Artificial Force Induced Reaction

2019/8/2

M1 Yuki Nishioka

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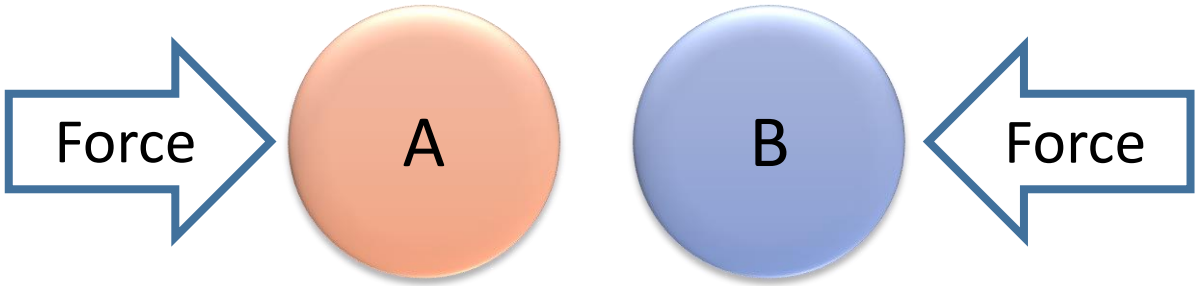
What is Artificial Force Induced Reaction(AFIR)?

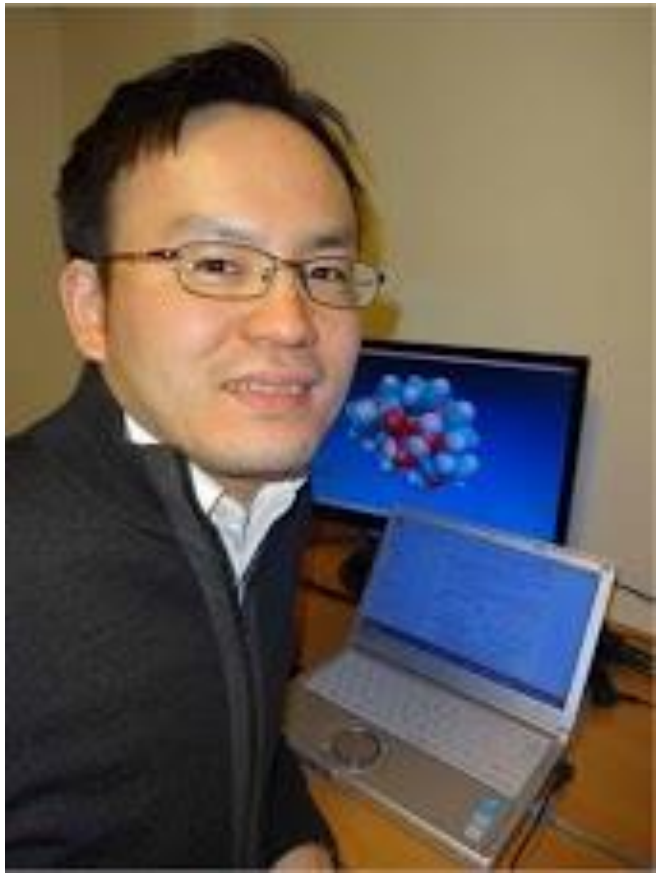
・One of the method of computational chemistry

・Prof. Maeda of Hokkaido University developed in 2010.

・In AFIR, artificial force is applied between the reactants to efficiently search the reaction path.



Satoshi Maeda



2002: B.S. from Tohoku University
2004: M.S. from Tohoku University
2007: Ph.D. from Tohoku University
2007-2010: Postdoc (JSPS PD), Tohoku University - Emory University - Kyoto University
2010-2012: Assistant Professor (Hakubi Project), Kyoto University
2012-2013: Assistant Professor, Hokkaido University
2014-2017: Associate Professor, Hokkaido University
2017-20xx: Professor, Hokkaido University
2017-20xx: Visiting Principle Investigator, National Institute for Materials Science (NIMS)
2018-2028: Director, Institute for Chemical Reaction Design and Discovery (WPI-ICReDD)

Source: https://sites.google.com/site/grrmgroup/satoshi-maeda

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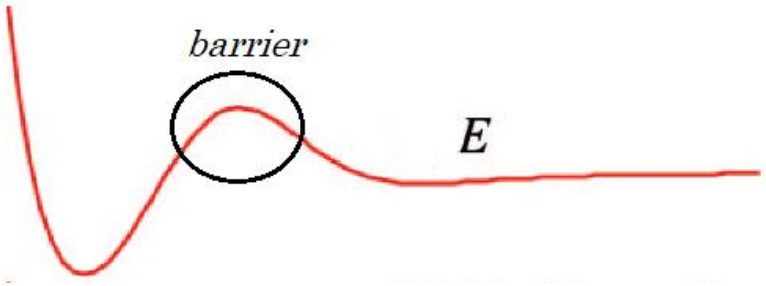
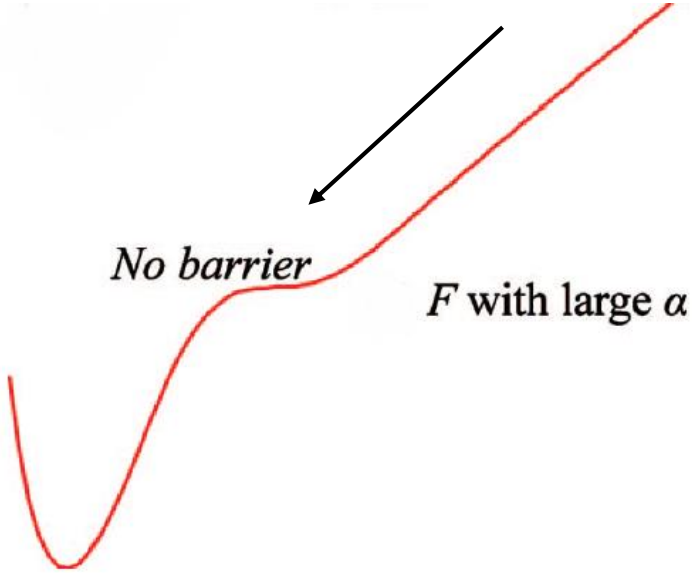
Overview of AFIR



Potential energy *E* as a function of r_{AB}(distance between A and B)



Artificial energy function *F* as a function of r_{AB}(distance between A and B)

$$F(r_{AB}) = E(r_{AB}) + \alpha r_{AB}$$

Satoshi Maeda and Keiji Morokuma *J. Chem. Phys*. **2010**, *132*, 241102

Function F

$$F(r_{AB}) = E(r_{AB}) + \alpha r_{AB}$$

$$F = E + \alpha \frac{\sum_{i \in A} \sum_{j \in B} \left[\left(R_i + R_j \right) / r_{ij} \right]^p r_{ij}}{\sum_{i \in A} \sum_{j \in B} \left[\left(R_i + R_j \right) / r_{ij} \right]^p}$$

E is potential energy.

$\alpha (\geq 0)$ is a parameter of magnitude of artificial attractive force.

$R_i \; and \; R_j$ are covalent radii of the ith and jth atoms, respectively.

r_{ij} is a distance between the ith and jth atoms.

p is arbitrary integer.

↑問題に対する調整項(p=6のときフィッティング良かった(P=6でなくてもよい。）)

Satoshi Maeda and Keiji Morokuma *J. Chem. Phys*. **2010**, *132*, 241102

Parameter α

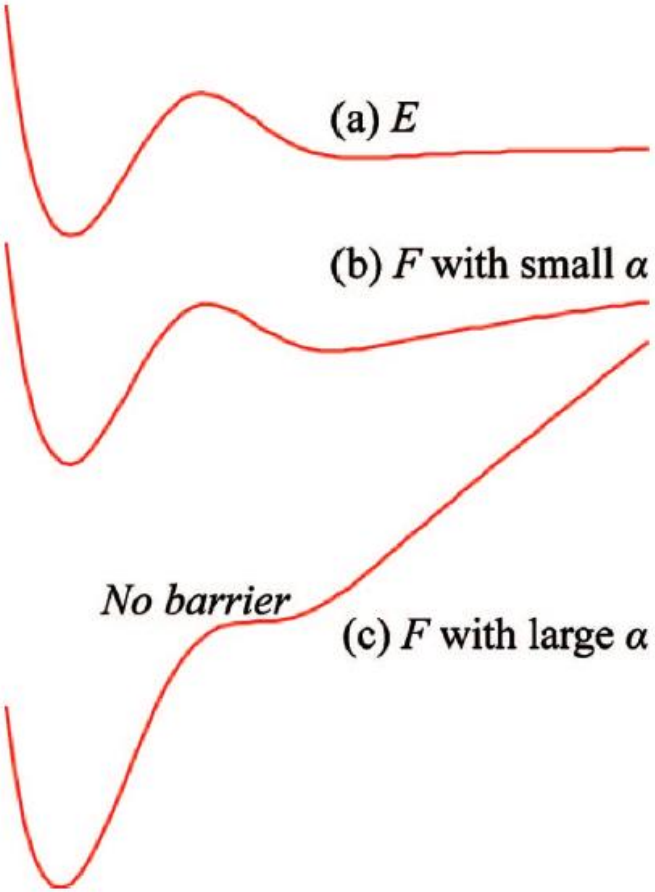
When both A and B are composed of single atom…

$$F = E + \alpha r_{AB}$$

The last term in this equation represents a constant artificial attractive force α between the atoms A and B.

Satoshi Maeda and Keiji Morokuma *J. Chem. Phys*. **2010**, *132*, 241102

Parameter α



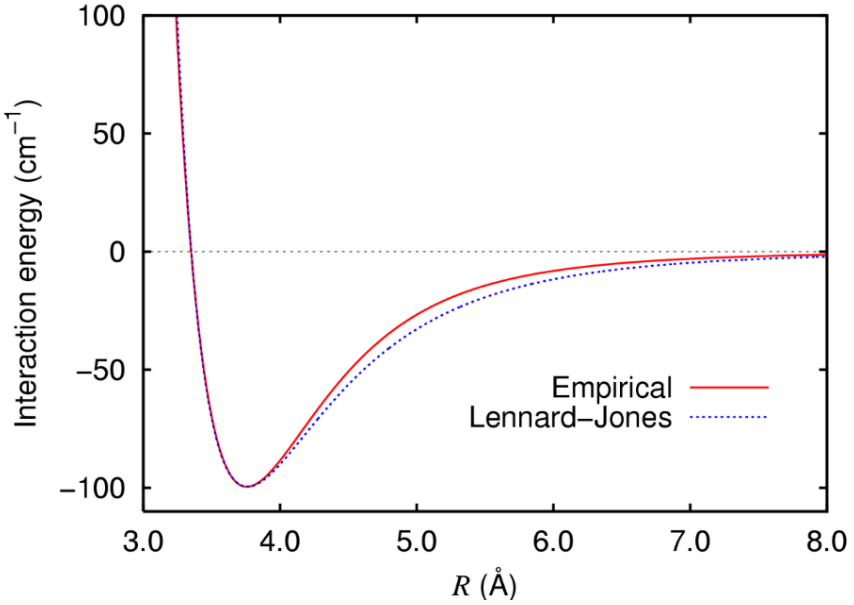
Typical diatomic potential curves
E and *F* with small α and large α

Rewrite α based on generic Lennard-Jones 6-12 potential

Satoshi Maeda and Keiji Morokuma *J. Chem. Phys*. **2010**, *132*, 241102

Lennard-Jones Potential

２つの原子間のポテンシャルエネルギーの経験的なもの



Potential energy between two argon atoms

Lennard-Jones potential is one of the empirical models representing the interaction potential energy between two atoms.

