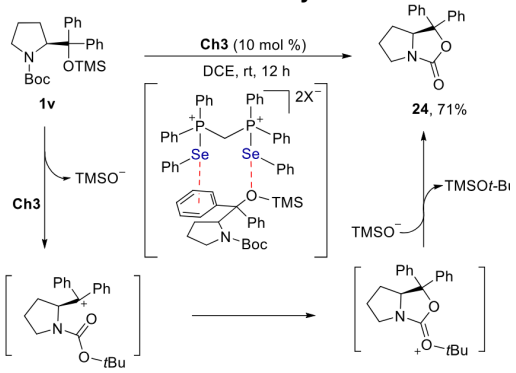
Friedel-Crafts Reaction



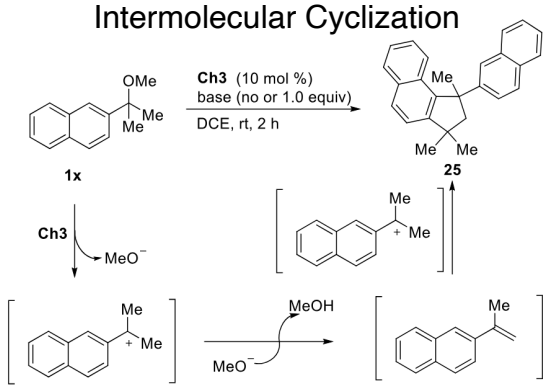
Coupling Reaction



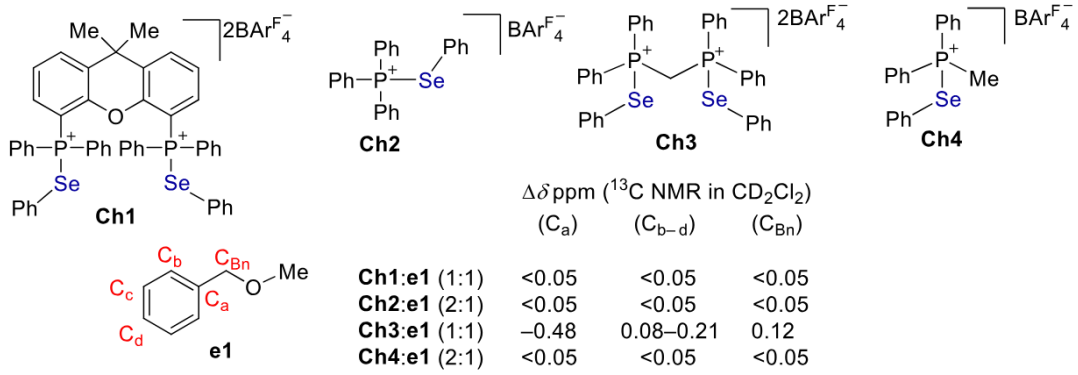
Intramolecular Cyclization



Intermolecular Cyclization

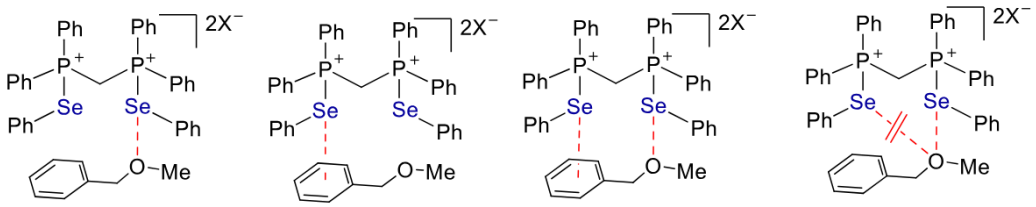


a



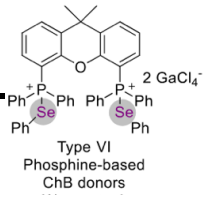
	Δδ ppm (^{13}C NMR in CD_2Cl_2) (C_a)	(C_{b-d})	(C_{Bn})
Ch1:**e1** (1:1)	<0.05	<0.05	<0.05
Ch2:**e1** (2:1)	<0.05	<0.05	<0.05
Ch3:**e1** (1:1)	–0.48	0.08–0.21	0.12
Ch4:**e1** (2:1)	<0.05	<0.05	<0.05

b



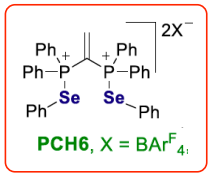
1) Wang, Y. *et. al.* **2023,** *14,* 6347

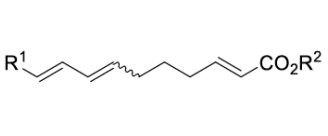
2. Chalcogen Bonding Catalyst



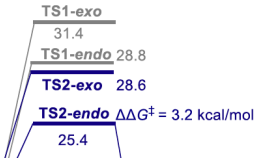
Type VI
Phosphine-based ChB donors

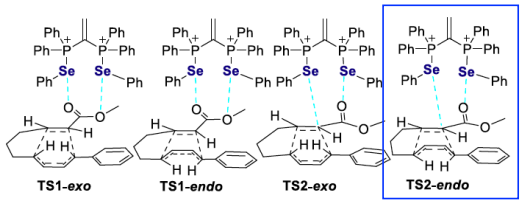
•Intramolecular Ester-based Diels-Alder Reaction (2024, Wang)[1]

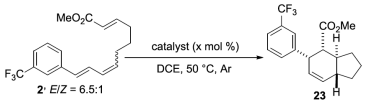




16 examples
up to 90% yield
>20:1 (endo:exo)







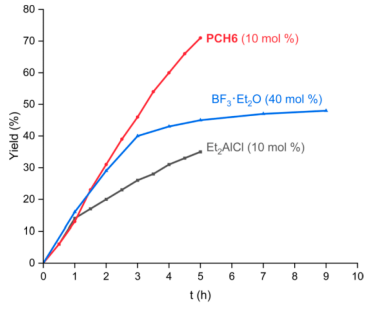
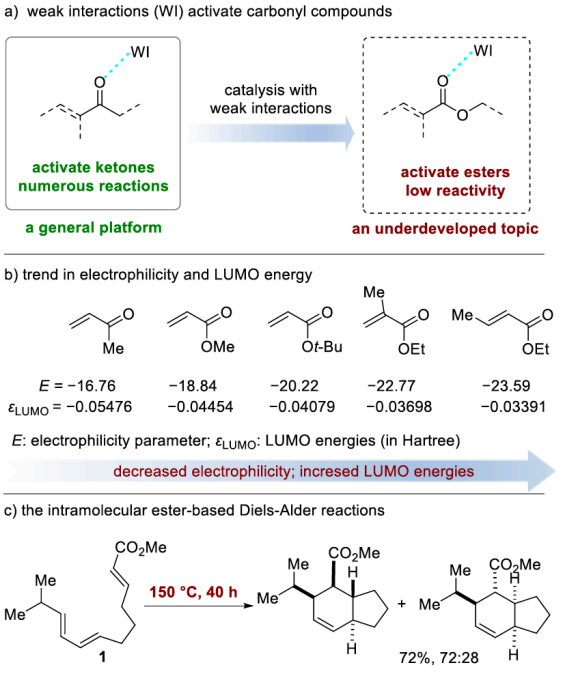


Figure 3. Catalytic efficiency of Lewis acids and PCH6.



1) Wang, Y. *et. al. J. Am. Chem. Soc.* **2024,** *146,* 13296