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# Catalytic Regioselectivity Control in Ring-Opening Cycloisomerization of Methylene- or Alkylidenecyclopropyl Ketones

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***Abstract:*** 2-Methylene- or alkylidenecyclopropanyl ketones were easily prepared by the regioselective cyclopropanation of allenes or the reaction of methylene-/alkylidenecyclopropanyllithium with *N*,*N*-dimethyl carboxylic acid amides. Due to the presence of the *exo*-cyclic C=C bond and the strained cyclopropane, their highly selective ring-opening cycloisomerization using $PdCl_2(CH_3CN)_2$, NaI (or $PdCl_2(CH_3CN)_2$ + NaI), and $Pd(PPh_3)_4$ as catalysts provided five different products, i.e., 4*H*-pyrans, 2,3,4-trisubstituted furans (or 4,5-disubstituted-3-alkylidene-2,3-dihydrofurans), and 2,3,4,5-tetrasubtituted furans (or 2,4,5-trisubstituted-3-alkylidene-2,3-dihydrofurans) in good yields, respectively, depending on the nature of the catalyst and reaction conditions. The less-substituted C=C bonds in these products can be highly selectively hydrogenated or hydroborated to afford new heterocyclic products stereoselectively. These three types of different reactions may proceed through a highly regioselective cleavage of a carbon−carbon single bond in the cyclopropane ring triggered by regioselective halometalation of the C=C bond and $\beta$-decarbopalladation, halogen anion attack on the nonsubstituted carbon atom of the cyclopropane ring, or the direct oxidative addition of the distal carbon−carbon single bond of the cyclopropane ring with Pd(0). In some cases substituent effects were successfully applied to synthesize 2*H*-pyrans **8** and 3-alkylidene-2,3-dihydrofurans **5**, which also provided some mechanistic information.

## Introduction

Selective synthesis of different products from the same materials by just choosing different catalysts is an interesting research topic for chemists.[1] Recently, much attention has been paid to methylenecyclopropanes (MCPs)[2−5] due to the presence of an *exo*-cyclic carbon−carbon double bond and a strained three-membered carbocycle. For the transition metal-mediated reactions, various reaction pathways, including oxidative addition of the distal or proximal C−C bond[6,7] and regioselective hydrometalation[8,9] or carbometalation[10,11] of the C=C bond, have been observed in the transition-metal-catalyzed reactions of MCPs (Scheme 1).

Although the chloropalladation reaction of the C=C bond in MCPs with stoichiometric $PdCl_2(PhCN)_2$ has been studied,[12] no catalytic reaction involving halometalation has been reported. During the course of our systematic study of functionalized

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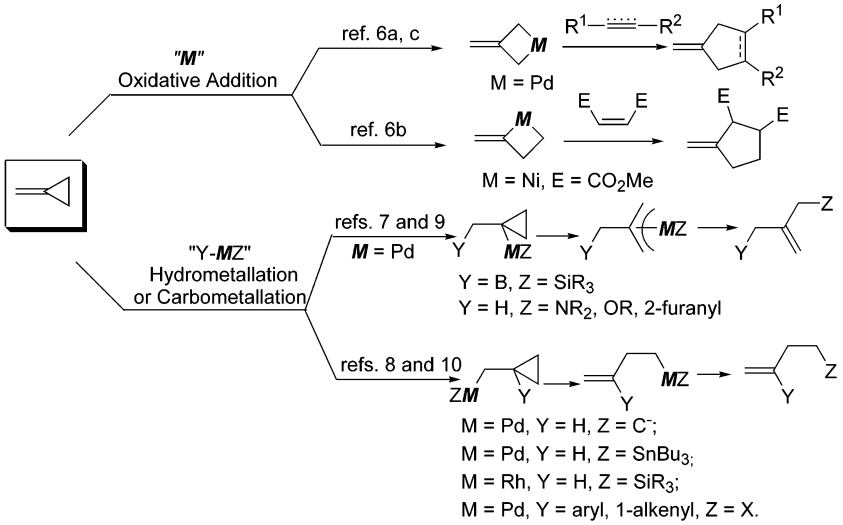
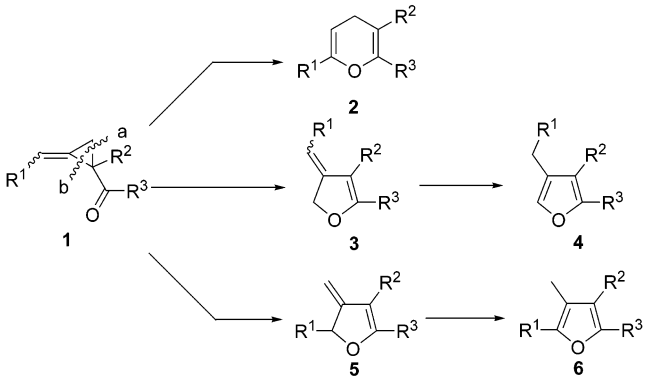
***Scheme 1.*** Transition Metal-Catalyzed Reactions of MCPs




***Scheme 2.*** Three Different Paths for the Catalytic Cycloisomerization of Alkylidenecyclopropyl Ketones **1**




allenes,[13] we were interested in the chemistry of its analogues, i.e., alkylidenecyclopropyl ketone **1**. In principle, due to the presence of the carbonyl group, the strained carbon−carbon single bonds a and b are further activated. In this paper, we wish to report the highly selective ring-opening cycloisomerization of methylene- or alkylidenecyclopropyl ketones under different reaction conditions leading to three types of different products **2**, **3** (or **4**), and **5** (or **6**), respectively (Scheme 2).

## Results and Discussion

**Synthesis of Starting Materials:** The starting alkylidenecyclopropyl ketones **1a**−**k** were easily prepared by the $Rh_2(OAc)_4$-catalyzed cyclopropanation[14] of the corresponding 1,2-allenes[15] with the α-diazo ketones **7a**−**e**[16] (Scheme 3). For **1f**, **1g**, and **1l**, only one isomer was observed. The stereochemistry of **1l** was determined by the X-ray diffraction study (Figure 1).[17] The corresponding ratios of *Z*/*E* isomers of other starting materials were determined by $^1$H NMR spectra. The configurations of the C=C bond of **1** in cases of mixtures were tentatively assigned based on the influence of the carbonyl group to the chemical shift of olefinic protons.[18]

The alkylidenecyclopropyl ketone **1m** and methylenecyclopropyl ketones **1n**−**y** were synthesized according to the method developed by Thomas, E. W. et al. except that the corresponding *N*,*N*-dimethyl amide was used instead of the lithium carboxylate (Scheme 4).[19]

**Ring-Opening Cycloisomerization under the Catalysis of $PdCl_2(CH_3CN)_2$. Formation of 4*H*-Pyrans:** We examined the cycloisomerization of methylenecyclopropyl ketone **1a** in the presence of a catalytic amount of $PdCl_2(CH_3CN)_2$.[20] The reaction was completed within 15 min at rt in acetone to afford 4*H*-pyran **2a**, which is air-sensitive (entry 1, Table 1).

This transformation is general for the alkylidenecyclopropyl ketones **1a**−**h** and **1m** under the catalysis of 5 mol % $PdCl_2(CH_3CN)_2$ in acetone at rt (Table 1). In some cases, benzene is a better solvent. For example, the reaction of **1c** in $CH_2Cl_2$ afforded **2c** in 80% yield, while the same reaction in acetone afforded **2c** in 69% yield (entries 3 and 4, Table 1). The reaction of **1d**, which contains the TBS-protected hydroxyl group, gave **2d** in 85% yield in benzene (entry 5, Table 1). The presence of electron-withdrawing group $R^2$ is not necessary, since the reaction of **1m** also occurred well to afford **2m** in 70% yield (entry 10, Table 1). It should be noted that the 2*H*-pyran **8**-type products (see the equation in Table 1) were not formed in these cases.

