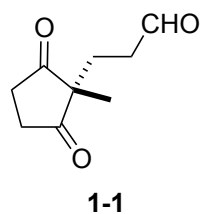
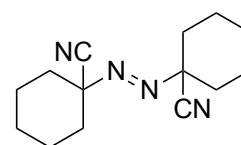
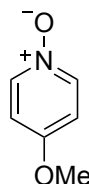
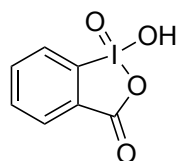
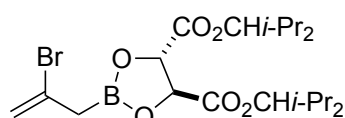
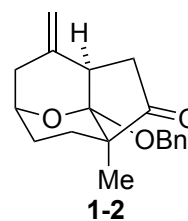


Problem 1

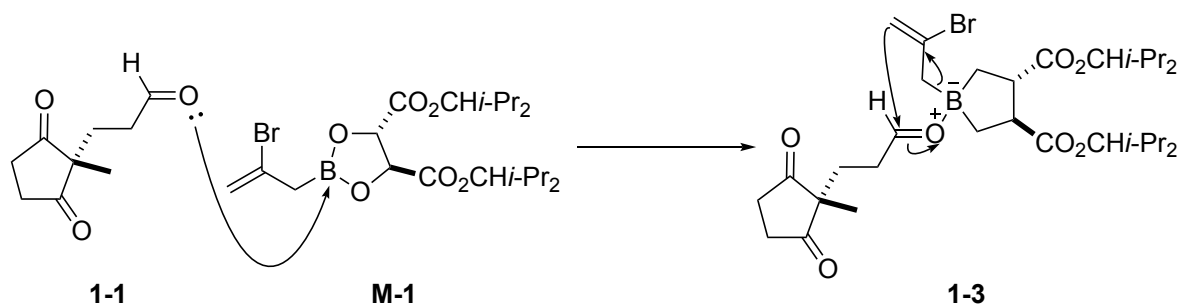


1. **M-1** (4.0 eq), MS 4A, toluene/pentane (3/1), -95 °C, 85% (80% ee)
2. BnOH (1.0 eq), MsOH (1.0 eq), MS 4A, CH₂Cl₂, 22 °C, 94%
3. TMSOTf (1.2 eq), Et₃N (1.5 eq), CH₂Cl₂, 0 °C
4. IBX (1.5 eq), MPO (1.5 eq), DMSO, 22 °C, 82% over 2 steps
5. (TMS)₃SiH (3.4 eq), V-40 (0.4 eq), toluene, 110 °C, 78%

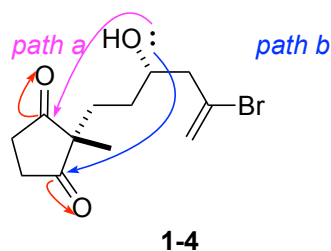


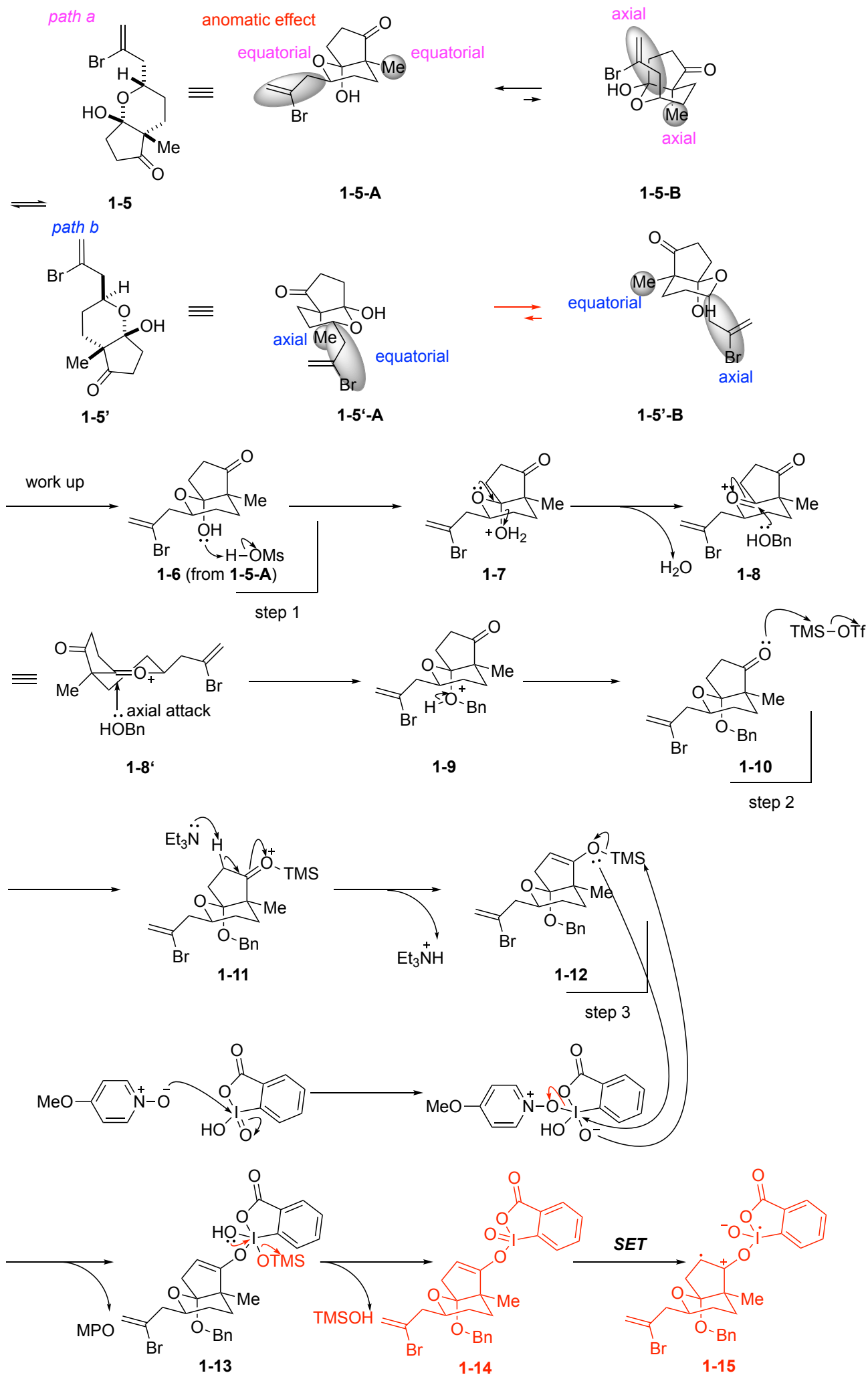
Lu, Z.; Zhang, X.; Guo, Z.; Chen, Y.; Mu, T.; Li, A. *J. Am. Chem. Soc.* **2018**, *140*, 9211.