Potential energy U is

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{p} - \left(\frac{\sigma}{r}\right)^{q}\right].$$

Especially, when $q = 6, p = 12$, it is called Lennard-Jones 6-12 potential.

Ronald A. Aziz *J. Chem. Phys*. **2010**, 99, 4518

Source: https://ja.wikipedia.org/wiki/レナード-ジョーンズ・ポテンシャル

Parameter α

$$\alpha = \frac{\gamma}{\left[2^{-1/6} - \left(1 + \sqrt{1 + \gamma/\varepsilon}\right)^{-1/6}\right] R_0}$$

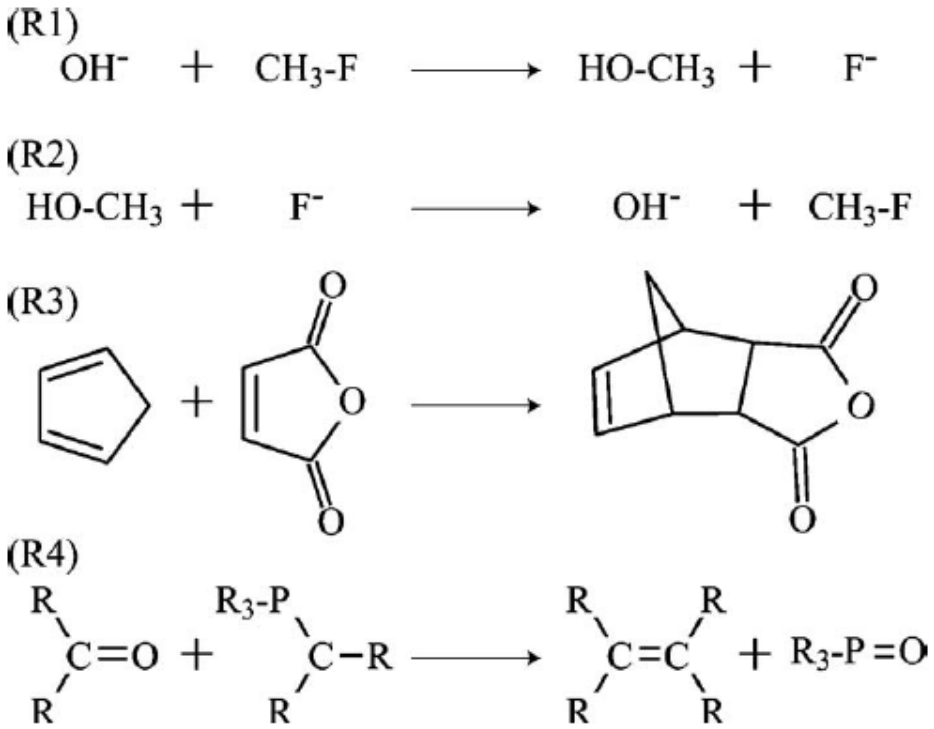
γ is a parameter related to collision energy on the Lennard-Jones potential.
Prof. Maeda used R_0 and ε to be the values for argon clusters($R_0 = 3.8164$ Å, $\varepsilon = 1.0061$ kJ/mol).

However, this conversion itself is not essential.

Satoshi Maeda and Keiji Morokuma *J. Chem. Phys*. **2010**, *132*, 241102

Four well-known Reaction

力をかける向きは自身で指定？
ラジカル的な反応は検証できる？
励起なども



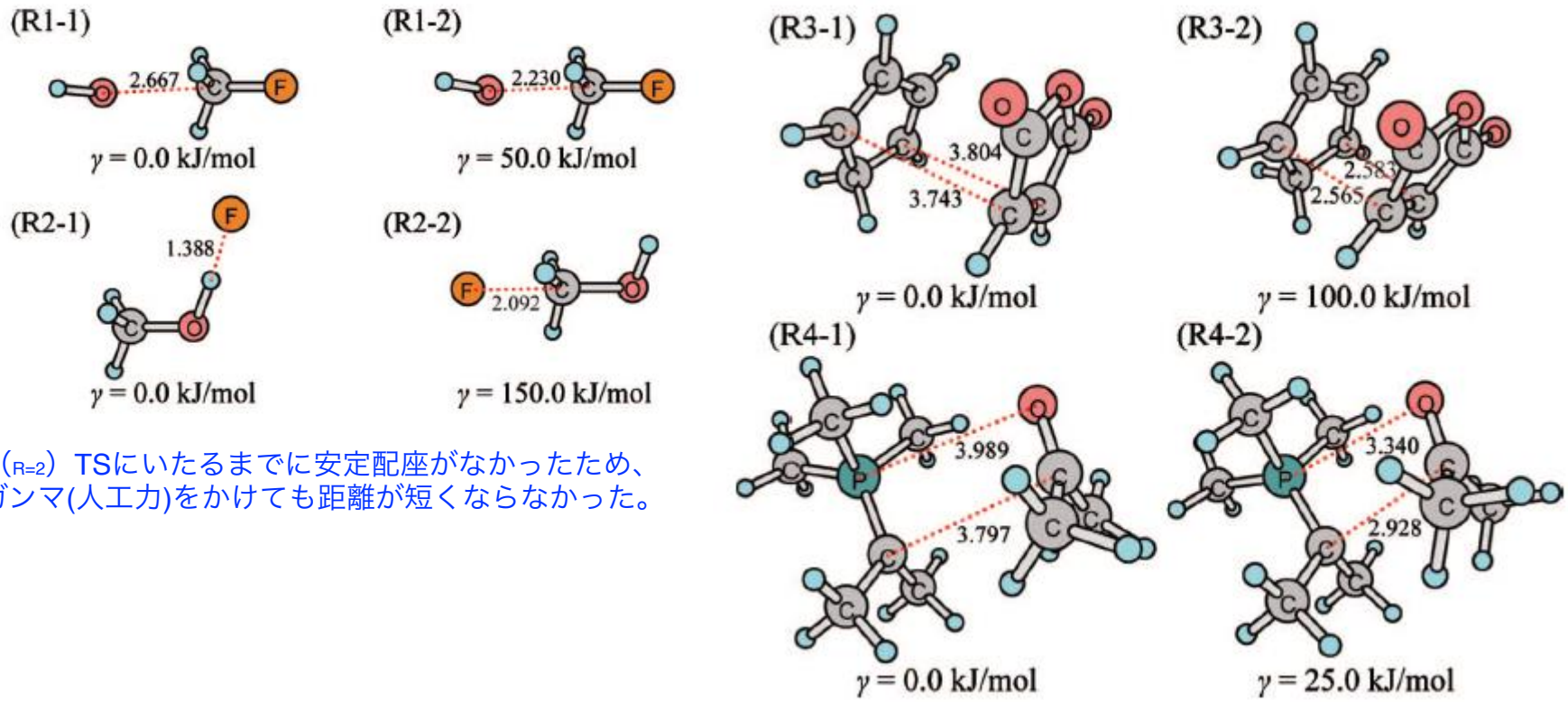
Starting from $\gamma = 0\ \mathrm{kJ/mol}$, authors increased γ by $50\ \mathrm{kJ/mol}$ until a minimization converges to a product side for each reaction.

R1: $\gamma = 100\ \mathrm{kJ/mol}$
R2: $\gamma = 200\ \mathrm{kJ/mol}$
R3: $\gamma = 150\ \mathrm{kJ/mol}$
R4: $\gamma = 50\ \mathrm{kJ/mol}$

⇨ γ_0

Satoshi Maeda and Keiji Morokuma *J. Chem. Phys*. **2010**, *132*, 241102

Four well-known Reaction

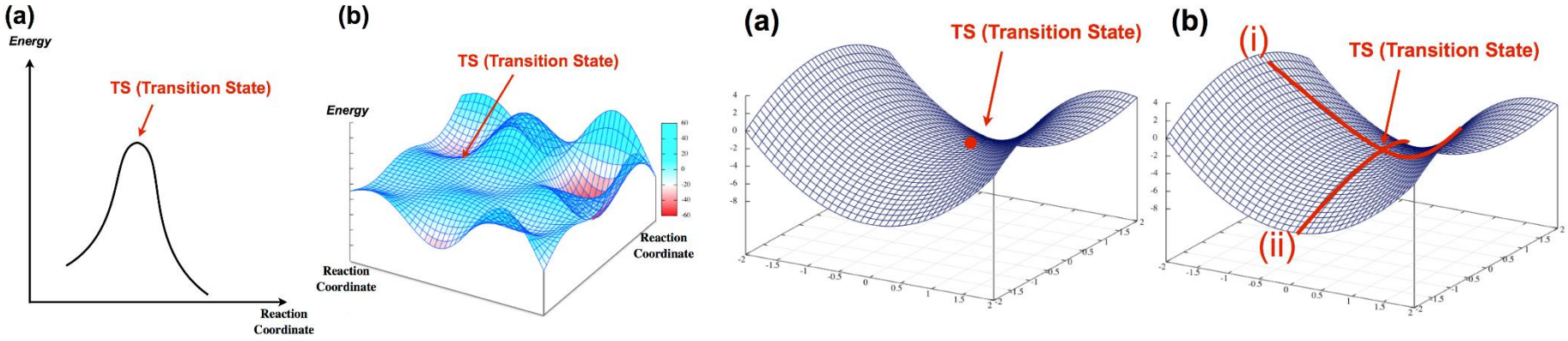


（$_{R=2}$）TSにいたるまでに安定配座がなかったため、
ガンマ(人工力)をかけても距離が短くならなかった。

Satoshi Maeda and Keiji Morokuma *J. Chem. Phys*. **2010**, *132*, 241102

Intrinsic Reaction Coordinate(IRC) Calculation

IRC…"the reaction coordinate as a curve passing through the initial and the transition points and orthogonal to energy equipotential contour surface"(Kenichi Fukui, 1970)