With the hydroboration−oxidation reaction of **2**, a series of cyclic alcohols **9** can be prepared highly stereoselectively (Scheme 5). The stereochemistry of **9** was established by the X-ray diffraction study of **9g** (Figure 2).[21] The hydroboration of the cyclic tetrasubstituted C=C bond was not observed.

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(17) X-ray data for compound **1l**: $C_{12}H_{11}O_3SCl$, MW = 270.72, monoclinic, space group *P*2(1)/*n*, Mo Kα, final R indices [$I > 2\sigma(I)$], R1 = 0.0494, wR2 = 0.0755, $a$ = 11.3404(19) Å, $b$ = 10.0567(17) Å, $c$ = 12.770(2) Å, α = 90°, β = 115.267(3)°, γ = 90°, $V$ = 1317.0(4) Å$^3$, $T$ = 293(2) K, $Z$ = 4, reflections collected/unique: 7763/3016 ($R_{int}$ = 0.1005), parameters 199. CCDC 228763 contains the supplementary crystallographic data.

(18) *Tables of Spectral Data for Structure Determination of Organic Compounds*; Prestch, E., Clerc, T., Seibl, J., Simon, W. (Translator: Biemann, K.); Springer-Verlag: Berlin, 1983; p. H-215.

(19) **1m**−**y** were prepared according to the following reference with slight modification; i.e., the corresponding *N*,*N*-dimethyl amide was used instead of the lithium carboxylate: Thomas, E. W.; Szmuszkovicz, J. R. *J. Org. Chem.* **1990**, *55*, 6054.

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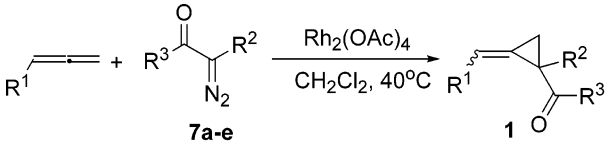
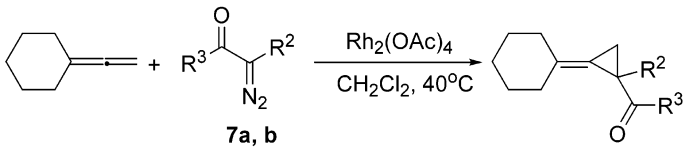
***Scheme 3.*** Synthesis of Starting Materials **1a**−**l**




**1a**: $R^1$ = *n*-$C_7H_{15}$, $R^2$ = $CO_2Et$, $R^3$ = $CH_3$, 52%
**1b**: $R^1$ = *n*-$C_4H_9$, $R^2$ = $CO_2Et$, $R^3$ = $CH_3$, 43%
**1c**: $R^1$ = Bn, $R^2$ = $CO_2Et$, $R^3$ = $CH_3$, 56%
**1d**: $R^1$ = $TBSO(CH_2)_3$, $R^2$ = $CO_2Et$, $R^3$ = $CH_3$, 41%
**1e**: $R^1$ = *n*-$C_7H_{15}$, $R^2$ = $COCH_3$, $R^3$ = $CH_3$, 28%
***E*-1f**: $R^1$ = *n*-$C_7H_{15}$, $R^2$ = $SO_2Ph$, $R^3$ = $CH_3$, 38%
***E*-1g**: $R^1$ = *n*-$C_4H_9$, $R^2$ = $SO_2Ph$, $R^3$ = $CH_3$, 26%
**1h**: $R^1$ = *n*-$C_7H_{15}$, $R^2$ = $CO_2Et$, $R^3$ = Ph, 40%
***E*-1l**: $R^1$ = Cl, $R^2$ = $SO_2Ph$, $R^3$ = $CH_3$, 10%




**1j**: $R^2$ = $CO_2Et$, $R^3$ = $CH_3$, 57%
**1k**: $R^2$ = $COCH_3$ $R^3$ = $CH_3$, 22%

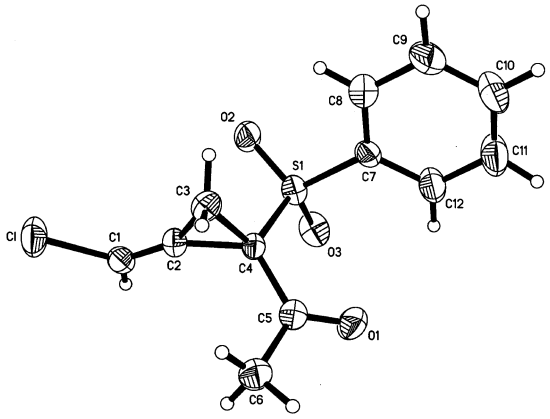
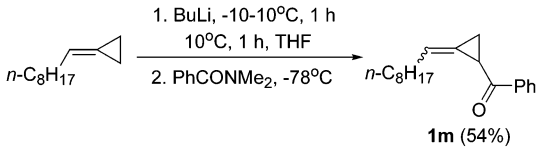
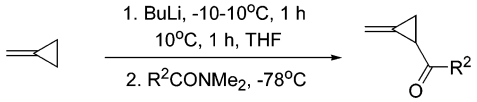



***Figure 1.*** ORTEP representation of ***E*-1l**.

***Scheme 4.*** Synthesis of Starting Materials **1m**−**y**

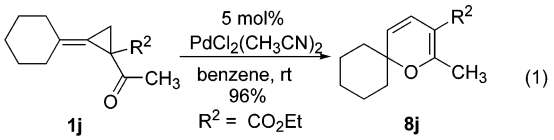



**1n**: $R^2$ = Ph, 89%; **1t**: $R^2$ = *p*-$IC_6H_4$, 73%;
**1o**: $R^2$ = *p*-$CH_3C_6H_4$, 89%; **1u**: $R^2$ = 1-Naphthyl, 77%;
**1p**: $R^2$ = *p*-$CH_3OC_6H_4$, 87%; **1v**: $R^2$ = 2-furyl, 79%;
**1q**: $R^2$ = *p*-$FC_6H_4$, 88%; **1w**: $R^2$ = $PhC_2H_4$, 57%;
**1r**: $R^2$ = *p*-$ClC_6H_4$, 95%; **1x**: $R^2$ = *p*-$MeOC_6H_4C_2H_4$, 46%;
**1s**: $R^2$ = *p*-$BrC_6H_4$, 70%; **1y**: $R^2$ = $BnOC_3H_6$, 87%.

A one-pot reaction of **1a**−**c** with 5 mol % $PdCl_2(CH_3CN)_2$ in $CH_2Cl_2$ followed by highly selective Pd/C-catalyzed hydrogenation afforded dihydropyran derivatives **10a**−**c** (Scheme 6), indicating the high regioselectivity of this hydrogenation step.

Furthermore, it is interesting to observe that in the presence of $PdCl_2(CH_3CN)_2$ the cycloisomerization of **1j** afforded 2*H*-pyran **8j** in 96% yield (eq 1).