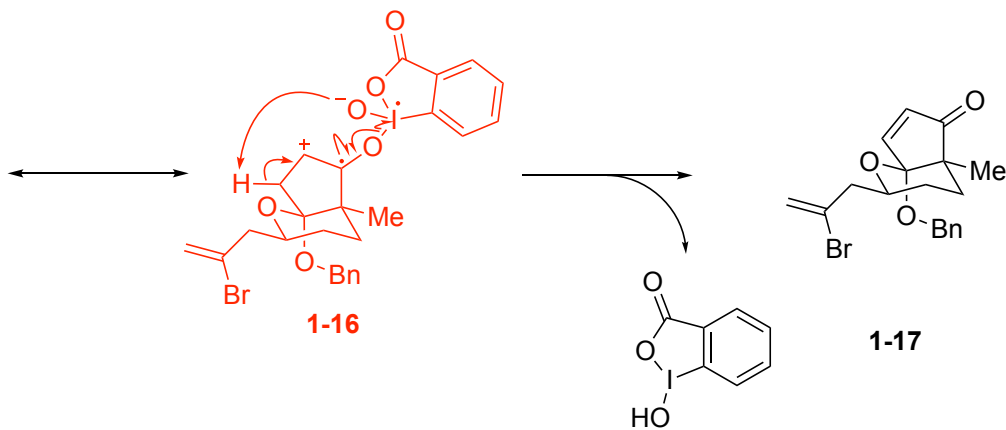
Answer 1



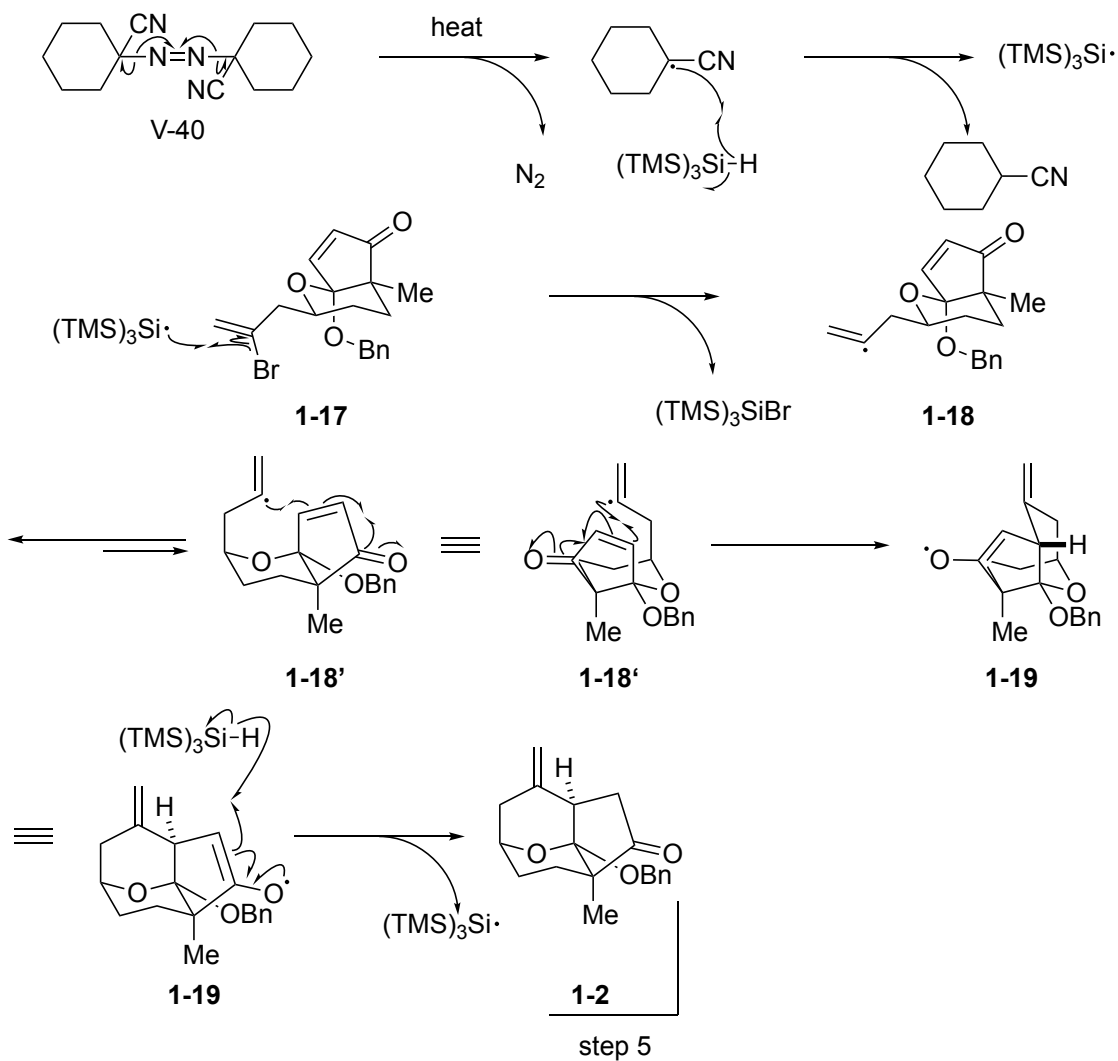
Discussion 1



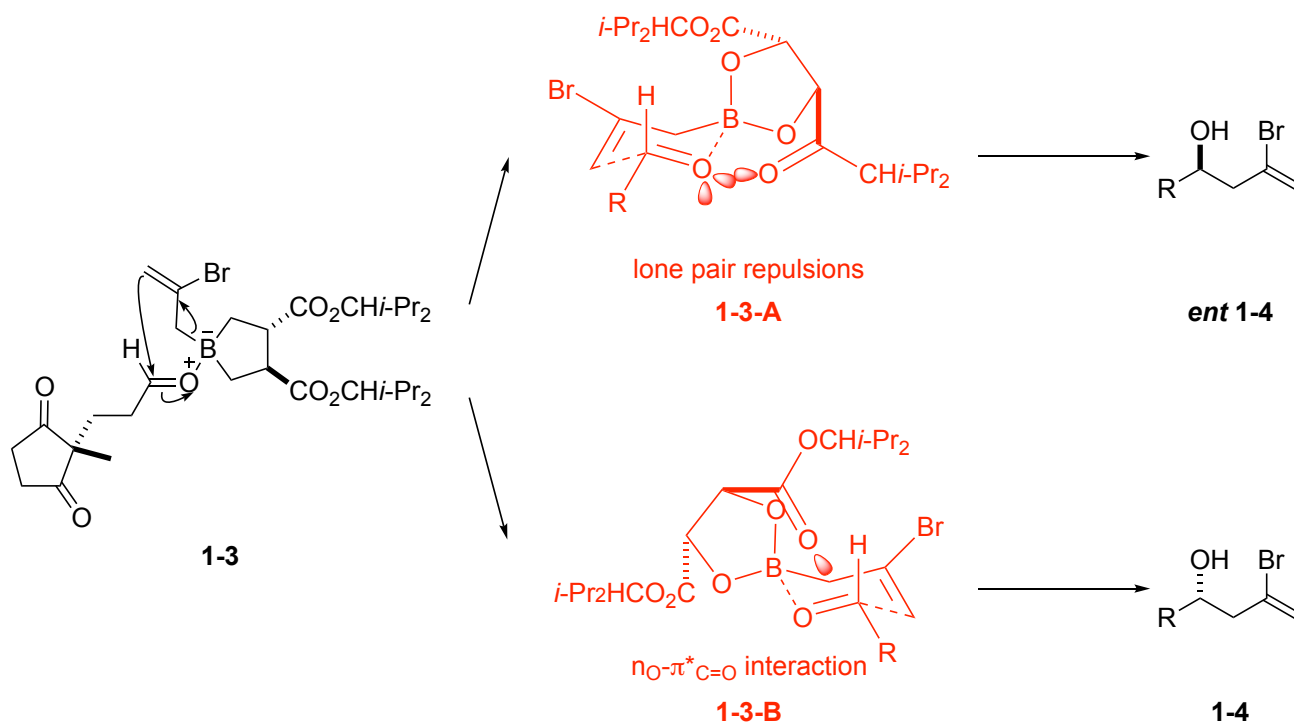




For proof of **SET** mechanism, please see appendix.



Discussion 1-1
Enantioselective Allylation



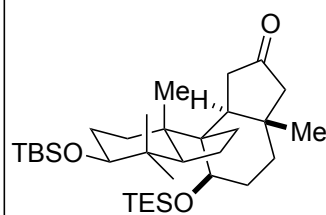
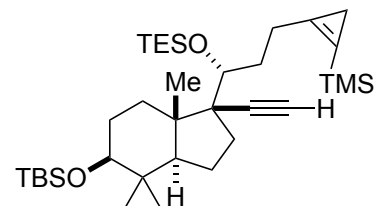
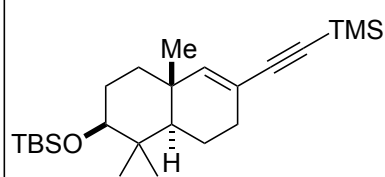
Repulsive n/n lone pair interaction make **1-3-A** unfavored, a stabilizing interaction between the ester carbonyl group and the aldehyde carbonyl carbon make **1-3-B** favored.