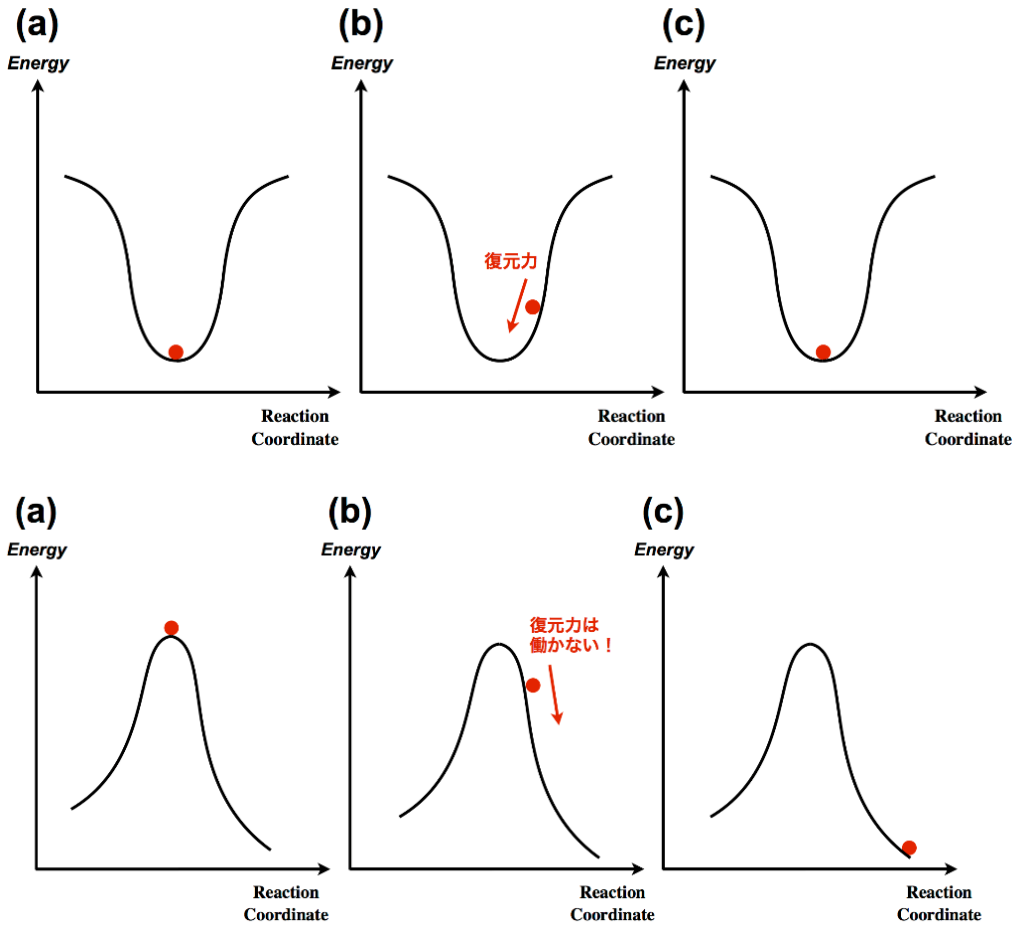
Kenichi Fukui, *J. Phys*. *Chem.* **1970**, *74*, 23, 4161

Kazuhiro Ishida *et al. J. Chem. Phys*. **1977**, 66, 2153

Source: https://computational-chemistry.com/top/blog/2016/01/11/transition-state/

Intrinsic Reaction Coordinate(IRC) Calculation

ヘッス行列を用いて定義

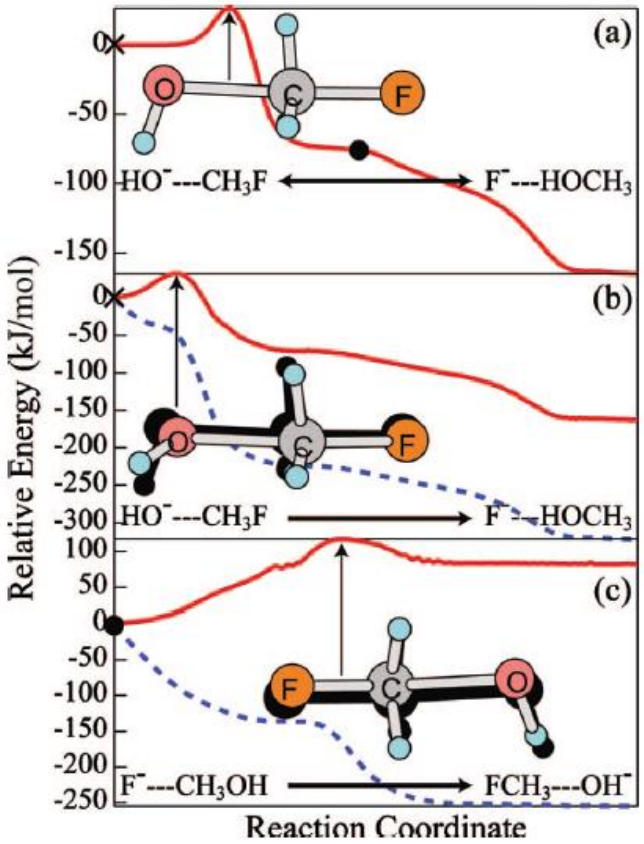


Kenichi Fukui, *J. Phys. Chem.* **1970**, *74*, 23, 4161

Kazuhiro Ishida *et al. J. Chem. Phys*. **1977**, 66, 2153

Source: https://computational-chemistry.com/top/blog/2016/01/11/transition-state/

R1 and R2



(a)…IRC profile
(b)
Blue dashed curve…a profile of *F*
with $\gamma = 100$ kJ/mol starting from R1-1
Red solid curve…a profile of *E*
(c)
Blue dashed curve…a profile of *F*
with $\gamma = 200$ kJ/mol starting from R2-1
Red solid curve…a profile of *E*

R1 → 133 gradients and 2 Hessians
R2 → 90 gradients and 2 Hessians

Satoshi Maeda and Keiji Morokuma *J. Chem. Phys*. **2010**, *132*, 241102

Optimizations Starting from Random Orientation

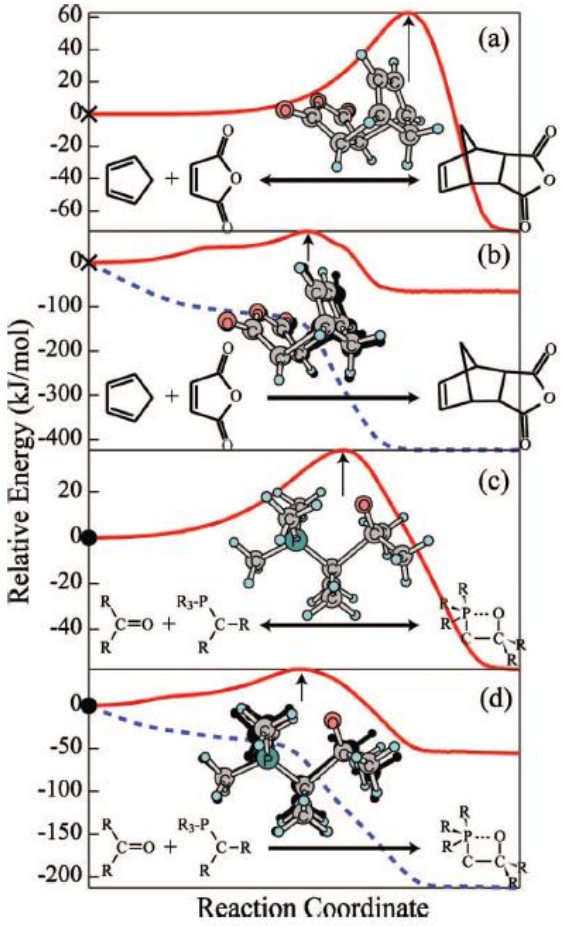
New procedure…optimizations starting from random orientations for R1 and R2 at $\gamma = 100\ \mathrm{kJ/mol}$, where generation of random orientation was terminated when last ten optimizations converged to the structures which were already found in earlier optimizations.

R1 → 1943 gradients and 49 Hessians
R2 → 1355 gradients and 39 Hessians

GRRM
Conventional method ⟹
R1 → 25758 gradients and 747 Hessians
R2 → 24230 gradients and 653 Hessians

Satoshi Maeda and Keiji Morokuma *J. Chem. Phys*. **2010**, *132*, 241102

R3 and R4



(a)…IRC profile of R3
(b)
Blue dashed curve…a profile of *F*
with $\gamma = 150\ \mathrm{kJ/mol}$ starting from R3-1
Red solid curve…a profile of *E*
(c)…IRC profile of R4
(d)
Blue dashed curve…a profile of *F*
with $\gamma = 50\ \mathrm{kJ/mol}$ starting from R4-1
Red solid curve…a profile of *E*

R3 → 103 gradients and 2 Hessians
R4 → 148 gradients and 2 Hessians

Satoshi Maeda and Keiji Morokuma *J. Chem. Phys*. **2010**, *132*, 241102

Short Summary

・AFIR is an efficient algorithm to obtain a TS of A+B→X type reaction

・Conventional methods don’t have an ability to systematically predict geometries of TS on quantum chemical potential energy surfaces. AFIR can be used in automated prediction of unknown reaction pathways.

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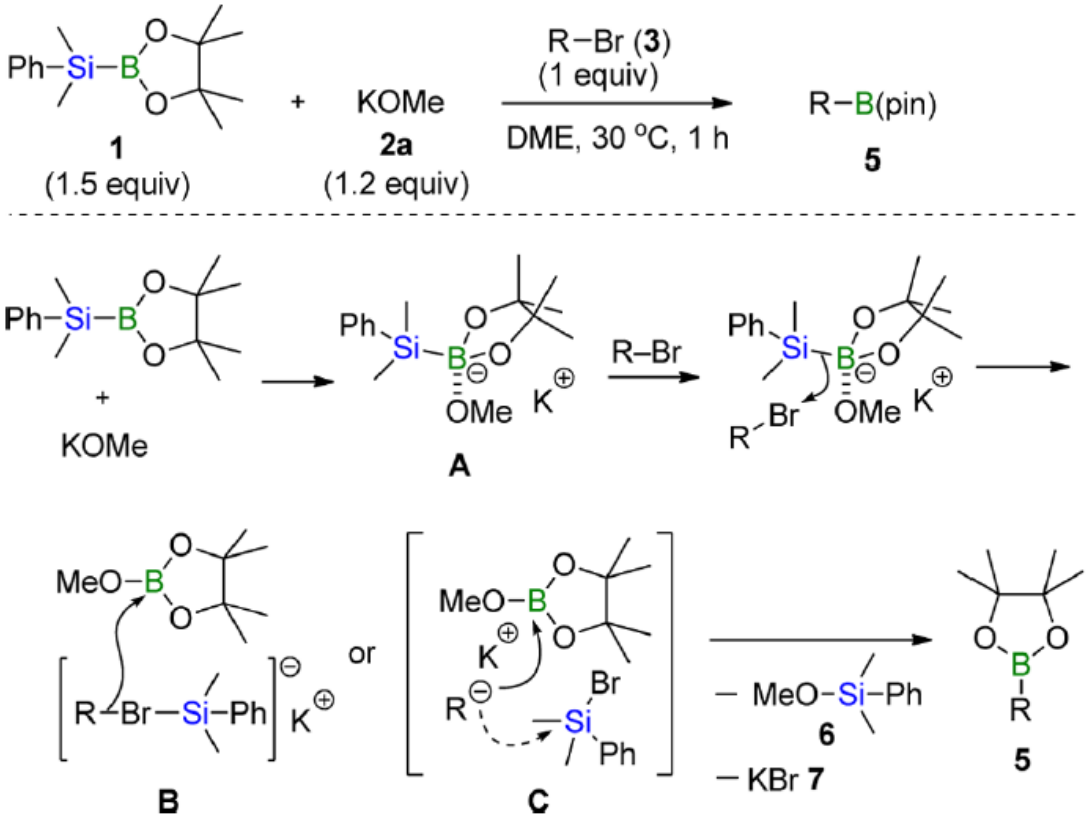
The Anomalous Formal Nucleophilic Borylation of Organic Halides with Silylborane