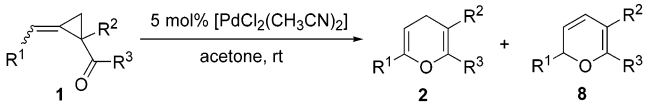

(1)

Based on these results, a plausible mechanism was proposed for the transformation (Scheme 7). Regioselective chloropalladation of **1** with $PdCl_2$ affords intermediate **11**, which would undergo $\beta$-decarbopalladation forming palladium enolate **12**. *Endo*-mode insertion of the C═C bond into the oxygen-palladium bond in **12** would generate **13**. An alternative pathway leading to intermediate **13** would be the oxypalladation to form the cationic bicyclic Pd intermediate **12A**, which would subsequently lead to **13A** and **13** via rearrangement.[22] If $R^4$ = H, the regiospecific $\beta$-$R^4$ elimination of **13** and hydropalladation with a reversed regioselectivity of **14** would afford **17**.[23] After these steps, 4*H*-pyrans **2** would be formed via $\beta$-dechloropalladation. If $R^4 \neq$ H, $\beta$-$H^a$ elimination of the proton atom at the 4-position and hydropalladation of **15** with a reversed regioselectivity and $\beta$-dechloropalladation would form **8**.

To probe the real nature of this $PdCl_2(MeCN)_2$-catalyzed isomerization of **1**, we designed the deuterium-labeling experiment to study the possible mechanism we proposed. With deuterated compound **18**, **19** (76% D incorporation) with the

(21) X-ray data for compound **9g**: $C_{16}H_{22}O_4S$, MW = 310.40, monoclinic, space group *P*2(1)/*c*, Mo K$\alpha$, final R indices [$I > 2\sigma(I)$], R1 = 0.0553, wR2 = 0.1280, $a$ = 17.931(4) Å, $b$ = 8.4053(16) Å, $c$ = 10.938(2) Å, $\alpha$ = 90°, $\beta$ = 94.494(3)°, $\gamma$ = 90°, $V$ = 1643.5(5) Å$^3$, $T$ = 293(2) K, $Z$ = 4, reflections collected/unique: 9438/3824 ($R_{int}$ = 0.0457), no observation [$I > 2\sigma(I)$] 3824, parameters 257. CCDC 190370 contains the supplementary crystallographic data.
(22) We thank the referees for the suggestion of this possibility.
(23) (a) Bender, D. D.; Stakem, F. G.; Heck, R. F. *J. Org. Chem.* **1982**, *47*, 1278. (b) Larock, R. C.; Lu, Y.; Bain, A. C. *J. Org. Chem.* **1991**, *56*, 4589. (c) Ma, S.; Yu, Z. *Angew. Chem., Int. Ed.* **2003**, *42*, 1955.

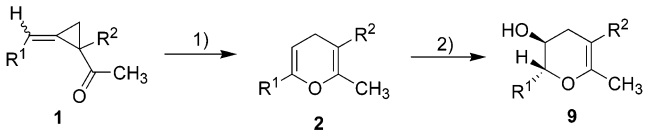
***Table 1.*** Regioselective Cycloisomerization of Ketones **1** under the Catalysis of Pd(II) Leading to 4*H*-Pyrans **2**[a]




| entry | 1 R¹ | 1 R² | 1 R³ | time (min) | yield of **2** (%) |
|---|---|---|---|---|---|
| 1 | $C_7H_{15}$ | $CO_2Et$ | Me (**1a**) | 15 | 80 (**2a**) |
| 2 | $C_4H_9$ | $CO_2Et$ | Me (**1b**) | 15 | 75 (**2b**) |
| 3 | Bn | $CO_2Et$ | Me (**1c**) | 15 | 69 (**2c**) |
| 4[b] | | **1c** | | 10 | 80 (**2c**) |
| 5[c] | $TBSO(CH_2)_3$ | $CO_2Et$ | Me (**1d**) | 10 | 85 (**2d**) |
| 6 | $C_7H_{15}$ | $COCH_3$ | Me (**1e**) | 40 | 60 (**2e**) |
| 7[c] | $C_7H_{15}$ | $SO_2Ph$ | Me (**1f**) | 40 | 56 (**2f**) |
| 8 | $C_4H_9$ | $SO_2Ph$ | Me (**1g**) | 15 | 91 (**2g**) |
| 9[c] | $C_7H_{15}$ | $CO_2Et$ | Ph (**1h**) | 30 | 96 (**2h**) |
| 10[c] | $C_8H_{17}$ | H | Ph (**1m**) | 15 | 70 (**2m**) |

[a] Unless otherwise specified, all reactions were carried out by using **1** (0.5 mmol) in the presence of 5 mol % $[PdCl_2(CH_3CN)_2]$ in 2 mL of acetone at rt. [b] The solvent used was $CH_2Cl_2$. [c] The solvent used was benzene.

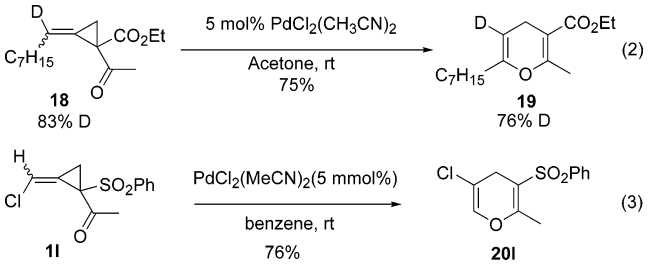
***Scheme 5.*** $PdCl_2(MeCN)_2$-Catalyzed Cycloisomerization of **1** and the Subsequent Selective Hydroboration




1) 5 mol% $PdCl_2(CH_3CN)_2$, acetone, rt, 15 min;
2) a) $BH_3{\cdot}SMe_2$, THF, 0°C-rt, 1 h; b) NaOH-$H_2O_2$, 0°C-rt, 6 h.

**1a**: $R^1 = C_7H_{15}$, $R^2 = CO_2Et$ — 59% (**9a**)
**1b**: $R^1 = C_4H_9$, $R^2 = CO_2Et$ — 59% (**9b**)
**1c**: $R^1$ = Bn, $R^2 = CO_2Et$ — 54% (**9c**)
**1d**: $R^1 = (CH_2)_3OTBS$, $R^2 = CO_2Et$ — 37% (**9d**)
**1f**: $R^1 = C_7H_{15}$, $R^2 = SO_2Ph$ — 55% (**9f**)
**1g:** $R^1 = C_4H_9$, $R^2 = SO_2Ph$ — 64% (**9g**)

deuterium at the 3-position was isolated in 76% yield (eq 2).




To some extent, this result confirmed the process from **13** to **17** via $\beta$-$R^4$ ($R^4$ = D, $R^1 = C_7H_{15}$) elimination and deuteriopalladation of **14** with a reversed regioselectivity. Another evidence for the mechanism was offered by the reaction of **1l** (eq 3). The structure of the corresponding product **20l** was confirmed by the direct X-ray diffraction study (Figure 3).[24]

**Cycloisomerization under the Catalysis of NaI in the Presence or Absence of $PdCl_2(CH_3CN)_2$. Formation of 4-Alkylidene-2,5-Dihydrofurans and 2,3,4-Trisubstituted Furans.** During the course of screening of the reaction conditions for the isomerization reaction of **1n**, it is surprising and interesting to observe that the isomerization of **1n** in refluxing acetone in the presence of $PdCl_2(CH_3CN)_2$ and 2.0 equiv of sodium iodide afforded 2-phenyl-4-methylfuran **4n** in 80% yield. LiBr or $Bu_4NBr$ also showed a similar effect, albeit yields of **4n** were lower, while LiCl showed no effect (Scheme 8).