For more details, please see:

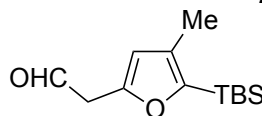
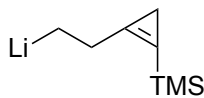
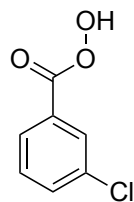
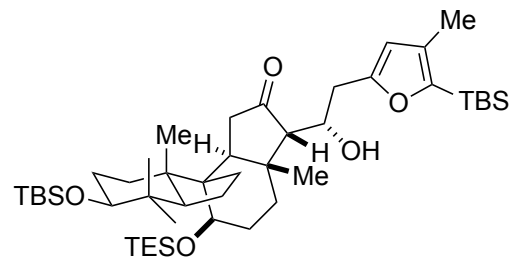
Gung, B. W.; Xue, X.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, *124*, 10692.

Problem 2

1. *m*-CPBA (2.0 eq), CH₂Cl₂, -30 °C to 0 °C
2. BF₃·Et₂O (0.05 eq), CH₂Cl₂, 0 °C, 65% over 2 steps
3. CeCl₃ (1.3 eq), **M-2** (1.3 eq), THF, -98 °C to -60 °C, 75%
4. TESOTf (1.2 eq), Et₃N (3.0 eq), CH₂Cl₂, -78 °C to 0 °C; K₂CO₃ (10.0 eq), MeOH, rt, 98%