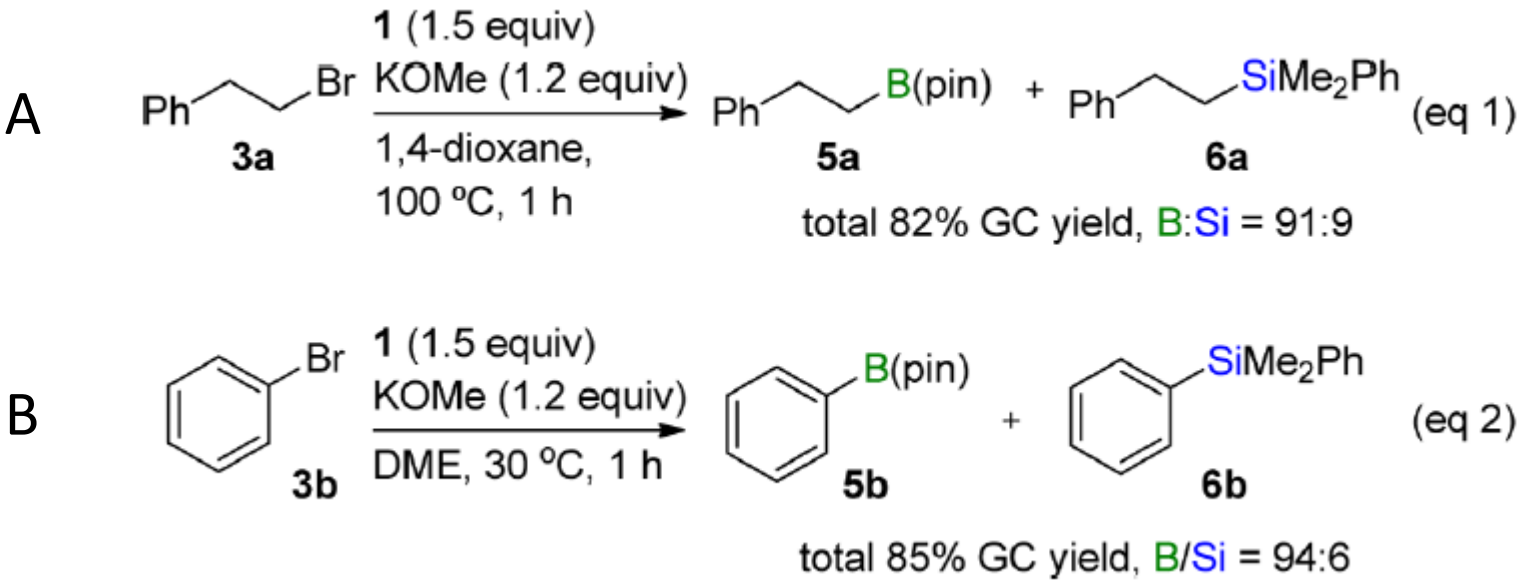
Scheme 1. Proposed Reaction Mechanism of Formal Boryl Substitution of Organic Bromine Compounds (R = Aryl or Alkyl) with Silylborane and Alkoxy Base



The mechanism of this reaction has not yet been elucidated.

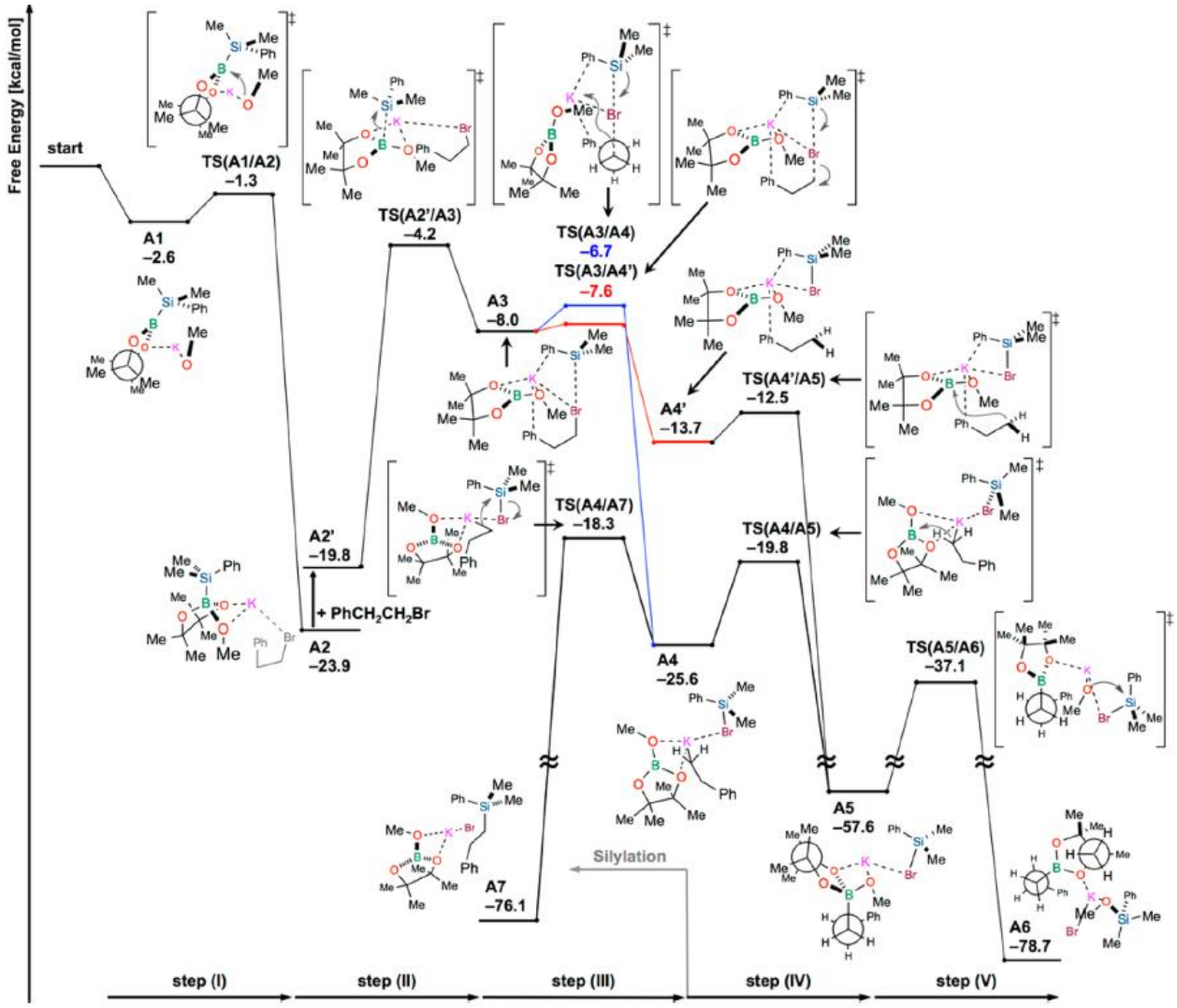
Rhohei Uematsu *et al*. *J. Am. Chem. Soc*. **2015**, *137*, 4090

The Anomalous Formal Nucleophilic Borylation of Organic Halides with Silylborane



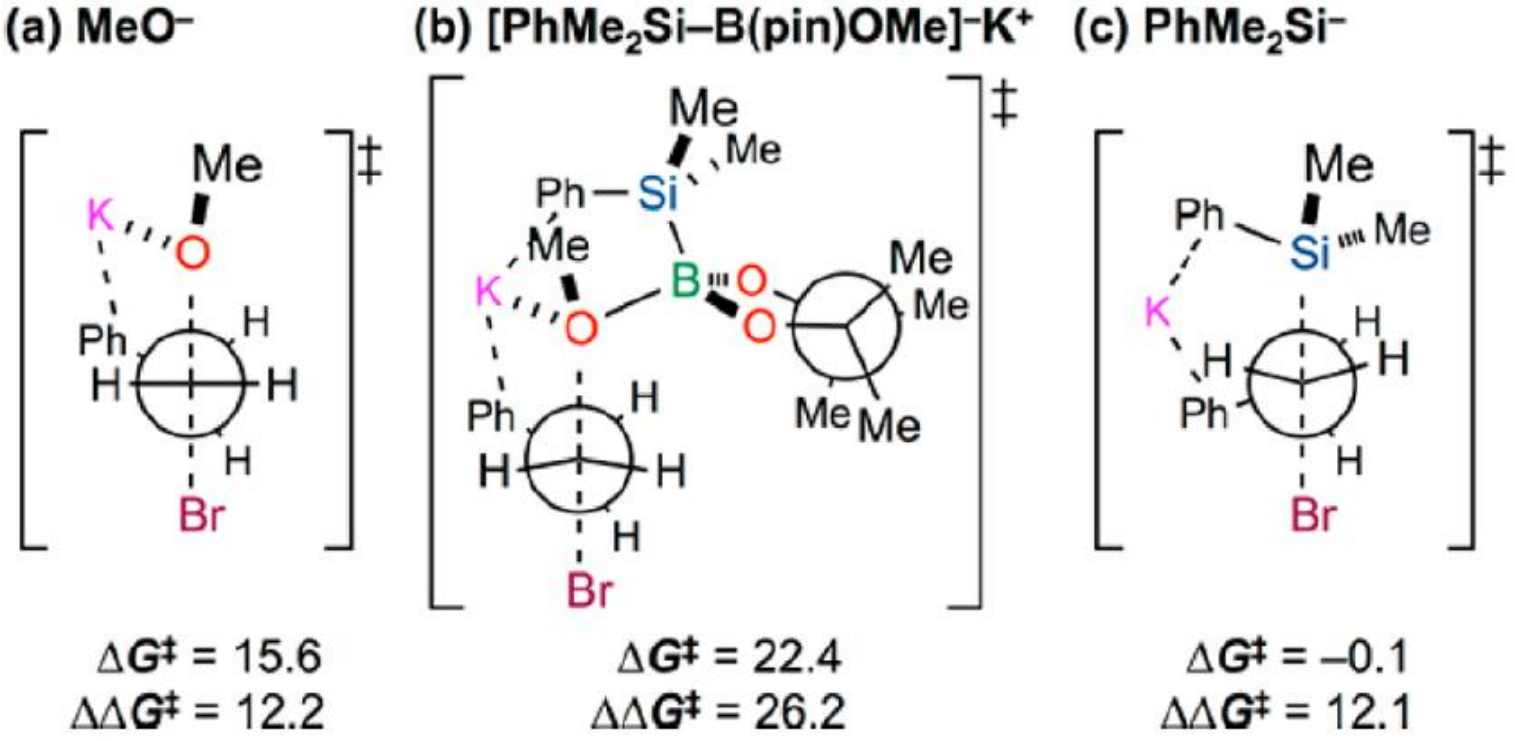
Rhohei Uematsu *et al*. *J. Am. Chem. Soc*. **2015**, *137*, 4090

