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High-Valent Palladium-Promoted Formal Wagner–Meerwein Rearrangement

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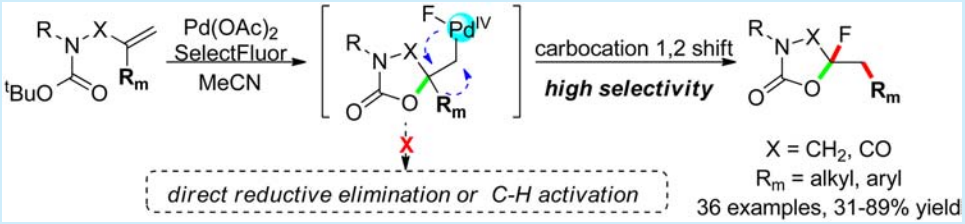
Supporting Information

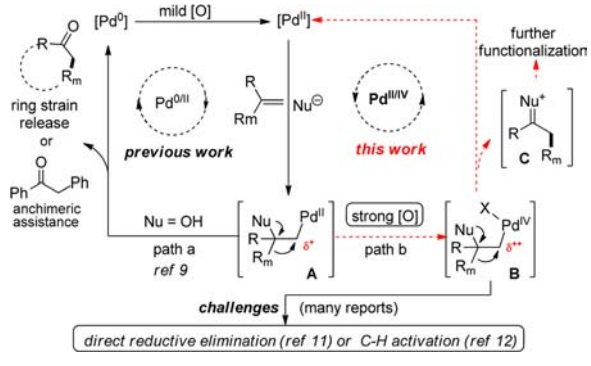


ABSTRACT: An oxy-palladation, formal Wagner–Meerwein rearrangement and fluorination cascade has been established for generating fluorinated oxazolidine-2,4-diones and oxazolidin-2-ones. The reaction has a broad substrate scope in which both aryl and alkyl groups can be utilized as efficient migrating groups. Experimental evidence suggests that the reaction is initiated by *anti*-oxy-palladation of the olefin, followed by oxidative generation of an alkyl Pd^{IV} intermediate and a concerted migration–fluorination.

The Wacker process, reported in 1959, inspired an era of research in palladium catalysis which demonstrated the powerful utility of Pd^0/Pd^{II} catalysis in organometallic chemistry.[1] In the past decade, processes mediated by high-valent palladium[2] have emerged as flexible protocols that complement the traditional low-valent reactions. Benefiting from the fundamental studies on high-valent palladium complexes, the enhanced reductive elimination[3,4] and inhibited β-elimination features[5] are now well understood and have been widely applied to a number of challenging reactions, such as the formation of C–halogen (heavy),[6] C–F,[7] and C–CF_3[8] bonds.

A survey of the literature on palladium chemistry reveals an interesting variation of the Wacker process, the Pd^0/Pd^{II} cycle (Scheme 1).[9] For the olefin substrate containing a strained ring, the Wacker intermediate **A** undergoes a 1,2-migration process to produce ring-expanded ketone product in good yield. Also, in an isolated case, 1,1-diphenylethylene undergoes a similar migration process benefiting from the anchimeric assistance to produce benzyl phenyl ketone in low yield.[9,10] No further study on this topic has been subsequently reported probably due to the intrinsic limitation of Pd^0/Pd^{II} catalytic efficiency.

Scheme 1. Formal Wagner–Meerwein Rearrangement in Wacker–Tsuji Oxidation



We speculated that under strong oxidative conditions (Pd^{II}/Pd^{IV} cycle, Scheme 1) the Wacker intermediate **A** could be converted to the Pd^{IV} intermediate **B**. The enhanced positive charge at the α-carbon to palladium would facilitate the Wagner–Meerwein-type migration process and allow more efficient migration of versatile R_m groups without the additional driving force gained by releasing strained rings or anchimeric assistance. The challenges lie in the competition with the facile reductive elimination pathway of the Pd^{IV} complex, which has been demonstrated frequently in olefin difunctionalization reactions[11] and the potential C–H activation pathways involving Pd^{IV} intermediates.[12]