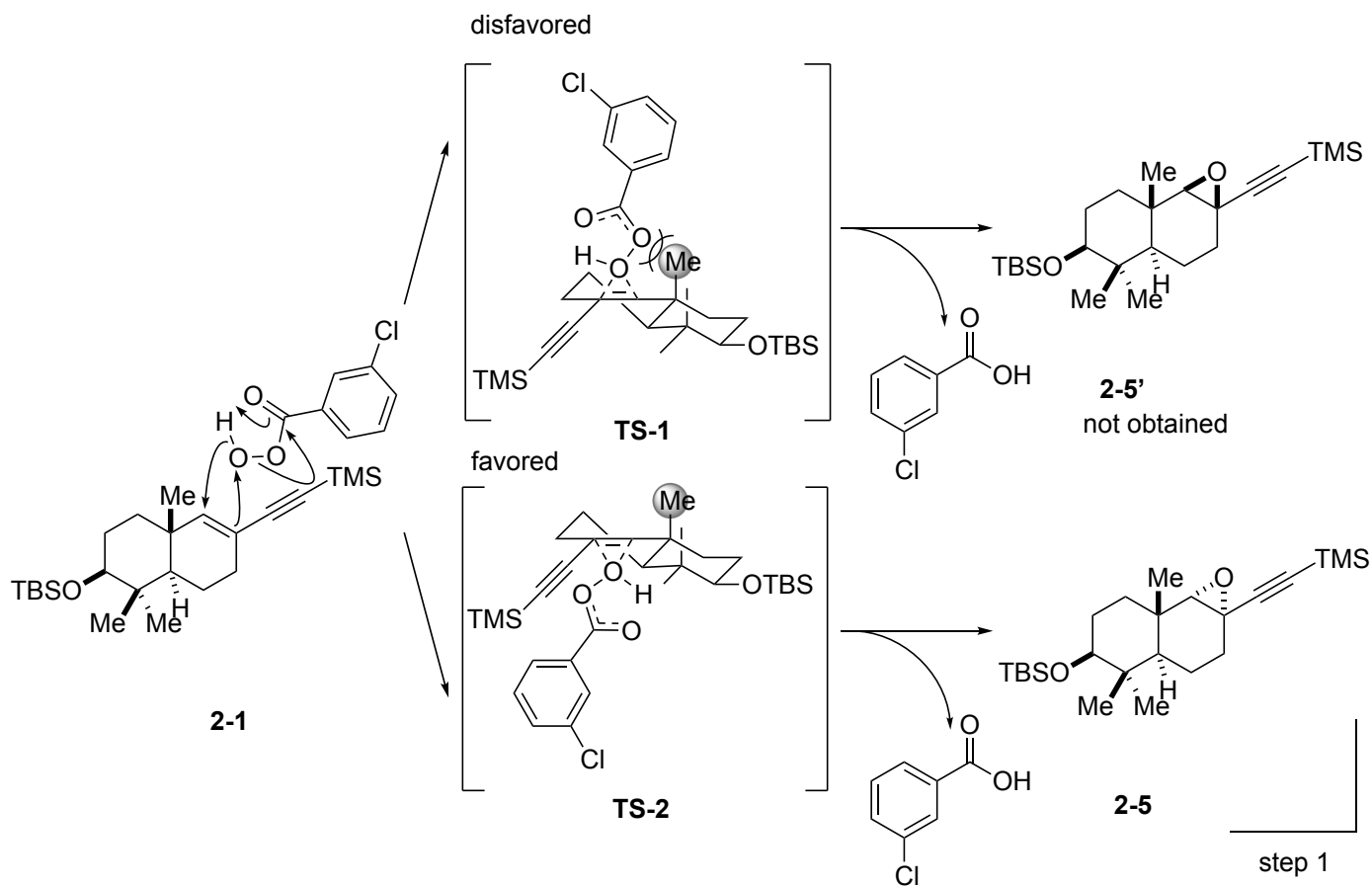


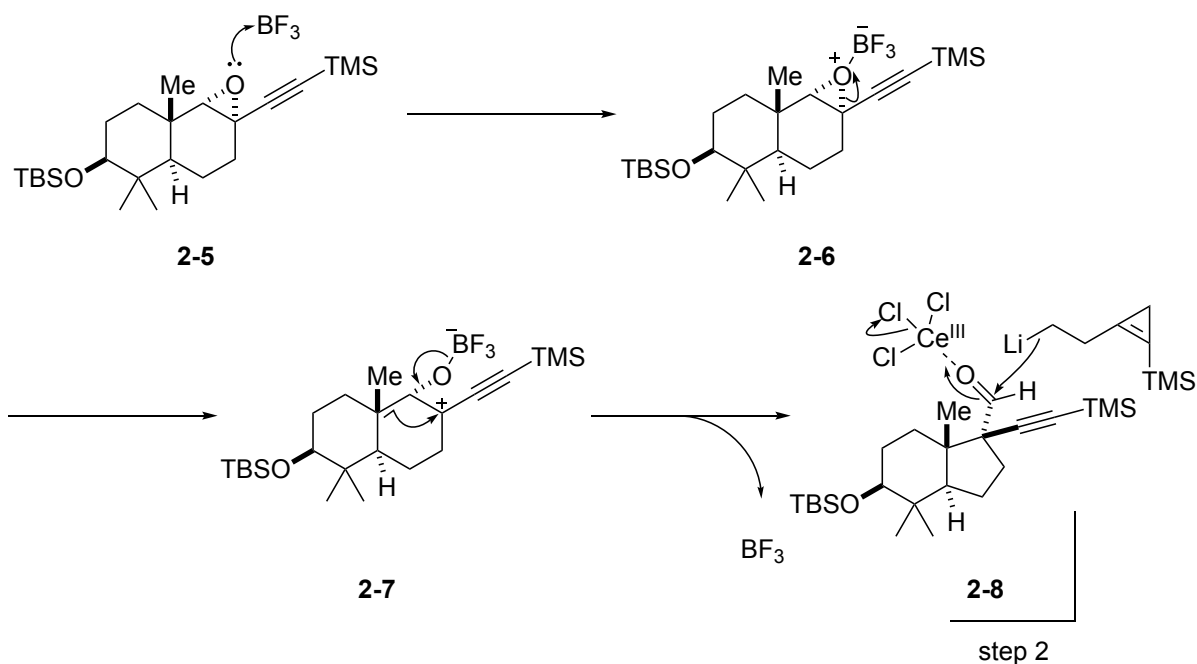
5. *n*-Bu₂BOTf (2.0 eq), *i*-Pr₂NEt (2.5 eq), CH₂Cl₂, -78 °C; then **M-3** (4.0 eq), -78 °C to -50 °C, 97%



Liang, X. T.; Chen, J. H.; Yang, Z. *J. Am. Chem. Soc.* **2020**, *142*, 8116.