Reaction Mechanism of Case A



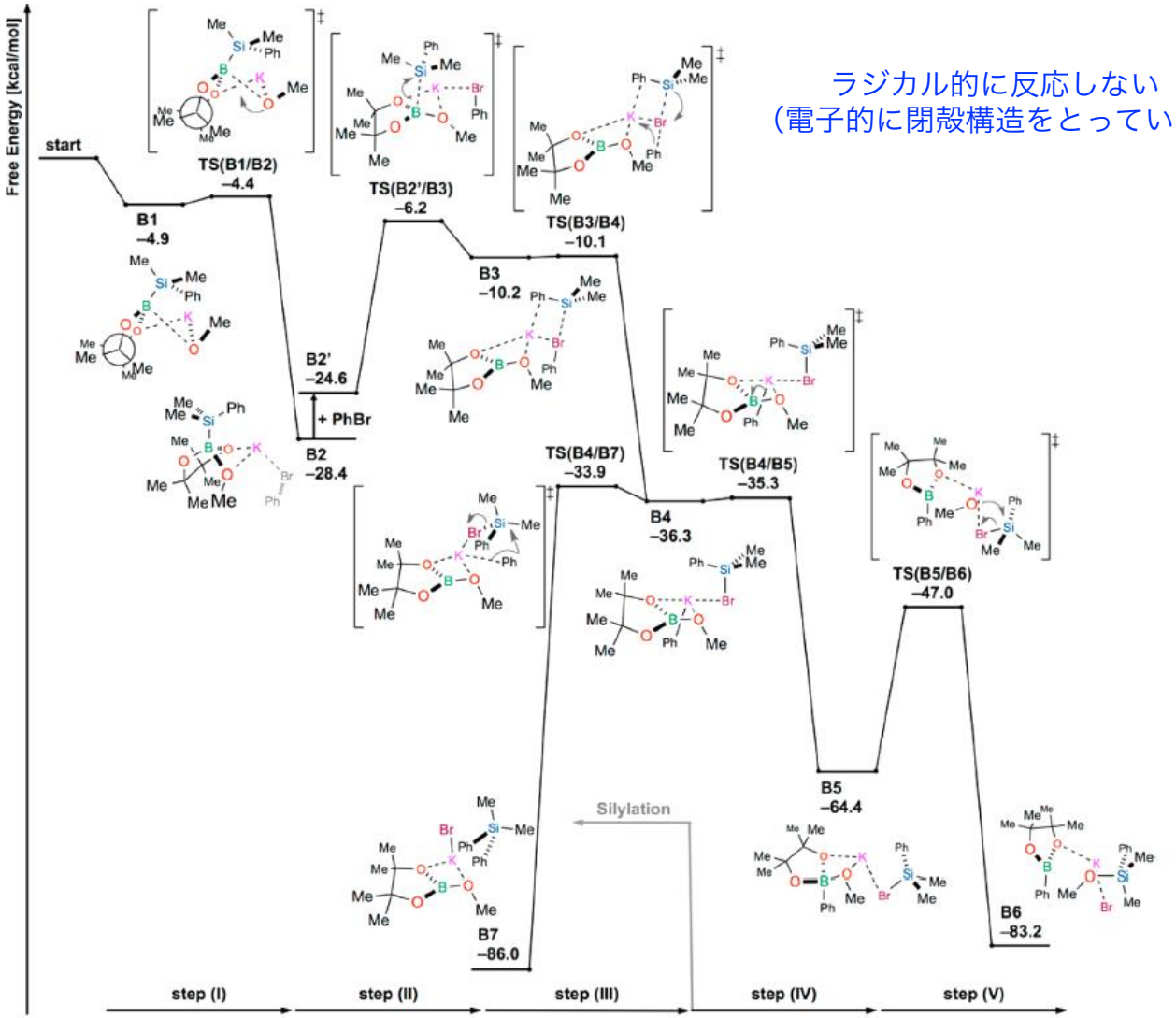
Rhohei Uematsu *et al*. *J. Am. Chem. Soc*. **2015**, *137*, 4090

Reaction Mechanism of Case A



Rhohei Uematsu *et al*. *J. Am. Chem. Soc*. **2015**, *137*, 4090

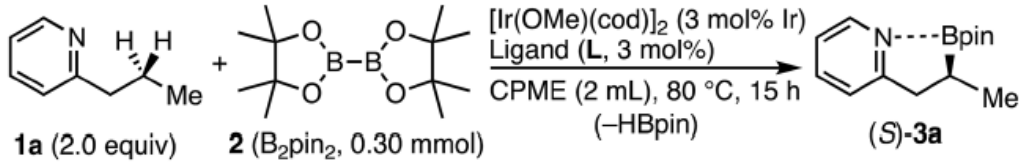
Reaction Mechanism of Case B



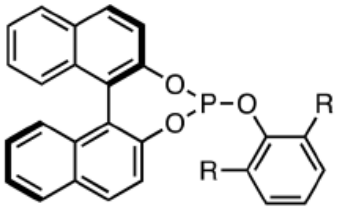
ラジカル的に反応しない
（電子的に閉殻構造をとっている）

Rhohei Uematsu *et al*. *J. Am. Chem. Soc*. **2015**, *137*, 4090

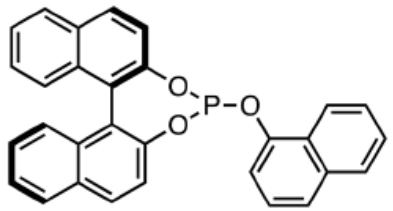
Iridium-Catalyzed Asymmetric Borylation of Unactivated Methylene C(sp3)–H Bonds



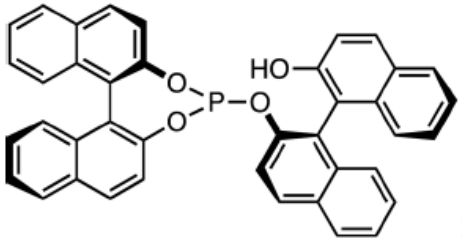
Ligand, Isolated yield of **4a** (based on **2**), % ee



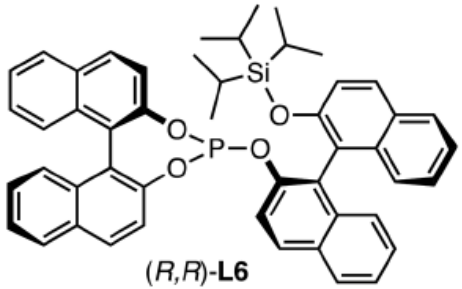
(*R*)-**L1** (R = H), trace (^{1}H NMR)
(*R*)-**L2** (R = Me), 30%, 30% ee
(*R*)-**L3** (R = Ph), 25%, 63% ee



(*R*)-**L4**, 49%, 76% ee



(*R*)-**L5**, 52%, 80% ee

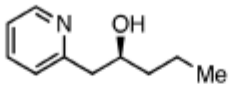
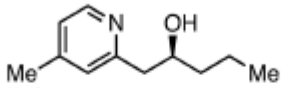
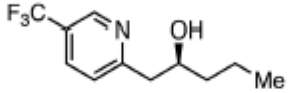
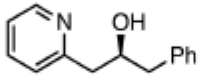
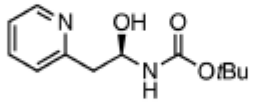
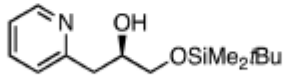
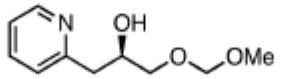
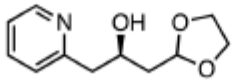
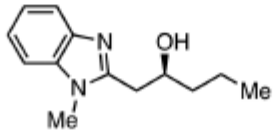
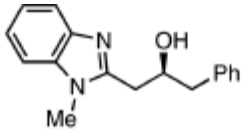
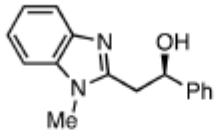
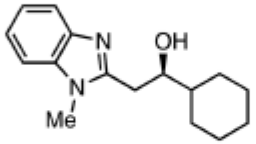
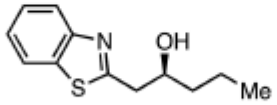
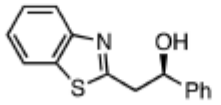
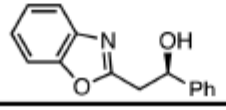


(*R,R*)-**L6**

55%, 90% ee[a]
75%, 98% ee (2,6-lutidine 20 mol%)
83%, 99% ee (2,6-lutidine 20 mol%, 3 equiv **1a**, 36 h)
96%, 99% ee (2 mol% Ir, 2,6-lutidine 20 mol%, 2 equiv **1a**, 36 h[b], **1.10 g** (*S*)-**4a**)

Ronald L. Reyes, *et al*. *J. Am. Chem. Soc*. **2019**, *141*, 6817

Substrate Scope

entry	oxidation product **4**		yield of **4** (%)[b]	ee of **4** (%)[c]
1[d]	**4b**		87	96 (*S*)
2[d]	**4c**		85	94 (*S*)
3[d,e]	**4d**		65	97 (*S*)
4	**4e**		75	93 (*S*)
5	**4f**		54	91 (*R*)
6[d]	**4g**		52	95 (*R*)
7	**4h**		78	94 (*R*)
8[d]	**4i**		53	92 (*R*)
9[e]	**4j**		95	93 (*S*)
10	**4k**		86	98 (*S*)
11[e]	**4l**		75	96 (*R*)
12[d]	**4m**		87	95 (*R*)
13[d,e]	**4n**		87	92 (*S*)
14[d]	**4o**		71	92 (*R*)
15[d,e]	**4p**		78	90 (*R*)

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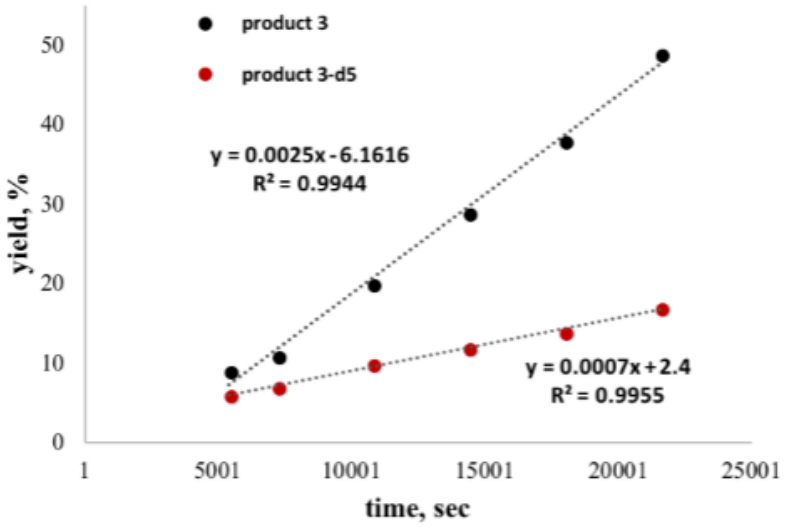
Kinetic Analysis



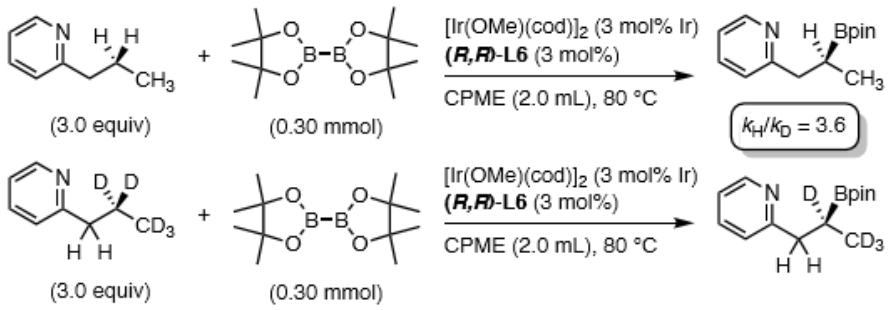


Figure S7: Initial Rate Data on the Formation of Alkylboronates **3** and **3-*d*$_4$**