To our delight, compound **1a** with a phenyl ring as the migrating group did react as anticipated with $Pd(OAc)_2$ as catalyst and Selectfluor (**F-1**) as oxidant in acetonitrile (Table 1). Fluorination occurred following the migration, providing compound **2a** in 70% yield. The structure was confirmed unambigously by X-ray analysis. The direct C–F reductive elimination process was successfully suppressed to produce the regioisomer **2a′** in a **2a′**/**2a** ratio of 1/13 (entry 1). $PdCl_2$, $Pd(OTFA)_2$, or $Pd(OPiv)_2$ provided either diminished yield or poor selectivity (entries 2–4). Neither **2a** nor **2a′** is observed in the absence

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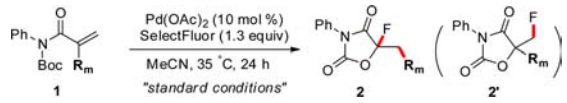
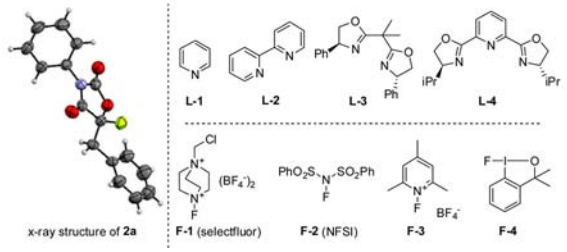
Table 1. Selected Results of Condition Optimization



entry	1	R_m	variation from "standard conditions" [a]	yield/% (2/2')[b]
1	1a	Ph	none	70[c] (13:1)
2	1a	Ph	$PdCl_2$ instead of $Pd(OAc)_2$	61 (13:1)
3	1a	Ph	$Pd(OTFA)_2$ instead of $Pd(OAc)_2$	67 (11:1)
4	1a	Ph	$Pd(OPiv)_2$ instead of $Pd(OAc)_2$	60 (6:1)
5	1a	Ph	without $Pd(OAc)_2$	n.d.[d]
6	1a	Ph	with 1 equiv $Pd(OAc)_2$, without Selectfluor	n.d.[d]
7	1a	Ph	with 10 mol % ligand[e]	trace[d]
8	1a	Ph	other oxidants[f, g] instead of Selectfluor	trace[d]
9	1a	Ph	other solvents[h] instead of MeCN	n.d.[d]
10	1b	Me	none	78[c] (>20:1)

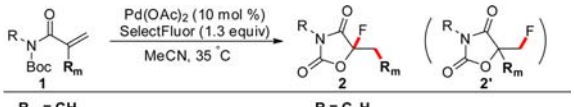


[a]Standard conditions: substrate **1** (0.1 mmol), $Pd(OAc)_2$ (10 mol %), Selectfluor (1.3 equiv), MeCN (2 mL), 35 °C, 24 h. [b]NMR yield with *N,N*′-dimethylacetamide as internal standard; ratio of **2**:**2**′ is given in parentheses. [c]Isolated yield of compound **2**. [d]Starting material **1a** was recovered. [e]**L-1**, **L-2**, **L-3**, and **L-4** were screened. [f]**F-2**, **F-3**, and **F-4** were screened. [g]A combination of 1 equiv of $PhI(OAc)_2$ and 1 equiv of AgF (or CsF) was screened. [h]DCM, water, EtOH, EtOAc, $MeNO_2$, and DMF were screened.

of the Pd catalyst (entry 5). A control experiment with a stoichiometric quantity of the Pd catalyst and no oxidant resulted in almost no reaction apart from slight decomposition of the Boc group (entry 6). It indicates that a Pd^0/Pd^{II} catalytic cycle is unlikely to work. Common N-σ-donor ligands such as pyridine and oxazoline derivatives basically inhibit the reaction (entry 7). When the oxidant is changed from Selectfluor to NFSI (**F-2**), a fluoropyridinium reagent (**F-3**), an iodonium reagent (**F-4**), or $PhI(OAc)_2$ with fluorine anion produced only a trace amount of product **2a** (entry 8). Solvent screening showed that acetonitrile was the only solvent that could efficiently facilitate this reaction (entry 9). Surprisingly, we found that a methyl group, which cannot participate in anchimeric assistance, can migrate in the reaction to produce the target product with even higher yield (78% yield, entry 10).