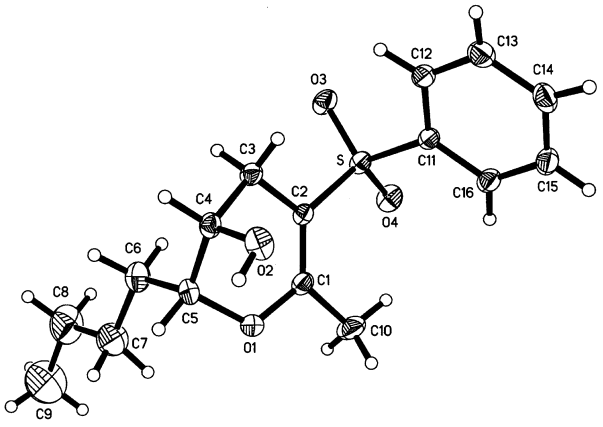
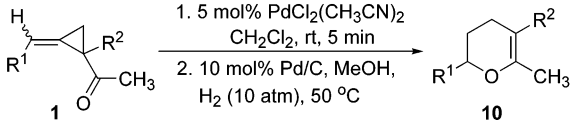



***Figure 2.*** ORTEP representation of **9g**.

***Scheme 6.*** $PdCl_2(MeCN)_2$-Catalyzed Cycloisomerization of **1a**−**c** and the Subsequent Selective Hydrogenation




**1a**: $R^1 = C_7H_{15}$, $R^2 = CO_2Et$ — 60% (**10a**)
**1b**: $R^1 = C_4H_9$, $R^2 = CO_2Et$ — 50% (**10b**)
**1c**: $R^1$ = Bn, $R^2 = CO_2Et$ — 54% (**10c**)

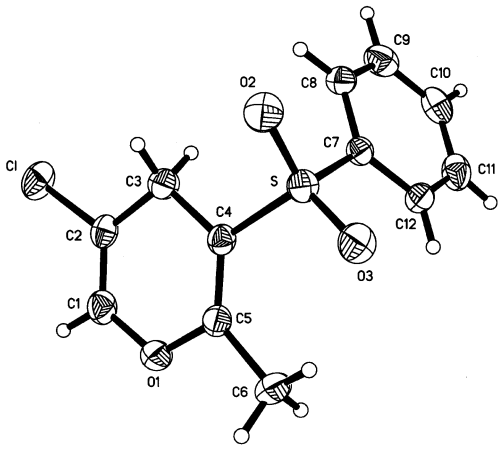
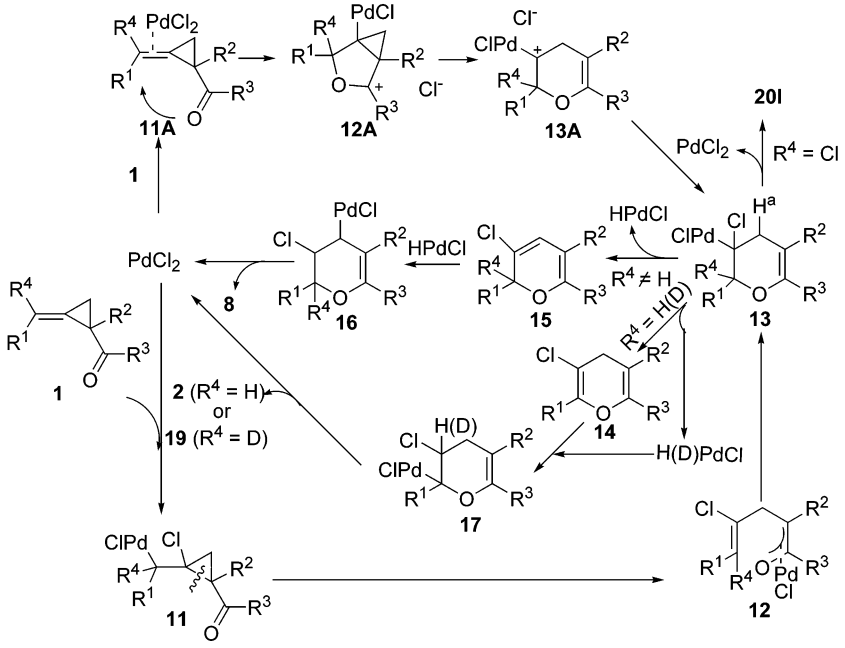



***Figure 3.*** ORTEP representation of **20l**.

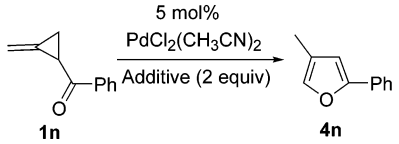
The cycloisomerization of methylene- and alkylidenecyclopropyl ketones **1** under the catalysis of $PdCl_2(CH_3CN)_2$ and sodium iodide afforded the corresponding 2,3,4-trisubstituted furans **3** in good to excellent yields (Table 2). The scope of the reaction is very broad: it is obvious that $R^1$ can be alkyl, benzyl, or H; $R^2$ can be $CO_2Et$, $SO_2Ph$, or H; $R^3$ group can be alkyl or aromatic groups with an electron-withdrawing or electron-donating group, indicating many functional groups could be tolerated.

(24) X-ray data for compound **20l**: $C_{12}H_{21}ClO_3S$, MW = 270.72, triclinic, space group *P*-1, Mo K$\alpha$, final R indices [$I > 2\sigma(I)$], R1 = 0.0422, wR2 = 0.1114, $a$ = 7.6277(7) Å, $b$ = 9.1238(9) Å, $c$ = 9.5937(9) Å, $\alpha$ = 82.377-(2)°, $\beta$ = 68.451(2)°, $\gamma$ = 75.268(2)°, $V$ = 600.01(10) Å$^3$, $T$ = 293(2) K, $Z$ = 2, reflections collected/unique: 3607/2625 ($R_{int}$ = 0.0260), no observation [$I > 2\sigma(I)$] 3607, parameters 191. CCDC 224467 contains the supplementary crystallographic data.

***Scheme 7.*** Mechanism of $PdCl_2(MeCN)_2$-Catalyzed Cycloisomerization of **1**



***Scheme 8.*** $PdCl_2(MeCN)_2$-Catalyzed Cycloisomerization of **1n** in the Presence of Different Additives



| | Conditions | Additive | $PdCl_2(CH_3CN)_2$ | Yield of **4n** (%) |
|---|---|---|---|---|
| 1 | THF, reflux | NaI | 5 mol% | 51 |
| 2 | Acetone, reflux | NaI | 5 mol% | 80 |
| 3 | Acetone, reflux | LiBr | 5 mol% | 63 |
| 4 | Acetone, reflux | $Bu_4NBr$ | 10 mol% | 57 |

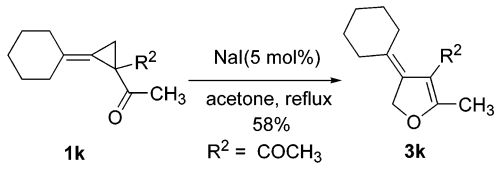
Furthermore, it is interesting to note that the reaction of **1e** gave 4-octylidene-4,5-dihydrofuran ***Z*-3e** (determined by the NOE study) in 55% yield together with the 2,3,4-trisubstituted furans **4e** (15%) within 1 h while the yield of **4e** reached up to 80% after 20.5 h, indicating that the reaction proceeded through the intermediacy of **3e** (Scheme 9). Further investigation indicated that both NaI (76%) and $PdCl_2(CH_3CN)_2$ (74%) can catalyze the transformation of ***Z*-3e** to **4e**.