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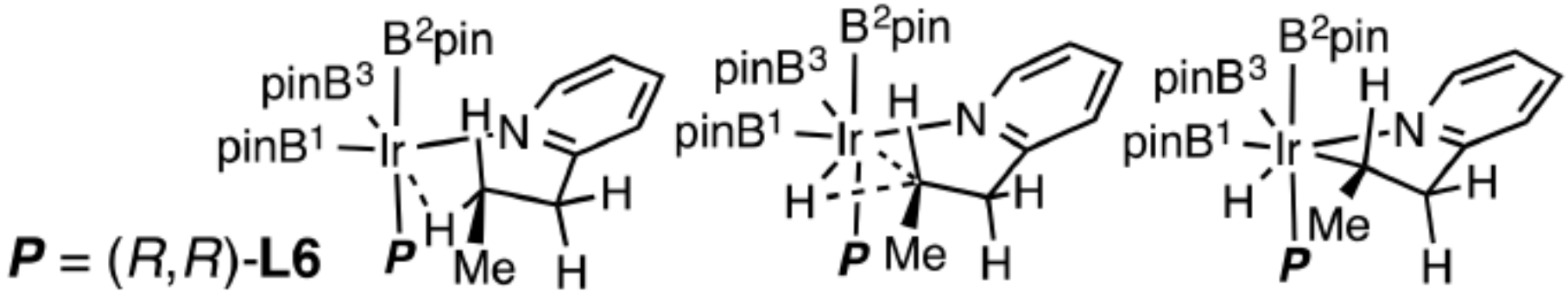
Chemical Diagrams

はじめ93個の構造が出てくる
そのうちえねるぎーの低い１０個を
その後の計算に使う。



配位の位置
水素原子の鏡像異性体
イリジウム錯体120度づつ捻って計算

３×4=12通り、手動で検討

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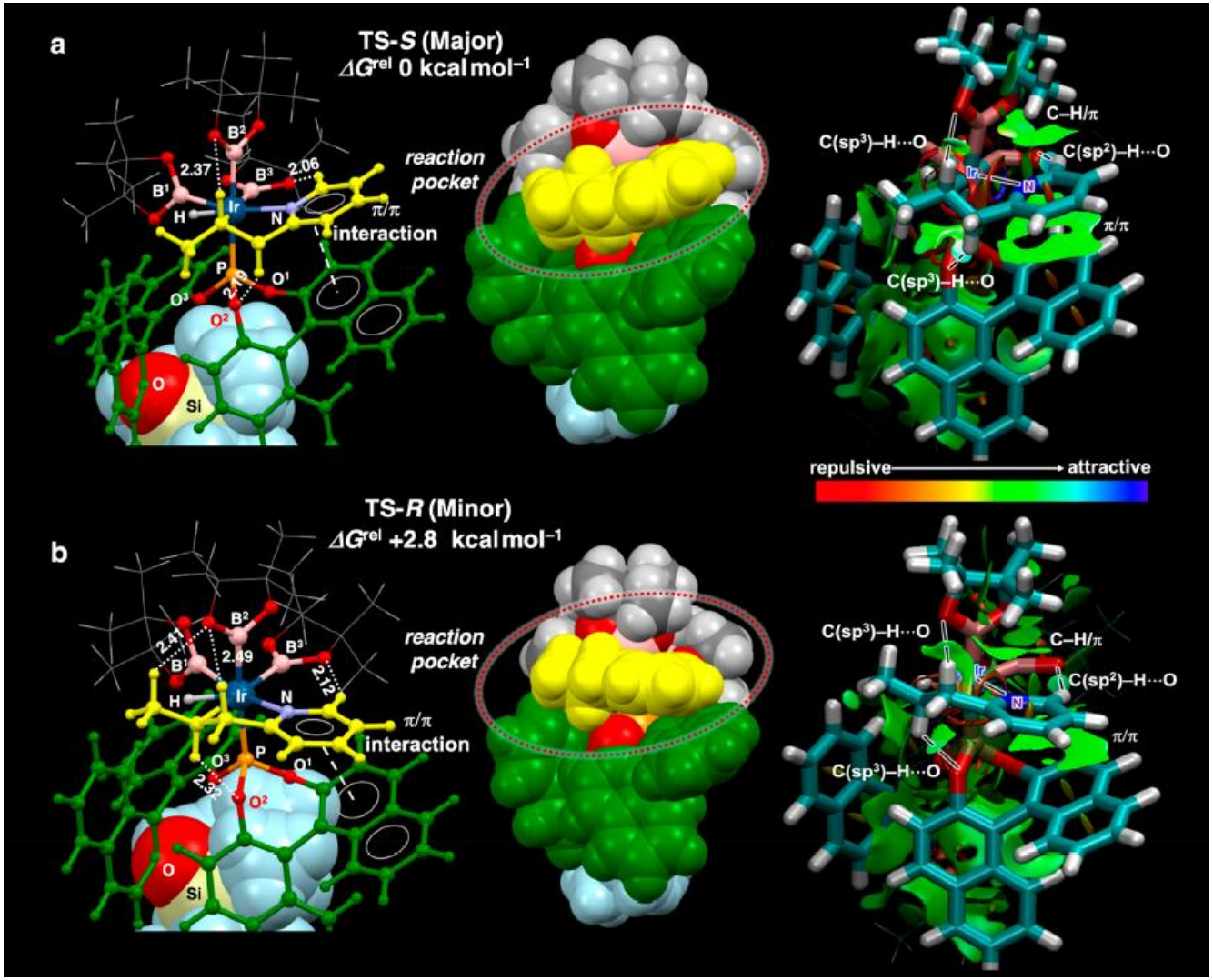
3-D Representations with Geometrical Features of the TS



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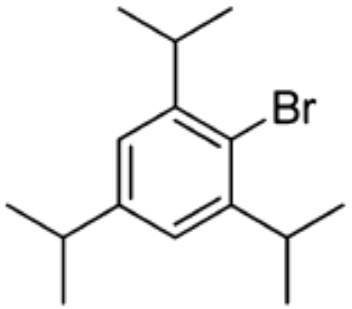
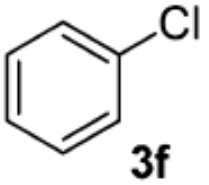
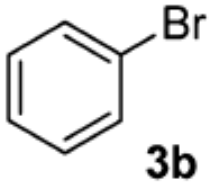
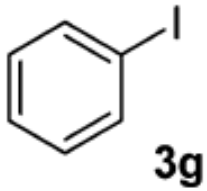
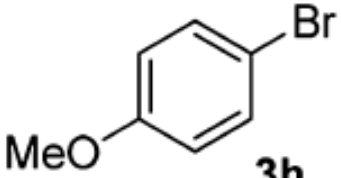
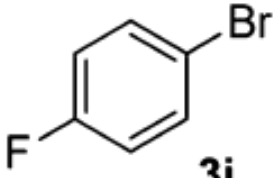
Summary

・AFIR is an efficient algorithm to obtain a Ts and reaction pathway reaction.

・Conventional methods cannot calculate unknown complex reaction, but AFIR can be used in automated prediction of unknown reaction pathways.

Appendix

Ar-X	 **3e**	 **3f**	 **3b**	 **3g**	
	 **3h**	 **3i**			
Base	KOMe **2a**	LiOMe **2b**	NaOMe **2c**	K(O-*t*-Bu) **2d**	Li(O-*t*-Bu) **2e**

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Appendix

S5-1. Steric Effect (R = $^{i}Pr_3C_6H_2$–)

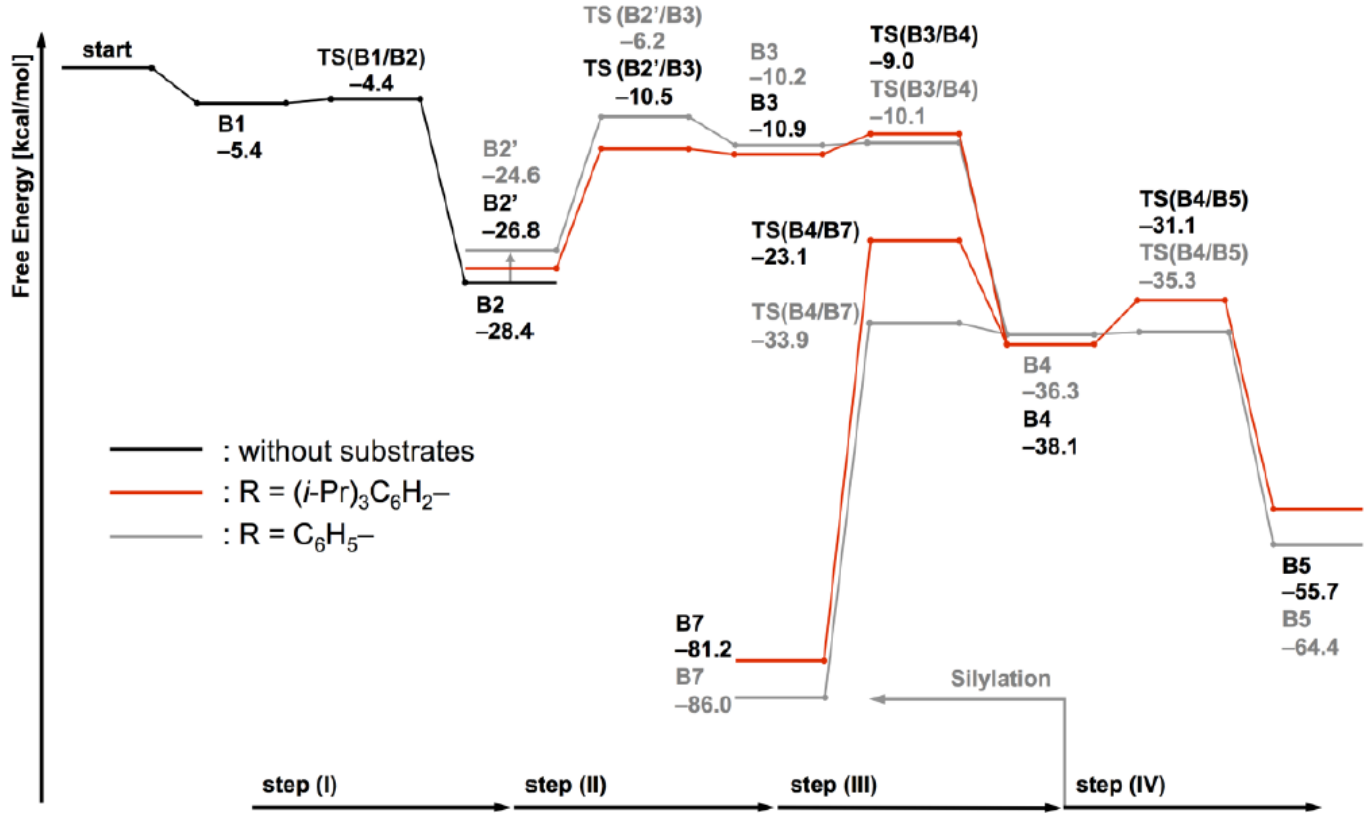

Figure S5-1. Reaction Pathways Leading to the B/Si Products with R = $^{i}Pr_3C_6H_2$