Answer 2



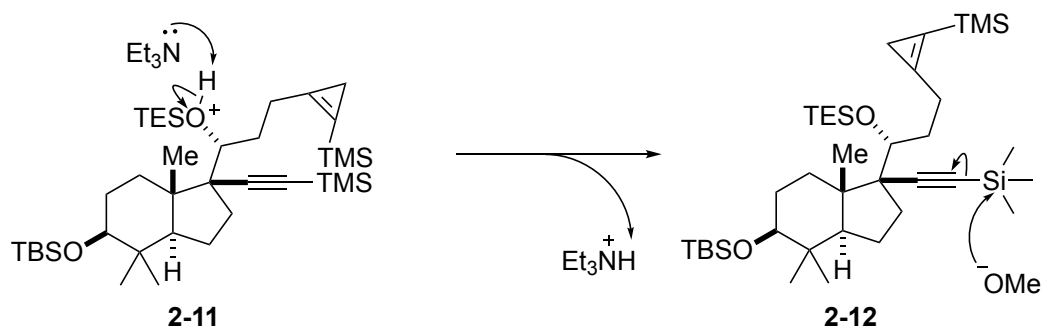
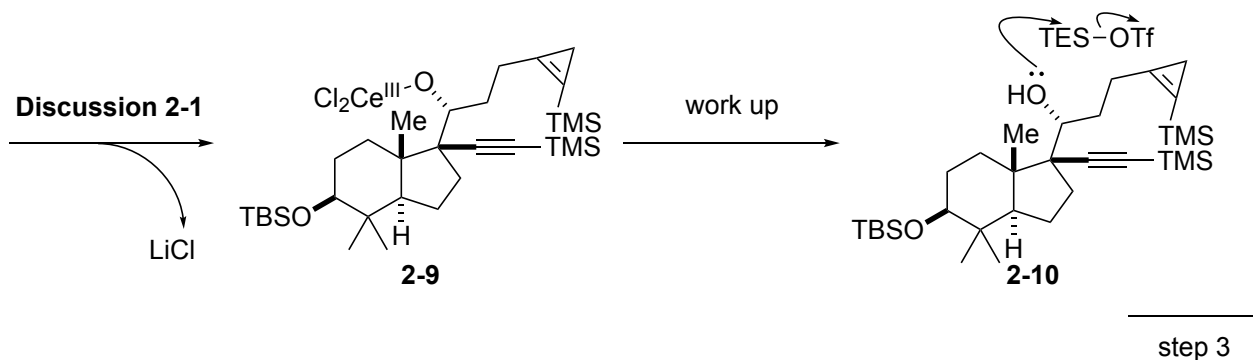


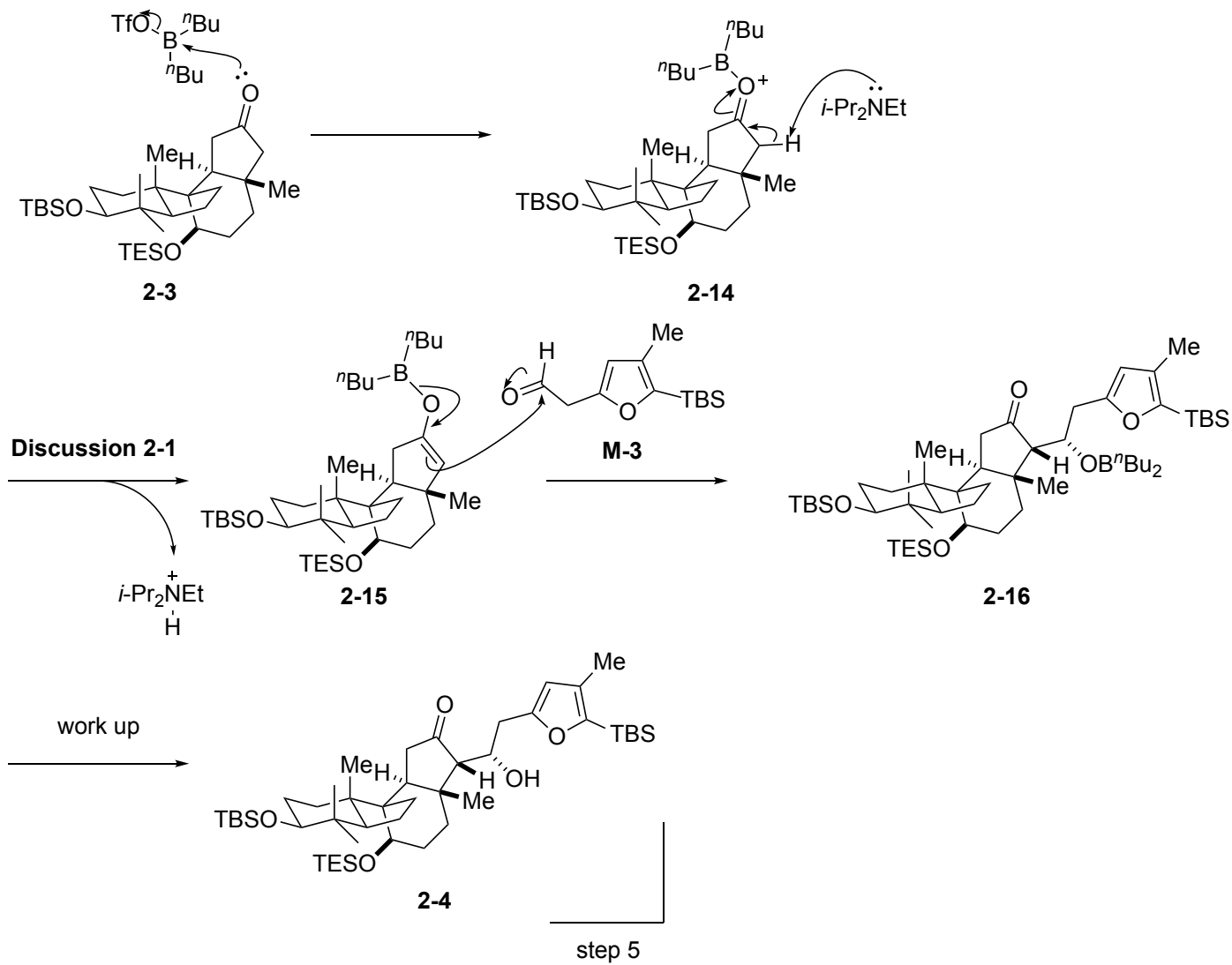
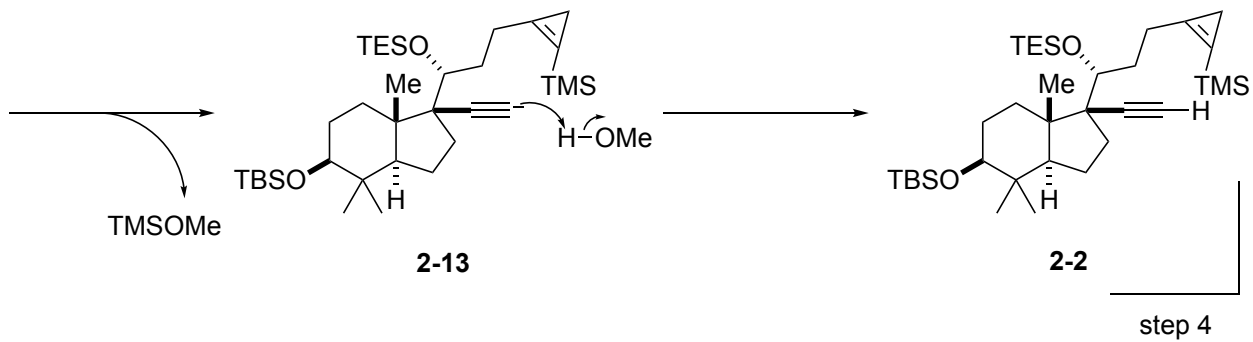
The rearrangement is through S_N1 , the oxygen is activated, then the carbon-oxygen bond begins to break and positive charge begins to build up on the more substituted carbon.