However, when **1a** was treated with 5 mol % of NaI alone, the nonisomerized 3-alkylidene-2,3-dihydrofuran **3a** was formed in 79% yield, indicating that the ring-opening cycloisomerization can also be induced by a catalytic amount of NaI. Some of the typical results are summarized in Table 3.

The structures of **3** were established by the X-ray diffraction study of **3g** (Figure 4).[25]

With more NaI and prolonged reaction time, although the reaction may not be as clean as that in the presence of a Pd(II) catalyst, the isomerized 1,2,3-trisubstituted furans were formed slowly. Some of these results are given in Table 4. In some cases 3 M HCl was added to induce the aromatization of **3** (entries 3, 5−7, Table 4)

The isomerization reaction of tetrasubstituted alkene **1k** in the presence of NaI occurred smoothly to afford the 3-cyclohexylidene-2,3-dihydrofuran **3k** in 58% yield. Here the isomerization of the *exo*-cyclic C═C bond did not occur due to presence of the cyclohexyl group even with prolonged reaction time (eq 4).



(4)

A rationale for this transformation was proposed as shown in Scheme 10. As compared to what is shown in Scheme 7, $X^-$ may act as a nucleophile to attack the C═C bond with an opposite regioselectivity followed by ring-opening to afford enolate-type intermediate **22**, which would undergo the intramolecular substitution reaction between the in situ formed allylic halide moiety and the enolate moiety to form **3**.[26] A C═C isomerization process would lead to 2,3,4-trisubstituted furans **4**.[8c] An alternative mechanism is that the direct attack of $X^-$ on the nonsubstituted carbon atom of the cyclopropane ring generates 2-alkylidenehomoallylic halide intermediate **23**,[27] which can then undergo a 5-*exo*-tet cyclization,[28] just as shown in path B.

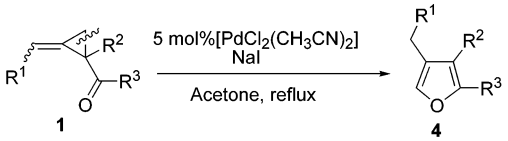
(25) X-ray data for compound **3g**: $C_{16}H_{20}O_3S$, MW = 292.38, triclinic, space group *P*-1, Mo Kα, final R indices [$I > 2\sigma(I)$], R1 = 0.0510, wR2 = 0.1042, $a$ = 7.9721(9) Å, $b$ = 9.2400(11) Å, $c$ = 11.3859(13) Å, α = 109.621(2)°, $\beta$ = 94.117(2)°, $\gamma$ = 101.647(2)°, $V$ = 764.84(15) Å$^3$, $T$ = 293(2) K, $Z$ = 2, reflections collected/unique: 4763/3441 ($R_{int}$ = 0.0368), no observation [$I > 2\sigma(I)$] 3441, parameters 239. CCDC 224466 contains the supplementary crystallographic data.

(26) (a) Negishi, E.; Coperet, S. M.; Ma, S.; Mita, T.; Sugihara, T.; Tour, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 5919. (b) Negishi, E.; Coperet, S. M.; Ma, S.; Mita, T.; Sugihara, T.; Tour, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 5904. (c) Gagnier, S. V.; Larock, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 4804.

(27) (a) Miller, R. D.; Mckean, D. R. *J. Org. Chem.* **1981**, *46*, 2412. (b) Dieter, R. K.; Pounds, S. *J. Org. Chem.* **1982**, *47*, 3174. (c) Lautens, M.; Han, W. *J. Am. Chem. Soc*. **2002**, *124*, 6312. (d) Alper, P. B.; Meyers, C.; Lerchner, A.; Siegel, D. R.; Carreira, E. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3186. For an account of nucleophilic ring-opening of cyclopropanes, see: Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66. We thank the referees for the suggestion of this possibility.

(28) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

***Table 2.*** Cycloisomerization of Ketones **1** under the Catalysis of Pd(II) Leading to Furans **3**[a]




| entry | 1 R[1] | 1 R[2] | 1 R[3] | NaI (equiv) | time (h) | yield of **4** (%) |
|---|---|---|---|---|---|---|
| 1 | $C_7H_{15}$ | $CO_2Et$ | Me (**1a**) | 2 | 10 | 74 (**4a**) |
| 2 | $C_4H_9$ | $CO_2Et$ | Me (**1b**) | 2 | 14 | 74 (**4b**) |
| 3 | Bn | $CO_2Et$ | Me (**1c**) | 2 | 13.5 | 78 (**4c**) |
| 4 | $TBSO(CH_2)_3$ | $CO_2Et$ | Me (**1d**) | 2 | 26 | 82 (**4d**) |
| 5 | $C_7H_{15}$ | $SO_2Ph$ | Me (**1f**) | 2 | 24 | 84 (**4f** + **3f**)[d] |
| 6[b] | | **1f** | | 0.2 | 6[c] | 89 (**4f**) |
| 7 | $C_4H_9$ | $SO_2Ph$ | Me (**1g**) | 2 | 24 | 76 (**4g** + **3g**)[e] |
| 8[b] | | **1g** | | 0.7 | 8.5[c] | 72 (**4g**) |
| 9 | $C_7H_{15}$ | $CO_2Et$ | Ph (**1h**) | 2 | 24 | 88 (**4h** + **3h**)[f] |
| 10[b] | | **1h** | | 1 | 8[c] | 82 (**4h**) |
| 11 | H | H | *p*-$MeC_6H_4$ (**1o**) | 2 | 6 | 73 (**4o**) |
| 12 | H | H | *p*-$MeOC_6H_4$ (**1p**) | 2 | 6 | 88 (**4p**) |
| 13 | H | H | *p*-$FC_6H_4$ (**1q**) | 2 | 12 | 84 (**4q**) |
| 14 | H | H | *p*-$ClC_6H_4$ (**1r**) | 2 | 12 | 69 (**4r**) |
| 15 | H | H | *p*-$BrC_6H_4$ (**1s**) | 2 | 10 | 76 (**4s**) |
| 16 | H | H | *p*-$IC_6H_4$ (**1t**) | 2 | 5 | 72 (**4t**) |
| 17 | H | H | 1-naphthyl (**1u**) | 2 | 6 | 83 (**4u**) |
| 18 | H | H | 2-furyl (**1v**) | 2 | 5 | 70 (**4v**) |
| 19 | H | H | $PhC_2H_4$ (**1w**) | 2 | 12 | 77 (**4w**) |
| 20 | H | H | *p*-$MeOC_6H_4C_2H_4$ (**1x**) | 2 | 11 | 72 (**4x**) |
| 21 | H | H | $BnOC_3H_6$ (**1y**) | 2 | 14 | 66 (**4y**) |

[a] Unless otherwise specified, the reaction was carried out using **1** (0.25−1.5 mmol) in the presence of 5 mol % $PdCl_2(CH_3CN)_2$ and sodium iodide in 2 mL of acetone under reflux. [b] 3 mL of 3 M HCl was added to the in situ formed product for aromatization. [c] The time referred to the Pd-catalyzed reaction only. [d] A mixture of **4f** and **3f** (**4f:3f** = 1:9.6) was formed. [e] A mixture of **4g** and **3g** (**4g:3g** = 3.2:1) was formed. [f] A mixture of **4h** and **3h** (**4h:3h** = 1:5.5) was formed.