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Appendix

S5-2. Halide Effect (X = Cl and I)

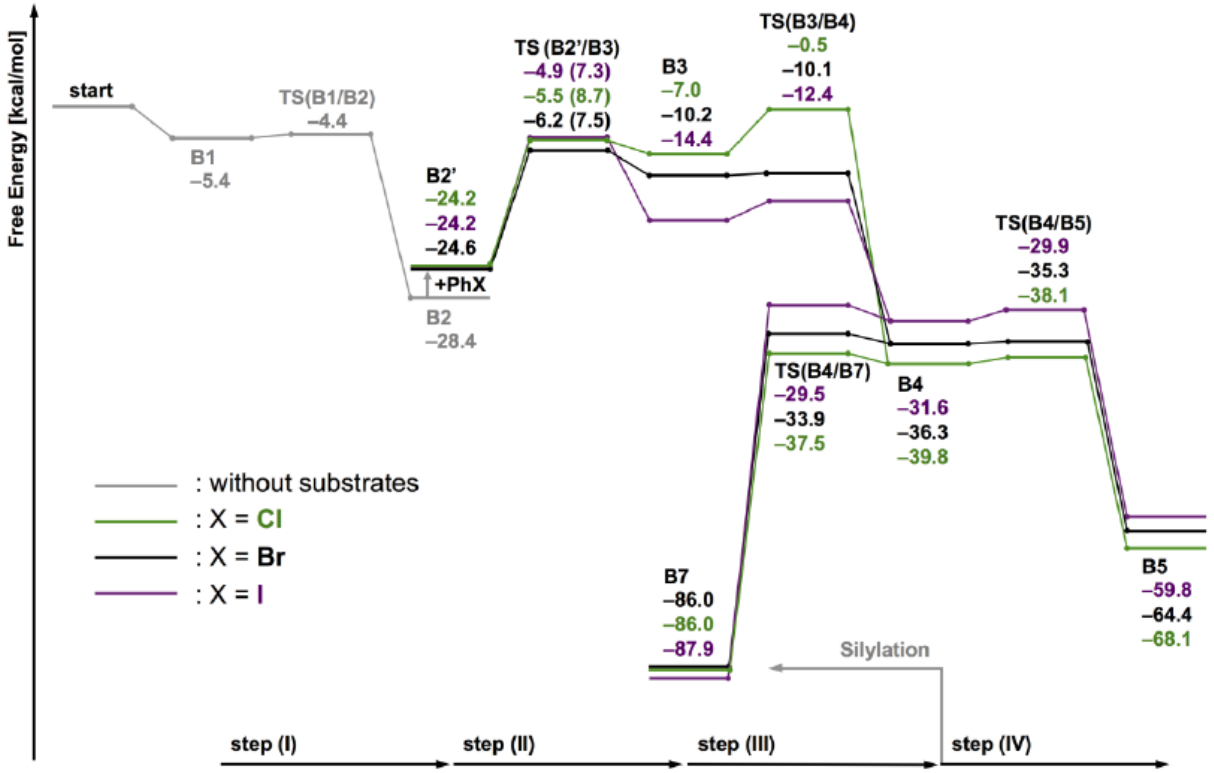

Figure S5-2. Reaction Pathways Leading to the B/Si Products with Different Substrates Ph-X (X = Cl and I)

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Appendix

S5-3. Base Effect (LiOMe, NaOMe, KO^{t}Bu, LiO^{t}Bu)

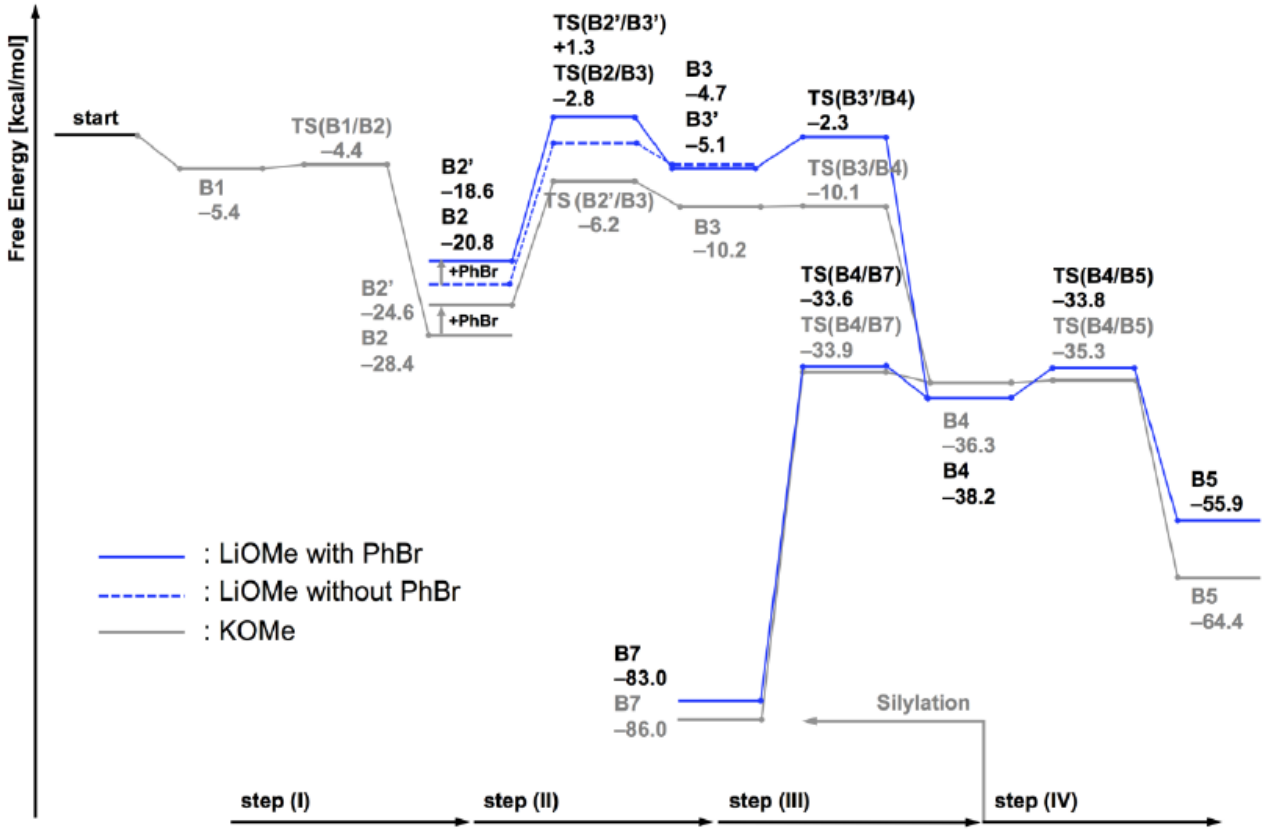

Figure S5-3-1. Reaction Pathways Leading to the B/Si Products with LiOMe

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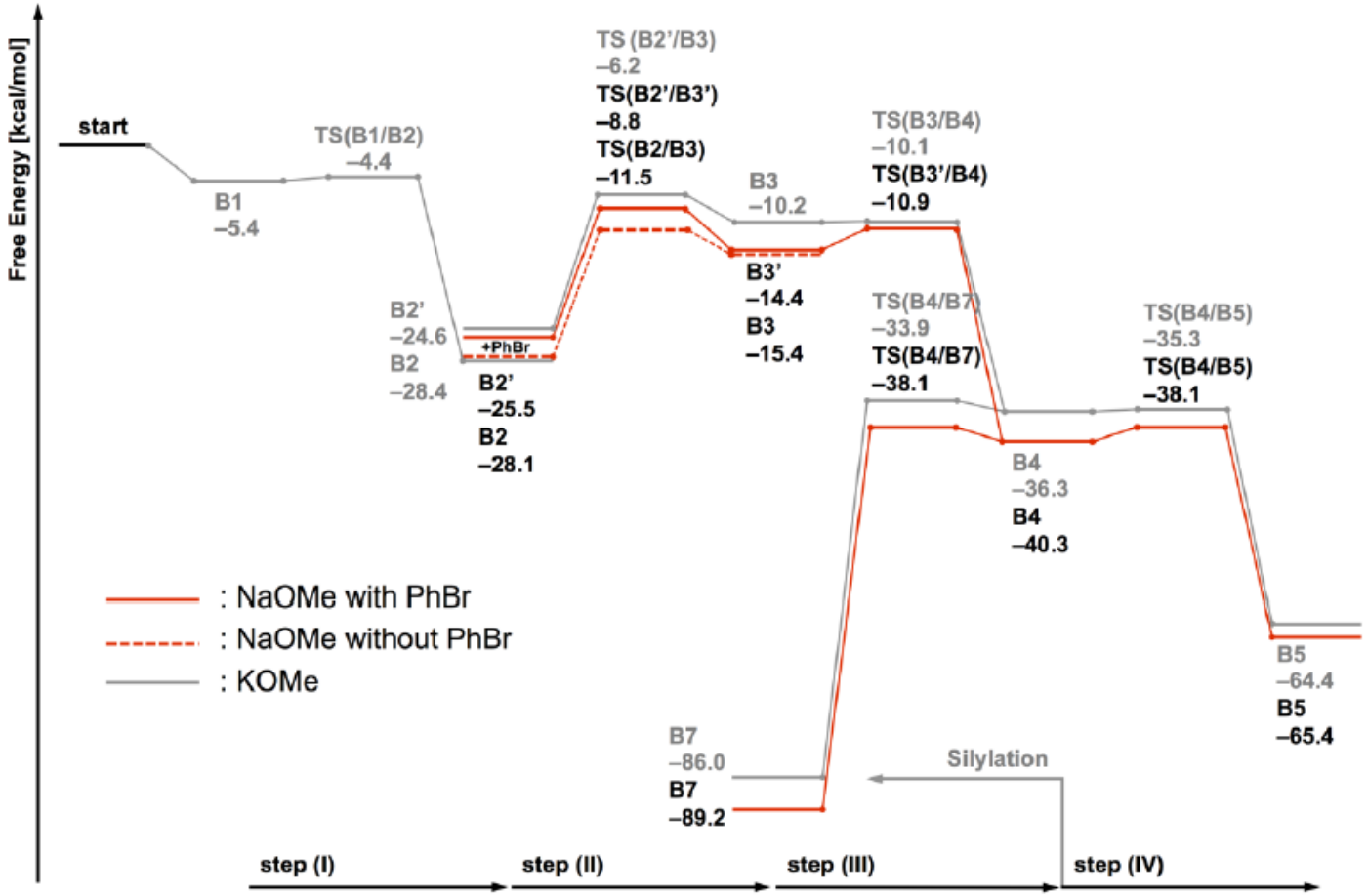