Through S_N1 , the orbital of migration part (C-C migration) is parallel to the plane of carbocation so the rearrangement is easy to conduct.

Through S_N1 , the oxygen is more electron rich so it is more willing to donate electrons to continue the rearrangement.

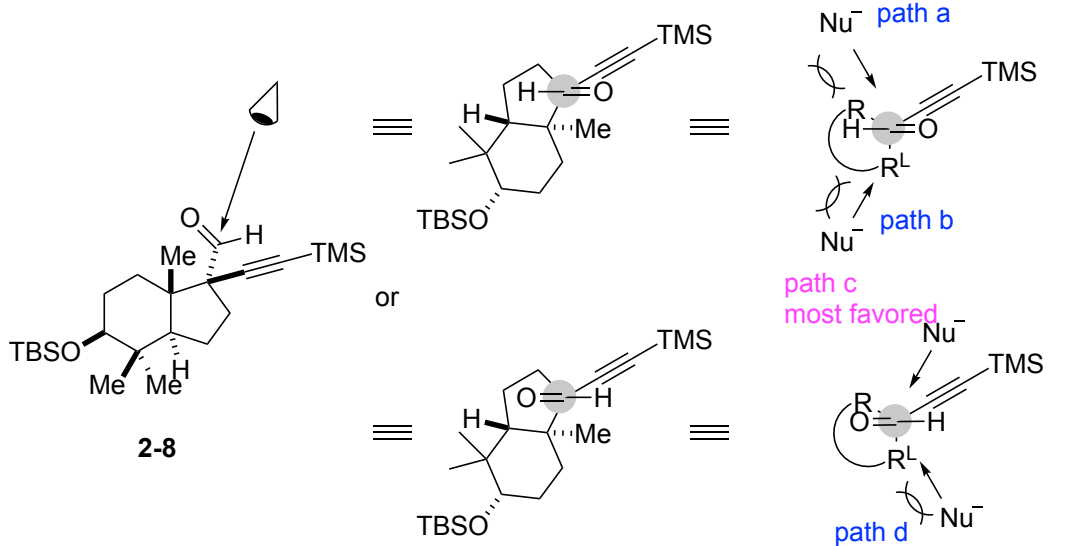
Reason of C-C migration instead of C-H migration: the orbital of C-C orbital is parallel to the plane of carbocation while the C-H orbital is perpendicular to the carbocation so the C-C is more willing to migrate.



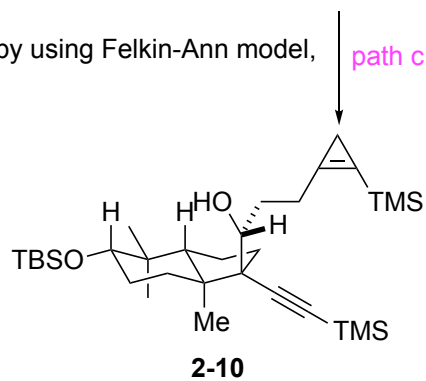


Discussion 2-1

Diastereoselective formation of **2-10**

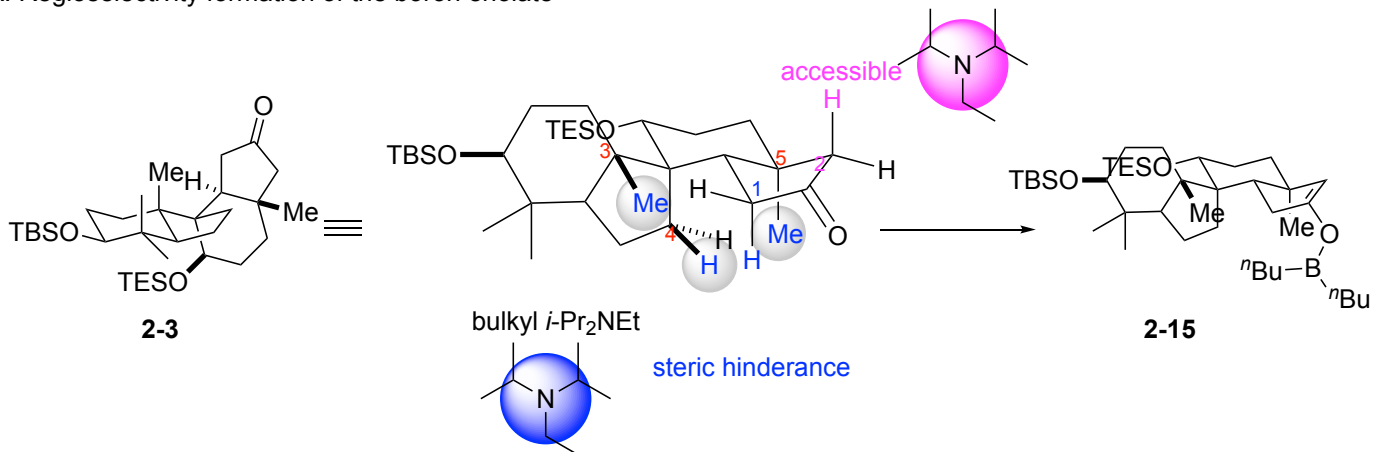


Diastereoselective formation of **2-10** can be explained by using Felkin-Anh model, only path c bearing the least steric hindrance.