***Scheme 9.*** $PdCl_2(MeCN)_2$-Catalyzed Cycloisomerization of **1e** in the Presence of NaI

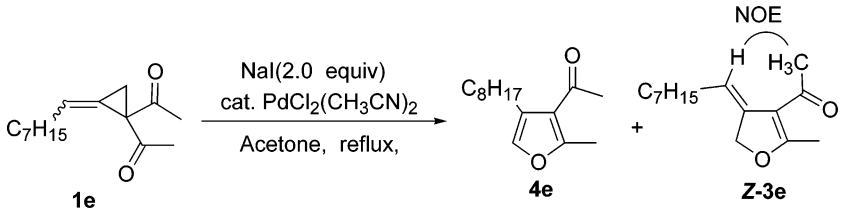
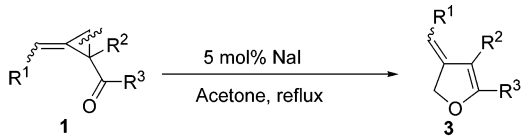



***Table 3.*** Cycloisomerization of Ketones **1** under the Catalysis of Sodium Iodide Leading to 3-Alkyliene-2,3-dihydrofurans **3**[a]




| entry | 1 R[1] | 1 R[2] | 1 R[3] | time (h) | yield of **3** (%) (*Z*/*E*) |
|---|---|---|---|---|---|
| 1 | $C_7H_{15}$ | $CO_2Et$ | Me (**1a**) | 11 | 79 (**3a**) (2.3:1) |
| 2 | $C_4H_9$ | $CO_2Et$ | Me (**1b**) | 3 | 46 (**3b**) (3:1) |
| 3 | Bn | $CO_2Et$ | Me (**1c**) | 2.5 | 80 (**3c**) (1.5:1) |
| 4 | $C_7H_{15}$ | $COCH_3$ | Me (**1e**) | 1.5 | 79 (**3e**) (1.9:1) |
| 5 | $C_4H_9$ | $SO_2Ph$ | Me (**1g**) | 2.5 | 78 (***E*-3g**)[b] |
| 6 | $C_7H_{15}$ | $CO_2Et$ | Ph (**1h**) | 2.5 | 79 (**3h**) (3.3:1) |

[a] Unless otherwise specified, the reaction was carried out using **1** (0.25−0.5 mmol) in the presence of 5 mol % sodium iodide in 2 mL of acetone under reflux. [b] Only one isomer was observed. The structure of ***E*-3g** was confirmed by the X-ray diffraction study (Figure 4).

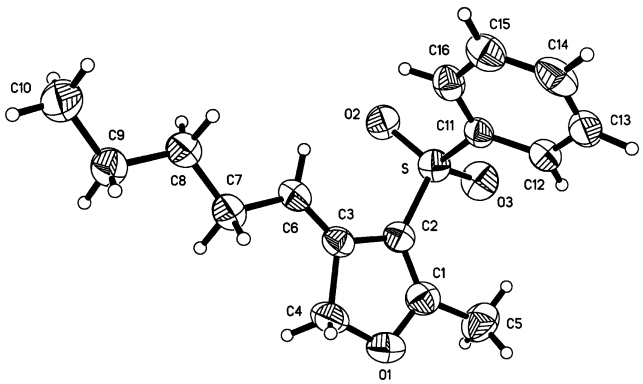
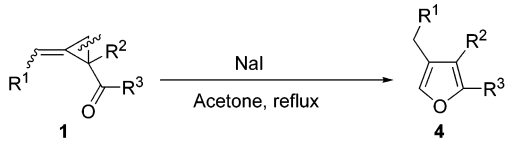



***Figure 4.*** ORTEP representation of **3g**.

**Cycloisomerization under the Catalysis of $Pd(PPh_3)_4$. Formation of 2,4,5-Trisubstituted 3-Alkylidene-2,3-dihydrofurans and 2,3,4,5-Tetrasubstituted Furans.** After studying the chemisty of **1** with a Pd(II) catalyst, we wish to explore the chemistry of **1** under a Pd(0) catalyst. The reaction of alkylidenecyclopropyl ketone **1a** in the presence of a catalytic amount of different Pd(0) catalyst in MeCN was examined, and the results were listed in Table 5. Under the catalysis of $Pd_2(dba)_2 \cdot CHCl_3$ together with a ligand and the treatment of the in situ

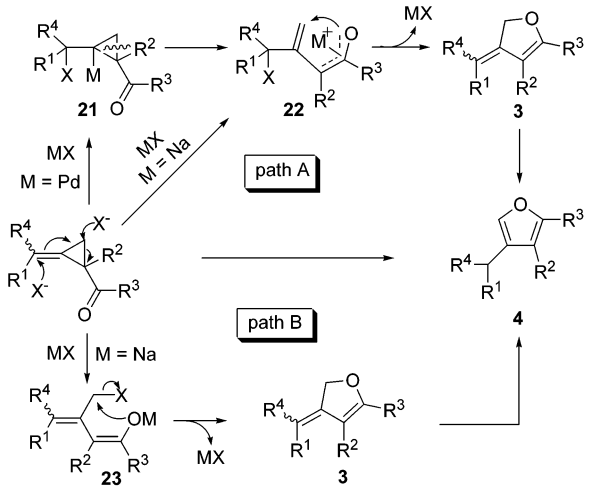
***Table 4.*** Cycloisomerization of Ketones **1** under the Catalysis of Sodium Iodide Leading to Furans **4**[a]




| entry | 1 R1 | 1 R2 | 1 R3 | NaI (equiv) | time (h) | yield of **4** (%) |
|---|---|---|---|---|---|---|
| 1 | $C_7H_{15}$ | $CO_2Et$ | Me (**1a**) | 1.0 | 24 | 75 (**4a**) |
| 2 | $C_4H_9$ | $CO_2Et$ | Me (**1b**) | 1.0 | 12 | 92 (**4b**) |
| 3[b] | Bn | $CO_2Et$ | Me (**1c**) | 0.05 | 2.5 | 79 (**4c**) |
| 4 | $TBSO(CH_2)_3$ | $CO_2Et$ | Me (**1d**) | 1.0 | 16 | 80 (**4d**) |
| 5[b] | $C_7H_{15}$ | $SO_2Ph$ | Me (**1f**) | 0.05 | 1.5 | 94 (**4f**) |
| 6[b] | $C_4H_9$ | $SO_2Ph$ | Me (**1g**) | 0.05 | 2.5 | 52 (**4g**) |
| 7[b] | $C_7H_{15}$ | $CO_2Et$ | Ph (**1h**) | 0.10 | 1.5 | 68 (**4h**) |
| 8 | H | H | Ph (**1n**) | 0.2 | 42 | 90 (**4n**) |
| 9 | H | H | *p*-$MeC_6H_4$ (**1o**) | 0.2 | 96 | 57 (**4o**) |
| 10 | H | H | *p*-$MeOC_6H_4$ (**1p**) | 0.2 | 144 | 61 (**4p**) |
| 11 | H | H | *p*-$FC_6H_4$ (**1q**) | 0.2 | 37 | 76 (**4q**) |
| 12 | H | H | *p*-$ClC_6H_4$ (**1r**) | 0.2 | 24 | 71 (**4r**) |
| 13 | H | H | *p*-$BrC_6H_4$ (**1s**) | 0.2 | 48 | 81 (**4s**) |
| 14 | H | H | *p*-$IC_6H_4$ (**1t**) | 0.2 | 24 | 73 (**4t**) |
| 15 | H | H | 1-naphthyl (**1u**) | 0.2 | 48 | 98 (**4u**) |
| 16 | H | H | 2-furyl (**1v**) | 0.2 | 30 | 78 (**4v**) |
| 17 | H | H | *p*-$MeOC_6H_4C_2H_4$ (**1x**) | 1.0 | 96 | 67 (**4x**) |
| 18 | H | H | $BnOC_3H_6$ (**1y**) | 0.2 | 96 | 24 (**4y**) |

[a] The reaction was carried out using **1** (0.25−0.5 mmol) in the presence of sodium iodide in 2 mL of acetone under reflux. [b] After the starting material was completely consumed, 3 mL of 3 M HCl was added to the solution and the mixture was stirred under rt as monitored by TLC.