Encouraged by these results, we sought to investigate the scope of substrates. As shown in Scheme 2, variously substituted phenyl groups on nitrogen were examined (**2b**–**l**). Both electron-donating and -withdrawing groups were well tolerated, giving good to high yields. A wide range of functional groups were compatible with this reaction, such as halogens (**2f**,**g**,**j**), an ester (**2k**), and a nitro group (**2l**). Interestingly, bulky substituents at the *ortho* position of the phenyl ring resulted in limited rotation of the aryl C–N bond, which led to the axial chirality. Diastereomers were observed for substrates with *o*-ethyl (**2c**), *o*-methoxyl (**2d**), and *o*-*tert*-butyl (**2e**) groups on the phenyl ring. In addition to the aryl groups, alkyl groups (**2m**,**n**)

Scheme 2. Substrate Scope of Activated Olefin[a]



$R_m = CH_3$	yield/%[b] (2 : 2')
2b R = C_6H_5	78 (>20:1)
2c R = 2-EtC_6H_4	80[c] (>20:1)
2d R = 2-OMeC_6H_4	71[d] (>20:1)
2e R = 2-^{t}BuC_6H_4	89[e] (>20:1)
2f R = 2-FC_6H_4	77 (>20:1)
2g R = 3-BrC_6H_4	78 (>20:1)
2h R = 4-MeC_6H_4	80 (>20:1)
2i R = 4-OMeC_6H_4	69 (>20:1)
2j R = 4-ClC_6H_4	76 (>20:1)
2k R = 4-COOMeC_6H_4	77 (>20:1)
2l R = 4-$NO_2C_6H_4$	74 (>20:1)
2m R= Bn	76 (>20:1)
2n R = cyclopentyl	67 (>20:1)

$R = C_6H_5$	yield/%[b] (2 : 2')
2o R_m = Et	63 (>20:1)
2p[f] R_m = ^{i}Pr	22 (17:1)
2q R_m = Bn	67 (>20:1)
2r R_m = C_8H_{17}	57 (>20:1)
2s R_m = cyclopropylCH$_2$	63 (>20:1)
2a R_m = Ph	70 (13:1)
R = 4-ClC_6H_4	yield/%[b] (2 : 2')
2t R_m = 3,5-di-MeC_6H_3	56 (5.6:1)
2u R_m = 4-OMeC_6H_4	12 (1:2.4)
2v R_m = 3-MeC_6H_4	54 (6.7:1)
2w[f] R_m = 4-FC_6H_4	58 (8.3:1)
2x[f] R_m = 4-COOEtC_6H_4	62 (13:1)
2y[f] R_m = 4-CHOC_6H_4	52 (13:1)

[a]Reaction conditions: substrate **1** (0.1 mmol), $Pd(OAc)_2$ (10 mol %), Selectfluor (1.3 equiv), MeCN (2 mL), 35 °C, 24 h. [b]Isolated yield of **2**, ratio of **2**:**2**′ given in parentheses as determined by ^{19}FNMR or ^{1}HNMR analysis of the crude products. des-Boc product and polymerization product were responsible for the low yield. [c]Diastereomeric ratio 50/50. [d]Diastereomeric ratio 65/35. [e]Diastereomeric ratio 79/21. [f]Reaction was conducted at 50 °C.

also performed well in this process. The scope of migrating group R_m was also investigated (Scheme 2). Encouragingly, ethyl (**2o**), benzyl (**2q**), octyl (**2r**), and even cyclopropylmethylene (**2s**) groups all migrate efficiently, producing the isomeric difunctionalized products. But the bulkier ^{i}Pr migrating group gave a significantly lower yield (**2p**). Aryl migrating groups were also examined (**2a**,**t**–**y**) and led to considerably reduced yields resulting from formation of byproduct **2**′. This pathway was attributed not only to the direct C–F reductive elimination but also to the regioselectivity associated with the nucleophilic opening of the phenonium intermediate,[13] showing the significant dependence on the electronic nature of the aryl migrating groups. Electron-donating substituents, such as methyl (**2t**,**v**), methoxyl (**2u**), and the π-electron-donating 4-fluoro (**2w**) group, gave diminished regioselectivity, while electron-withdrawing substituents, such as COOEt (**2x**) and CHO (**2y**) groups at the *para*-position, resulted in high regioselectivity. Instead of *tert*-butyl carbamates, isopropyl methacryloyl(phenyl)carbamate was used as the substrate, and the yield of **2b** dropped to 55%.