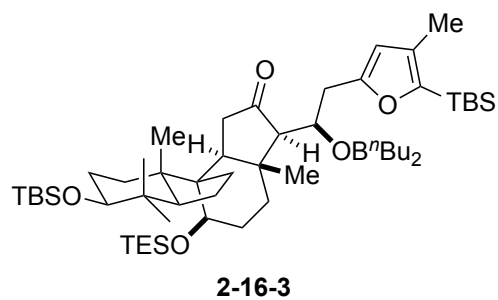
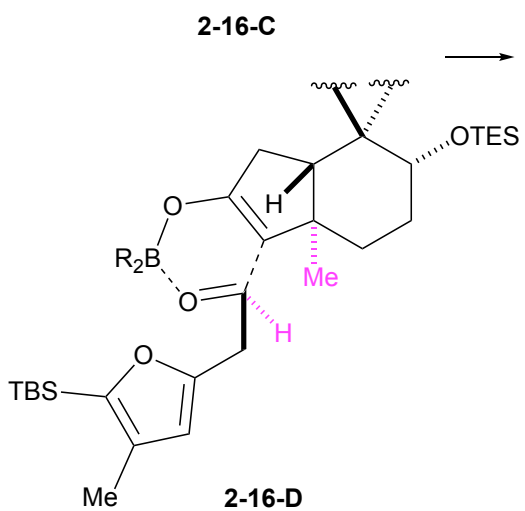
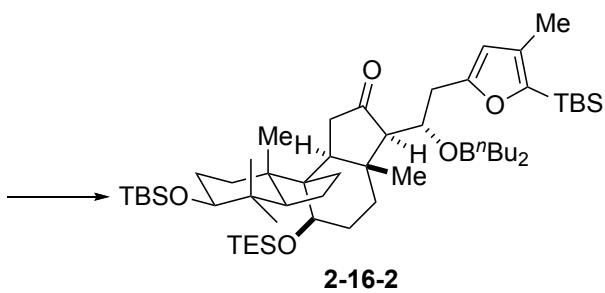
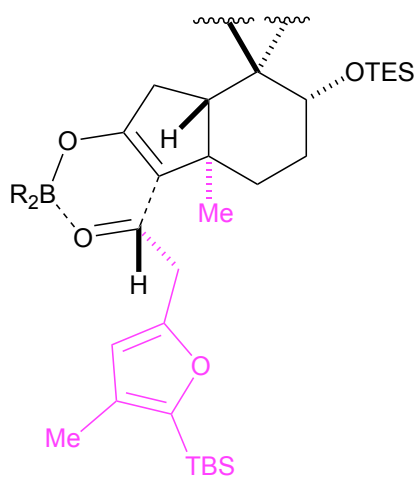
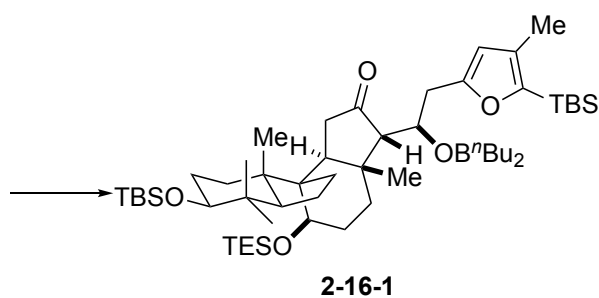
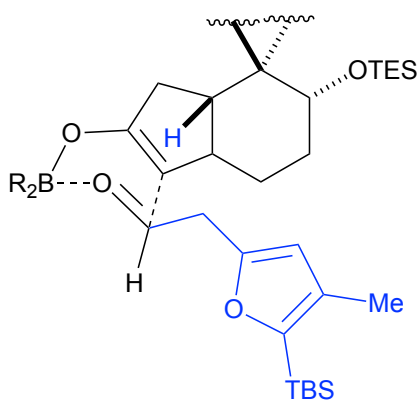
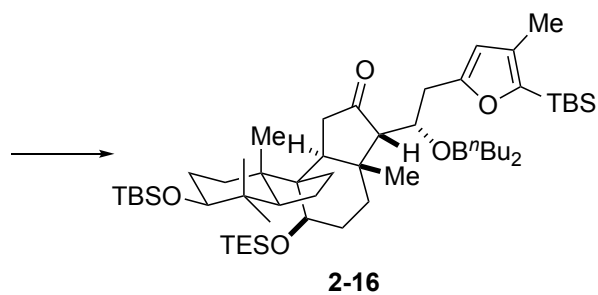
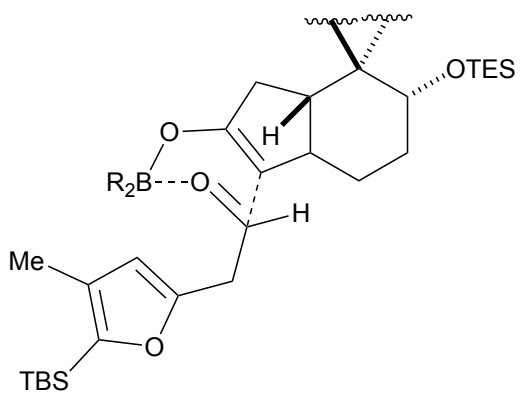
Discussion 2-2

A. Regioselectivity formation of the boron enolate



Regioselective formation of the boron enolate may be due to bulky $i\text{-Pr}_2\text{NEt}$ and steric hindrance experienced by C1 hydrogen atoms from the C3 and C5 methyl groups and C4 hydrogen atom, while C2 hydrogen atom is accessible.