***Scheme 10.*** Mechanism for the Conversion of Alkylidenecyclopropyl Ketones **1** to 2,3,4-Trisubstituted Furans




formed product with 3 M HCl, the reaction afforded a mixture of 2,3,4-trisubstituted furan **4a** and 2,3,4,5-tetrasubstituted furan **6a** with different ratios (entries 1−4, Table 5). It is quite surprising that with $Pd(PPh_3)_4$ as the catalyst tetrasubstituted furan **6a** was formed highly selectively in MeCN (entry 7, Table 5)! With $PPh_3$ as the catalyst, the reaction can also occur; however, instead of **4a** and **6a**, a mixture of **4a** and **3a** with a ratio of 1:29 was formed. The reaction can also proceed in the absence of any catalyst at 80 °C to afford a mixture of **4a** and **3a** in a 2.5:1 ratio (entry 6, Table 5). The solvent effect on the $Pd(PPh_3)_4$-catalyzed isomerization of **1** was shown in Table 6 with the best solvent being MeCN. Some of the typical examples under the catalysis of $Pd(PPh_3)_4$ in MeCN are summarized in Table 7.

If the reaction mixture was submitted directly to chromatography on silica gel without the treatment of 3 M HCl, the unisomerized 4-methylene-substituted furans **5** may be isolated (Table 8). In some cases, the reaction was carried out in the presence of $Et_3N$ to avoid the transformation of **5** to **6** (entries 1 and 4, Table 8). With cyclohexylidene-substituted cyclopropyl ketones **1j**−**k**, the isomerization of the *exo* C=C bond is not possible; thus, **5j**−**k** were formed in high yields respectively (Scheme 11).

Based on the isolation of **5**-type product, a mechanism was proposed (Scheme 12). The regiospecific oxidative addition of the distal C−C bond of **1** would afford palladacyclobutane intermadiate **24**, which may be transformed into enolate-type allylic palladium intermediate **25**.[6c,29] Reductive elimination or intramolecular allylic substitution of **25** at the more substituted terminal[30] would lead to **5**, which can be aromatized to give tetrasubstituted furans **6**.

In conclusion, we have observed three different types of reactions for ring-opening cycloisomerization of methylene- or alkylidenecyclopropyl ketones. With the application of different reaction conditions and catalysts, a highly selective formation of 4*H*-pyrans, 3-alkylidene-2,3-dihydrofurans (or 2,4- or 2,3,4-trisubstituted furans), and 2,3,4,5-tetrasubstituted furans (or 3-alkylidene-2,4,5-trisubstituted- 2,3-dihydrofurans) can be realized. Due to the easy availability of the starting materials and synthetic potential of these products, this methodology will show its utility in organic synthesis. Further studies in this area are being pursued in our laboratory.

## Experimental Section

**Starting Materials.** Alkyl-1,2-dienes used in this study were prepared from the reaction of alkyl Grignard reagents with propargyl bromide as reported.[15]

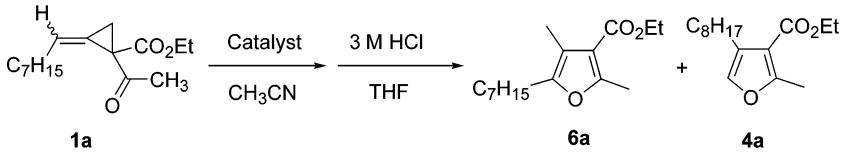
Diazo compounds **7a**−**e** were prepared from *p*-toluenesulfonyl azide with corresponding acyl substrates.[16]

**General Procedure for the Synthesis of Alkylidenecyclopropyl Ketones: (A) 1-(Ethoxycarbonyl)-2-(octylidene)cyclopropyl Methyl Ketone (1a):** A solution of 2-diazo-3-oxobutyric acid ethyl ester **7a** (1.97 g, 13 mmol) in 15 mL of $CH_2Cl_2$ was added with a syringe to a solution of deca-1,2-diene (13.51 g, 97 mmol) and $Rh_2(OAc)_4$ (20 mg, 0.9 mmol) in 5 mL of $CH_2Cl_2$ under reflux. After the addition was over, the mixture was stirred for 2 h under reflux. After 7.64 g (55 mmol) of deca-1,2-diene was recovered by distillation, the residue was purified by column chromatography on silica gel (hexane/ether = 10:1) to afford 1.80 g (52%) of **1a**: liquid; mixture of *Z*/*E* isomers, ratio = 2.5:1; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ [5.87−5. 97 (m, 0.71 H), 5.80−5.86 (m, 0.29 H)], 4.10−4.30 (m, 2 H), [2.33 (s, 0.87 H), 2.31 (s, 2.13 H)], 2.10−2.28 (m, 4 H), 1.36−1.50 (m, 2 H), 1.20−1.36 (m, 11 H), 0.82−0.90 (m, 3 H); MS *m*/*z* 266 ($M^+$, 3.32), 181 (100); IR (neat) 1723, 1708, 1295, 1091 $cm^{-1}$. Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 71.96; H, 10.01.

**1-(Ethoxycarbonyl)-2-(1′-deutrooctylidene)cyclopropyl Methyl Ketone (18):** The reaction of 2-diazo-3-oxobutyric acid ethyl ester **7a** (2.35 g, 15 mmol) with 3-deutro-1,2-heptadiene (5.32 g, 39 mmol) and $Rh_2(OAc)_4$ (33 mg, 0.075 mmol) afforded 1.66 g (41%) of **18** as an *E*/*Z* mixture (*Z*/*E* = 1.7:1). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.10−4.30 (m, 2 H), [2.33 (s, 1.06 H), 2.31 (s, 1.94 H)], 2.10−2.25 (m, 4 H),

(29) Binger, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 433.
(30) (a) Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 21969. (b) Minami, I.; Yuhara, M.; Tsuji, J. *Tetrahedron Lett.* **1987**, *8*, 629. (c) Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225. (d) Kadota, J.; Komori, S.; Fukumoto, Y.; Murai, S. *J. Org. Chem.* **1999**, *64*, 7523. (e) Kadota, J.; Chatani, N.; Murai, S. *Tetrahedron* **2000**, *56*, 2231.

***Table 5.*** Effects of Catalyst on the Pd(0)-Catalyzed Cycloisomerization of **1a**[a]

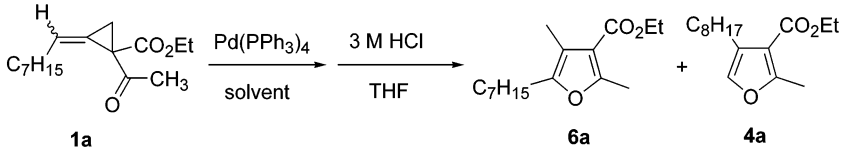



**1a** **6a** **4a**

| entry | catalyst | temp (°C) | time (h) | yield (%) (**6a**:**4a**) |
|---|---|---|---|---|
| 1 | $Pd_2(dba)_3$·$CHCl_3$/$PCy_3$ | 80 | 13.5 | 50 (1:2.5) |
| 2 | $Pd_2(dba)_3$·$CHCl_3$/P(α-furanyl)$_3$ | 80 | 13.5 | 47 (2.5:1) |
| 3 | $Pd_2(dba)_3$/(*t*-Bu)$_3$P | 80 | 12 | 39 (1:5.6) |
| 4 | $Pd_2(dba)_3$·$CHCl_3$/$PPh_3$ | 80 | 27.5 | 74 (9:1) |
| 5 | $PPh_3$(20 mmol %) | 80 | 42 | 47 (**4a**:**3a** = 1:29) |
| 6 | | 80 | 48 | 22 (**4a**:**3a** = 2.5:1) |
| 7 | $Pd(PPh_3)_4$ | 80 | 12 | 84 (50:1) |

[a] Unless otherwise specified, all reactions were conducted by using **1a** (0.25−0.5 mmol) with 5 mmol % catalyst in 3 mL of $CH_3CN$.