During the investigation, we found that compound **3a**, an unactivated olefin, was also compatible with this catalytic system to afford product **4a** in 58% yield with excellent regioselectivity with respect to **4a**′ (Scheme 3). This is particularly interesting because a background reaction exists without Pd catalyst, which leads to the formation of **4a**′ predominantly.[14] A brief investigation of substrate **3** was conducted (Scheme 3). A lower yield was obtained with 2-ethylphenyl substituents on nitrogen (**4b**). Phenyl rings with electron-withdrawing groups, such as 4-nitro (**4c**), 4-CN (**4d**), and perfluoro (**4e**) groups, all provided acceptable yields. Ts and Boc substituents were also tolerated well under the present catalytic system (**4f**,**g**). Further investigation showed that ethyl (**4h**) and benzyl (**4i**) groups are efficient migrating groups, affording the products in slightly lower yields. A phenyl migrating group led to poor regioselectivity due to the

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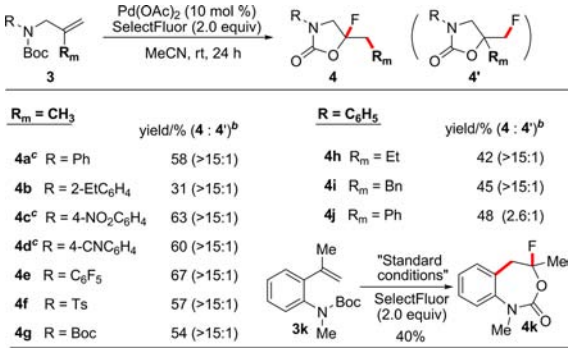
Scheme 3. Substrate Scope of Unactivated Olefin[a]

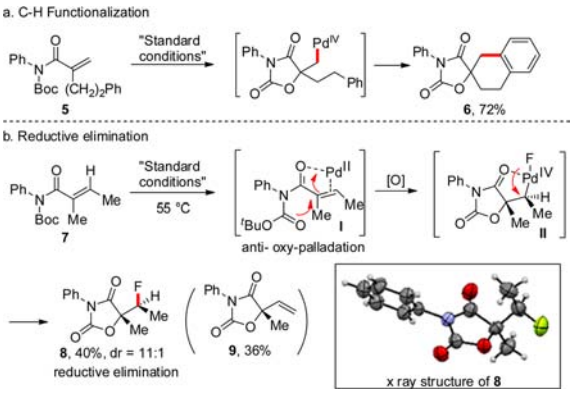


[a]Reaction conditions: substrate **3** (0.1 mmol), $Pd(OAc)_2$ (10 mol %), Selectfluor (2.0 equiv), MeCN (2 mL), rt, 24 h. [b]Isolated yield of **4**. Ratio of **4**:**4′** was given in parentheses and was determined by ^{19}F NMR analysis. des-Boc product and polymerization product were responsible for the low yield. [c]Reaction was conducted at 0 °C for 24 h then at rt for 24 h.

strong background reaction in the absence of Pd catalyst (**4j**).[14] In addition, when a homoallylic amine derivative, such as *tert*-butyl (3-methylbut-3-en-1-yl) phenylcarbamate, was used as substrate, no desired 6-membered cyclic product was observed. Substrate **3k**, containing an aryl ring and a methyl substituent, both of which are potential migrating groups, afforded compound **4k** as the major product.[15] Compound **4k′** was observed as the major byproduct, but no methyl migration product was detected. This result suggested that migration of the phenyl group is much more favorable than migration of the methyl group.[16] The lower yields observed for substrates with aryl migrating groups are probably due to side reactions.