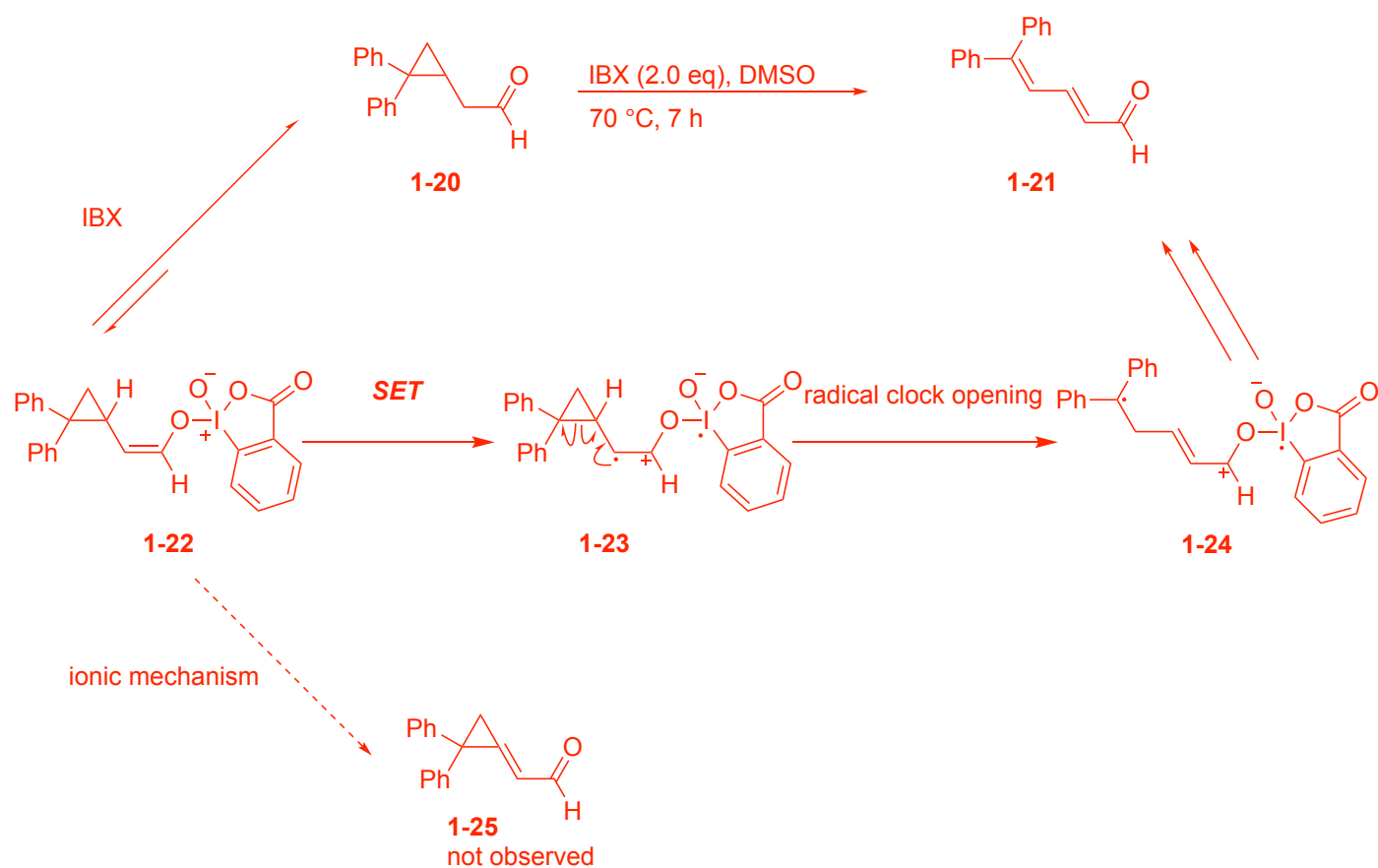
B. Diastereoselective formation of 2-16



Appendix:

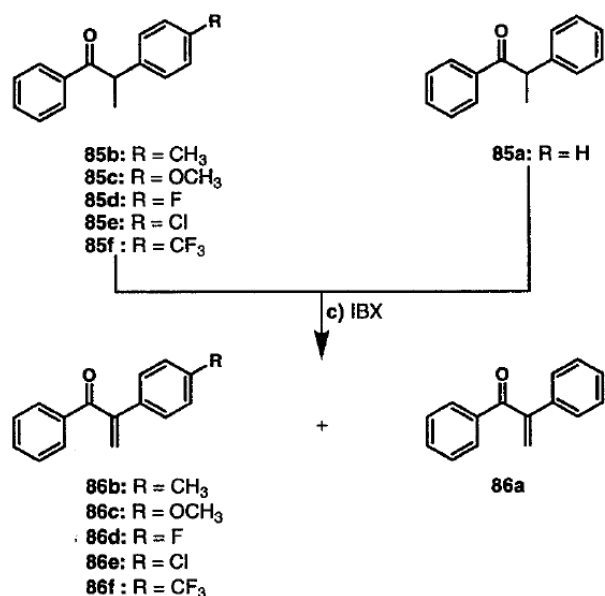
Proof of SET mechanism

1. Mechanistic probe



The authors sought evidence for the intermediacy of a radical species by using the well-established fragmentation of cyclopropyl methyl radicals. It has been shown that the rate constant for the opening of 2,2-diphenylcyclopropylmethyl radicals is significantly larger than that of the unsubstituted cyclopropyl methyl radical thus permitting a much more unequivocal assessment of the presence or absence of a radical, when its fragmentation is used as a mechanistic probe. The opening of the cyclopropyl ring was taken to provide strong support for a single electron-transfer mechanism for this process.

2. Hammett analysis



(c) IBX (2.5 equiv), *p*-TsOH (0.3 equiv), DMSO, 85 °C, 22h

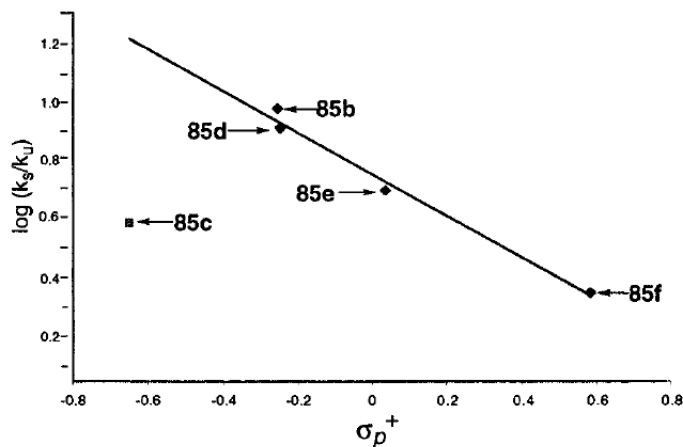


Figure 4. Plot derived using Hammett analysis of the competition reactions of substituted α -aryl ketones (**85b–f**) with ketone (**85a**). The gradient (ρ) = -0.75 and regression analysis give a value $R^2 = 0.99$.

k_u : rate constant of reaction **85a** \rightarrow **86a**; k_s : rate constants for reactions **85b–f** \rightarrow **86b–f**.

σ_+ : substituent constant (how the substituent is electron-withdrawing or -donating)

positive \rightarrow EWG negative \rightarrow EDG

ρ : reaction constant

negative ρ value: TS of rate determining step has lower electron density relative to the initial ground state

The methoxy-substituted ketone **85c** coordinates at the iodine center via the lone pair of electrons on the ethereal oxygen thus distorting the reaction progress and leading to a unique set of kinetic data for this compound.

The remaining data are strongly suggestive of a **SET** pathway. The magnitude of ρ is small, indicating only a slight dependence in this reaction on the polarizing influence of the aromatic substituents appended to the α carbon. This is consistent with a transition state bearing a radical cation and not a true oxonium ion at the center α to the carbonyl. The negative sign of ρ leads to the inference that the transition state is electron deficient when compared to the ground state which again is in accord with the proposed radical cation species.

For more details, please see:

Nicolaou, K. C.; Montagnon, T.; Baran, P. S.; Zhong, Y. L. *J. Am. Chem. Soc.* **2002**, *124*, 2245.