Figure S5-3-2. Reaction Pathways Leading to the B/Si Products with NaOMe

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Appendix

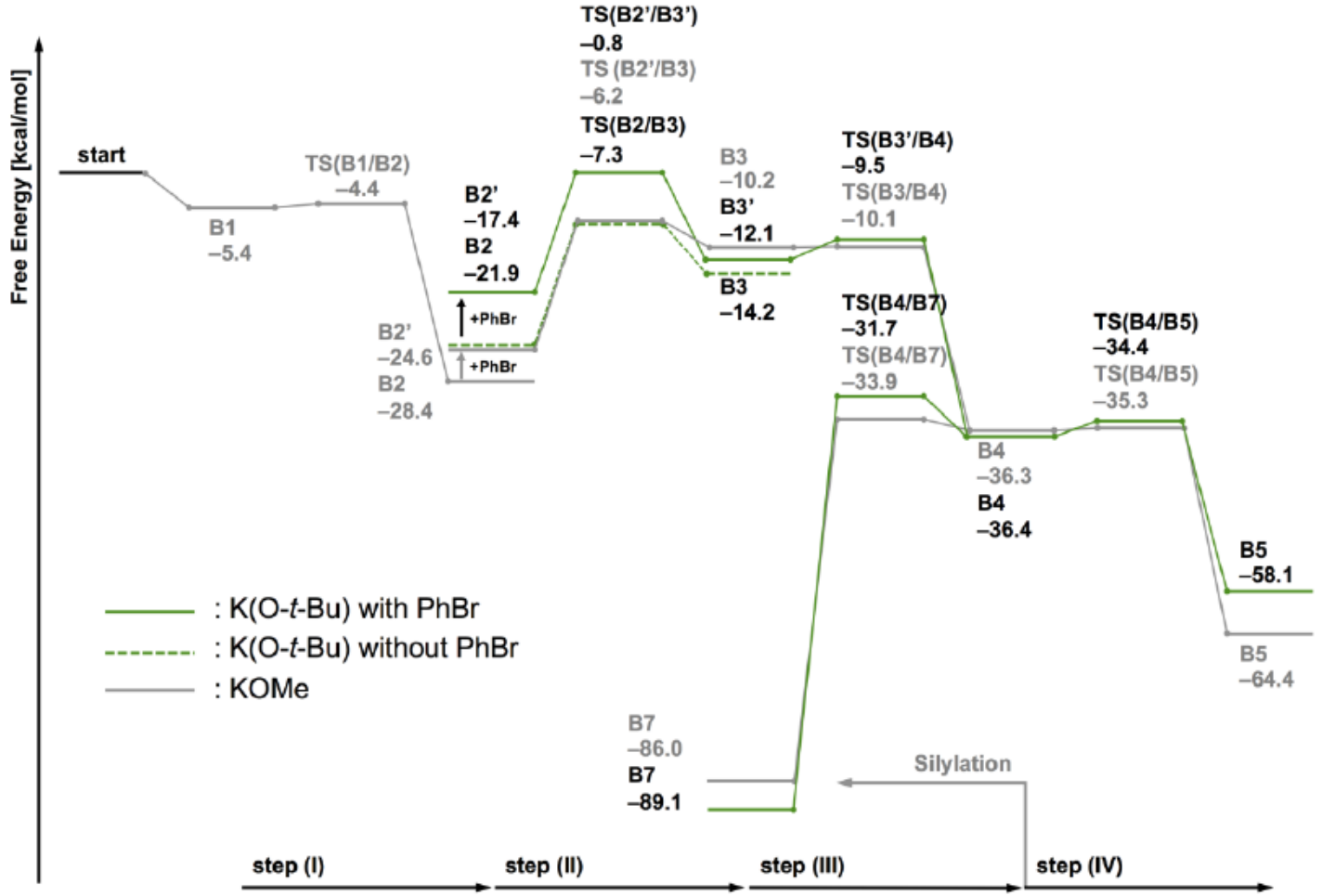

Figure S5-3-3. Reaction Pathways Leading to the B/Si Products with K(O-*t*-Bu)

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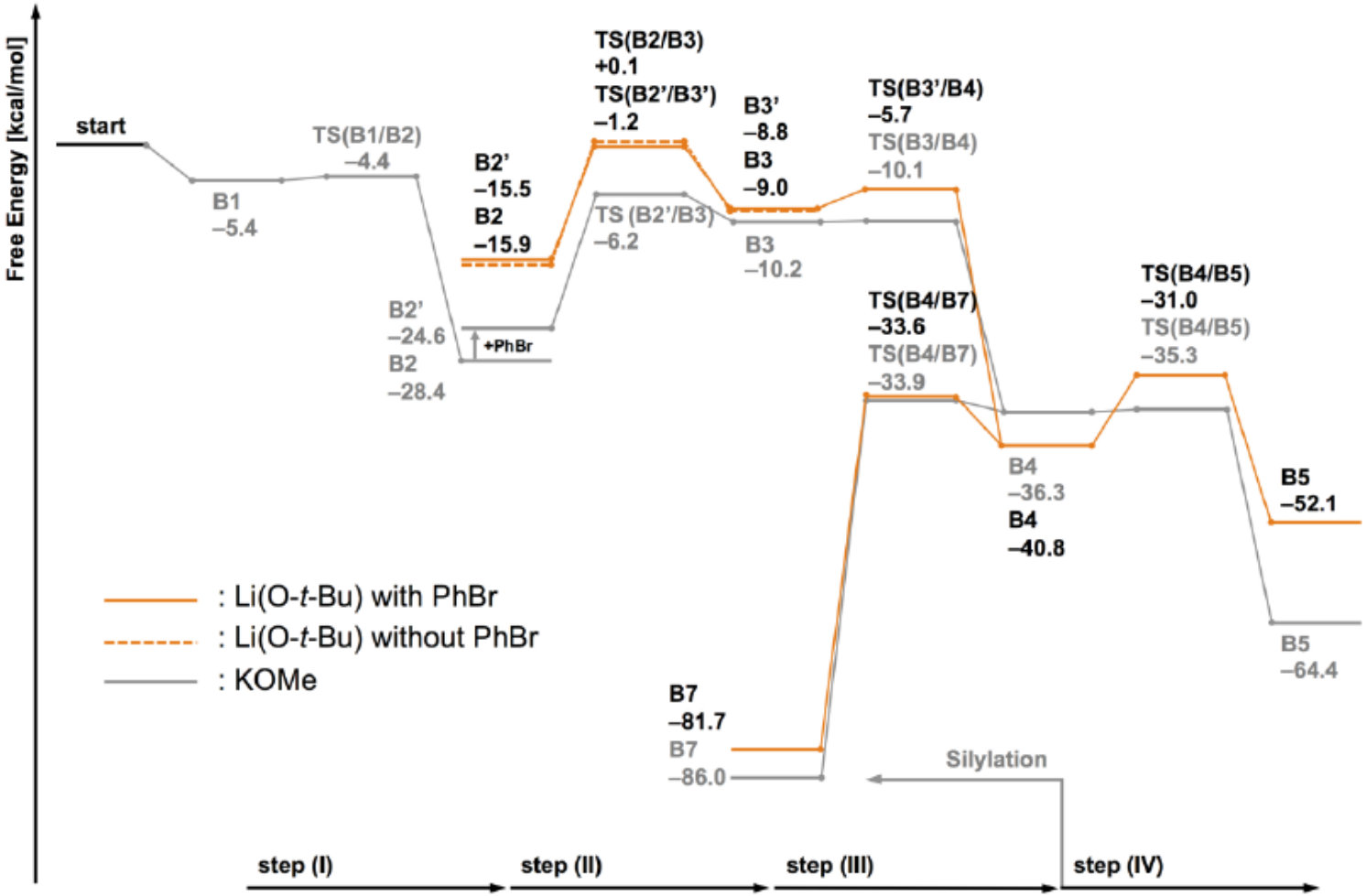

Figure S5-3-4. Reaction Pathways Leading to the B/Si Products with Li(O-*t*-Bu)

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Appendix

S5-4. Substitution Effect (R = *p*-F–C_6H_4– and *p*-MeO–C_6H_4–)

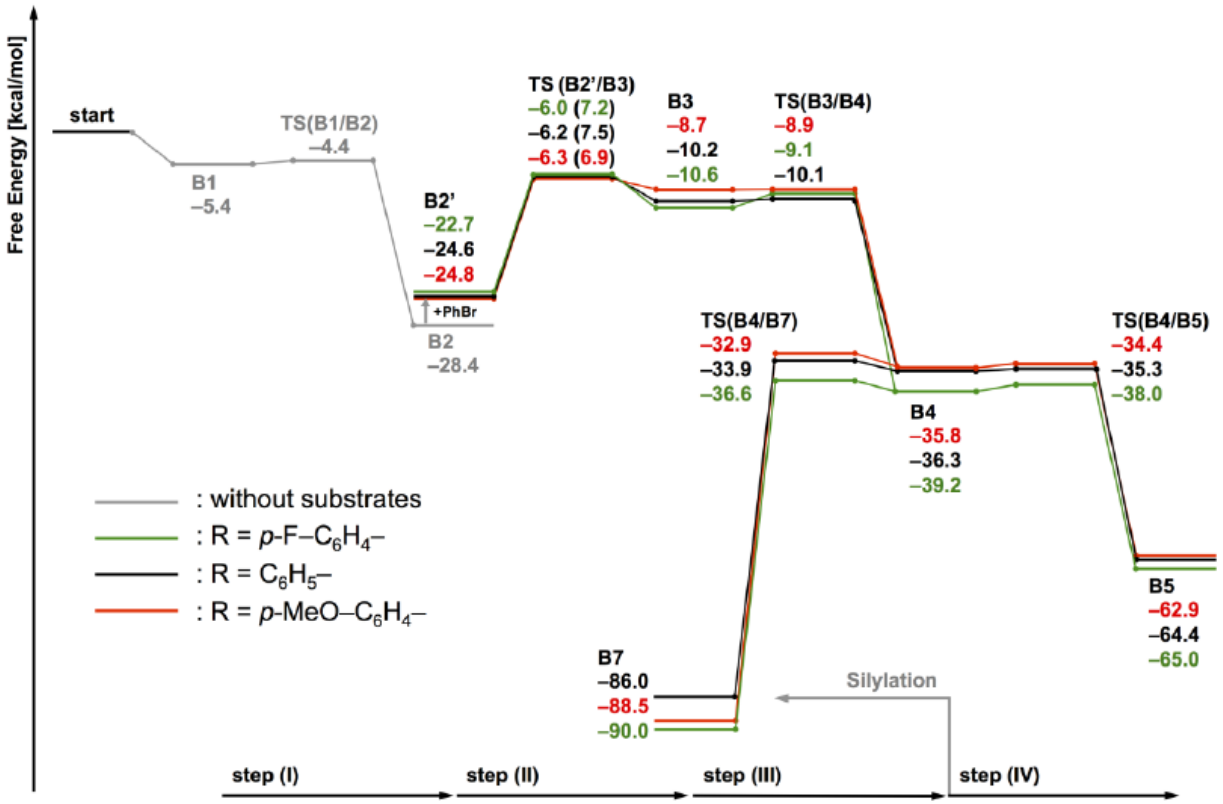

Figure S5-4. Reaction Pathways Leading to the B/Si Products with Different Substrates R–Br (R = *p*-FC_6H_4 and *p*-$MeOC_6H_4$)

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