The major reaction pathway varies with different substrates (Scheme 4). For example, the reaction with substrate **5** could

Scheme 4. Substrate-Controlled Reaction Pathways

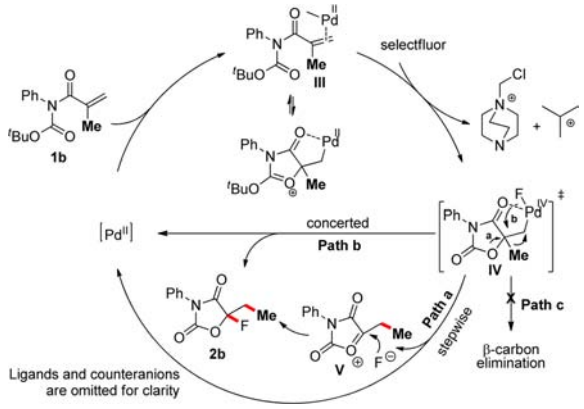


afford a spiro compound (**6**) via a C−H activation pathway (Scheme 4a).[17] With substrate **7**, a direct C−F reductive elimination product (**8**) (Scheme 4b) was isolated as the major product along with some β-hydrogen elimination byproduct (**9**). Both of these examples were rationalized in terms of the formation of a common Pd^{IV} intermediate. Kinetic issues are probably the reason for the different reaction pathways: for compound **5**, an intramolecular 6-membered-ring C−H activation is more likely to occur; for compound **7**, the positive charge stability and steric hindrance at α-carbon in intermediate **I** slow down the migration process leading to the direct reductive elimination product. The configuration of compound **8**, assigned unambiguously by X-ray structural analysis (see the Supporting Information (SI)), shows that an *anti*-oxy-palladation[18] followed by C−F bond-forming reductive elimination with retention of configuration is operating in the reaction.[19]

In order to reveal some details of the catalytic mechanism, CD_3 substituted compound **1b**-D_3 was prepared and examined, showing that the CD_3 group migrated. In addition, when competitive experiments of **1a** vs **1i** and **1a** vs **1v** were conducted, no scrambling was observed (Schemes S14 and S15).

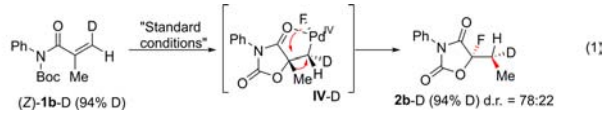
On the basis of these results, a working mechanism for the reaction is proposed in Scheme 5. First, coordination of the

Scheme 5. Proposed Mechanisms for the Isomeric Difunctionalization Reaction



substrate to the palladium catalyst generates a Pd^{II} complex (**III**).[20] Then oxy-palladation and oxidation probably occurred to generate a possible key Pd^{IV} intermediate (**IV**). The enhanced positive charge at the α-carbon to palladium may induce the Wagner−Meerwein rearrangement-type migration.[21] Trapping of the resulting intermediate (**V**) with a fluorine anion[22] produces the final product (**2b**) (path a). Alternatively, a concerted migration−fluorination process furnishing the catalytic cycle could also be envisaged (path b). Although the β-carbon elimination mechanism is thought to proceed in the Pd^0/Pd^{II} catalytic cycle, it is usually suppressed in Pd^{IV} complexes (path c).[5,23]

To probe the possibility of the existence of the two pathways (paths a and b) after the formation of intermediate **IV**, deuterated substrate (*Z*)-**1b**-D was prepared and subjected to the catalysis (eq 1). The resulting compound **2b**-D was observed



with a diastereomeric ratio of 78:22 and no H−D scrambling. It is very likely that both pathways are competing and the concerted process is dominant (path b). Otherwise, the alternative stepwise pathway (path a) via intermediate **V**-D would presumably result in a significant loss of stereochemical information from the complex **IV**-D. The configuration of the major diastereomer was determined by NMR analysis and is in accord with the structure assigned from mechanism analysis (see the SI).

In summary, an oxy-palladation and formal Wagner−Meerwein rearrangement cascade has been discovered and can be used for the construction of fluorinated oxazolidine-2,4-diones and oxazolidine-2-ones. Both aryl and alkyl groups were found to be capable of migration during the catalytic process. The reaction is

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proposed to occur through a Pd^{II}/Pd^{IV} catalytic cycle involving a concerted migration−fluorination process to furnish the final product. Further mechanistic research is in progress by our group to examine details of the reaction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02706.

Detailed experimental procedures and characterization data for all new compounds (PDF)
X-ray data for compound **2a** (CIF)
X-ray data for compound **8** (CIF)

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Notes

The authors declare no competing financial interest.

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(5) β-Elimination, including β-carbon elimination and β-H elimination, is inhibited for the Pd^{IV} complex. See ref 2d,e,g and references cited therein.

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(13) Compounds **2a** and **2a′** were also speculated to form via a pathway in Scheme S16 in the SI, see (a) Ilchenko, N. O.; Tasch, B. O.; Szabó, K. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 12897. (b) Reference 10b.

(14) When substrate **3a** or **3j** was subjected to the control experiment in the absence of Pd catalyst, product **4a′** (36%) or **4j′** (77%) was obtained as the major product along with some polymerization products.

(15) A similar reaction involving different conditions was reported recently; see: Ulmer, A.; Brunner, C.; Arnold, A. M.; Pöthig, A.; Gulder, T. *Chem. - Eur. J.* **2016**, *22*, 3660.

(16) For selected examples, see: (a) Winstein, S.; Morse, B. K.; Grunwald, E.; Schreiber, K. C.; Corse, J. *J. Am. Chem. Soc.* **1952**, *74*, 1113. (b) Brown, H. C.; Kim, C. J. *J. Am. Chem. Soc.* **1968**, *90*, 2082. In some cases, 1,2-alkyl shift was more favorable over 1,2-aryl shift to form a more stable carbocation transition state, see: (c) Gutiérrez-Bonet, Á.; Flores-Gaspar, A.; Martin, R. *J. Am. Chem. Soc.* **2013**, *135*, 12576.

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(18) It also corresponds to the general observation that weak coordinating nucleophiles prefer anti nucleophilic palladation to olefins. See: McDonald, R. I.; Liu, G.; Stahl, S. S. *Chem. Rev.* **2011**, *111*, 2981 and references cited therein.

(19) Previous reports showed that configurational retention of C−F bond-forming reductive elimination from the F−Pd^{IV} complex was observed. However, a S_N2-type reductive elimination may also operate during the process, which causes the decline of ee or dr values; see: Emer, E.; Pfeifer, L.; Brown, J. M.; Gouverneur, V. *Angew. Chem., Int. Ed.* **2014**, *53*, 4181. (b) See ref 7b.

(20) Substrate **1a** with stoichiometric $Pd(OAc)_2$ in the absence of Selectfluor resulted almost no reaction (Table 1, entry 6). It suggests the ^{t}Bu group leaving should occur after the oxidation step.

(21) The migration should proceed *anti*-periplanar to metal, analogous to the Baeyer−Villiger reaction: (a) Cárdenas, R.; Cetina, R.; Lagúnez-Otero, J.; Reyes, L. *J. Phys. Chem. A* **1997**, *101*, 192. (b) Okuno, Y. *Chem. - Eur. J.* **1997**, *3*, 212.

(22) The fluorine source may also come from the BF_4^- counteranion; see ref 13a.

(23) As far as we know, β-alkyl elimination without an additional driving force (such as ring strain release) has never been reported for transition-metal complexes. For relative reviews involving the topic of transition-metal-mediated β-carbon elimination, see: (a) (a) Jun, C.-H. *Chem. Soc. Rev.* **2004**, *33*, 610. (b) Ruhland, K. *Eur. J. Org. Chem.* **2012**, *2012*, 2683. Even for the Wacker process (hydrogen shift), evidence shows the migration proceeds via 1,2-hydride shift-type mechanism instead of β-H elimination. See: (c) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047. (d) Cornell, C. N.; Sigman, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2796. Moreover, the evidence that the cyclopropylmethylene group is also able to migrate without decomposition further excludes this process (Scheme 2, substrate **1s**).

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