***Table 6.*** Effects of Solvent on Cycloisomorization of **1a**[a]

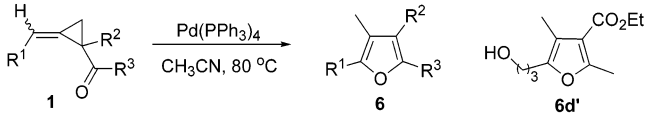



**1a** **6a** **4a**

| entry | solvent | catalyst | temp (°C) | time (h) | yield (%) (**6a**:**4a**) |
|---|---|---|---|---|---|
| 1[b] | THF | $Pd(PPh_3)_4$ | 80 | 14 | 72 (6.7:1) |
| 2 | acetone | $Pd(PPh_3)_4$ | reflux | 6 | 61 (12:1) |
| 3 | $CHCl_3$ | $Pd(PPh_3)_4$ | 80 | 10 | complicated |
| 4 | dioxane | $Pd(PPh_3)_4$ | 80 | 13 | 68 (40:1) |
| 5 | toluene | $Pd(PPh_3)_4$ | 80 | 12.5 | 79 (18:1) |
| 6 | DMF | $Pd(PPh_3)_4$ | 80 | 8.5 | 37 (3.5:1) |
| 7 | $CH_3CN$ | $Pd(PPh_3)_4$ | 80 | 12 | 84 (50:1) |

[a] Unless otherwise specified, all reactions were carried out by using **1a** (0.25−0.5 mmol) with 5 mmol % $Pd(PPh_3)_4$ in 3 mL of solvent. [b] 10 mol % $Pd(PPh_3)_4$ was used.

***Table 7.*** Cycloisomerization of Ketones **1** under the Catalysis of Pd(0) Leading to Furans **6**[a]

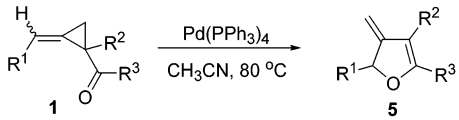



**1** **6** **6d'**

| entry | **1** R[1] | **1** R[2] | **1** R[3] | time (h) | yield of **6** (%) |
|---|---|---|---|---|---|
| 1 | $C_7H_{15}$ | $CO_2Et$ | Me (**1a**) | 12 | 84 (**6a**) |
| 2 | $C_4H_9$ | $CO_2Et$ | Me (**1b**) | 12 | 78 (**6b**) |
| 3[b,c] | $TBSO(CH_2)_3$ | $CO_2Et$ | Me (**1d**) | 22 | 62 (**6d′**) |
| 4 | $C_7H_{15}$ | $COCH_3$ | Me (**1e**) | 13 | 75 (**6e**) |
| 5 | $C_7H_{15}$ | $SO_2Ph$ | Me (**1f**) | 29 | 74 (**6f**) |
| 6[b] | $C_7H_{15}$ | $CO_2Et$ | Ph (**1h**) | 48 | 77 (**6h**) |

[a] Unless otherwise specified, the reaction was carried out using **1** (0.25−0.5 mmol) in the presence of 5 mol % $Pd(PPh_3)_4$ in 4 mL of $CH_3CN$ under 80 °C. After the starting material was completely consumed, the solvent was evaporated. Then 3 mL of THF and 3 mL of 3 M HCl were added to the residue, and the mixture was stirred under rt as monitored by TLC. [b] 10 mol % $Pd(PPh_3)_4$ was used. [c] The TBS group was removed due to the presence of HCl; thus, the product was **6d′**.

***Table 8.*** Cycloisomerization of Ketones **1** under the Catalysis of Pd(0) Leading to **5** with an *exo*-Cyclic Carbon−Carbon Double Bond[a]




**1** **5**

| entry | **1** R[1] | **1** R[2] | **1** R[3] | time (h) | yield of **5** (%) |
|---|---|---|---|---|---|
| 1[b] | $C_7H_{15}$ | $CO_2Et$ | Me (**1a**) | 14.5 | 90 (**5a**) |
| 2 | $TBSO(CH_2)_3$ | $CO_2Et$ | Me (**1d**) | 12 | 90 (**5d**) |
| 3 | $C_7H_{15}$ | $SO_2Ph$ | Me (**1f**) | 13 | 86 (**5f**) |
| 4[b,c] | $C_7H_{15}$ | $CO_2Et$ | Ph (**1h**) | 34 | 70 (**5h**) |

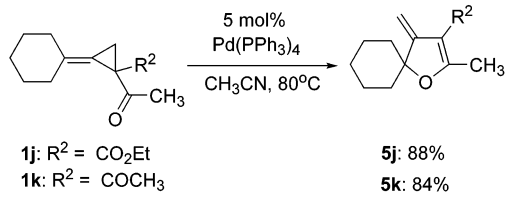
[a] Unless otherwise specified, the reaction was carried out using **1** (0.25−0.5 mmol) in the presence of 5 mol % $Pd(PPh_3)_4$ in 4 mL of $CH_3CN$ under 80 °C. [b] 0.2−0.5 mL $Et_3N$ was added to avoid the isomerization from **5** to **6**. [c] 10 mol % $Pd(PPh_3)_4$ was used.

1.36−1.50 (m, 2 H), 1.20−1.36 (m, 11 H), 0.82−0.94 (m, 3 H); MS *m*/*z* 267 ($M^+$, 0.87), 43 (100); IR (neat) 1721, 1708, 1294, 1101 $cm^{-1}$. HRMS calcd for $C_{16}H_{25}DO_3$: 267.19447. Found: 267.19612.

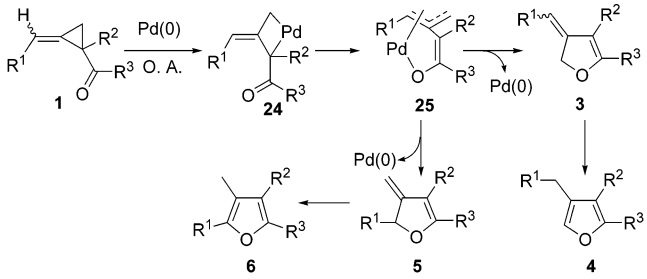
**(B) 1-(Ethoxycarbonyl)-2-(pentylidene)cyclopropyl Methyl Ketone (1b):** The reaction of 2-diazo-3-oxobutyric acid ethyl ester **7a** (3.15 g, 20 mmol) with hepta-1,2-diene (13.53 g, 141 mmol) and $Rh_2(OAc)_4$ (20 mg + 18 mg + 10 mg, 0.11 mmol) afforded 1.91 g (43%) of **1b**: liquid; mixture of *Z*/*E* isomers, ratio = 2.1:1; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ [5.87−5.95 (m, 0. 68 H), 5.80−5.87 (m, 0.32 H)], 4.13−4.30 (m, 2 H), [2.34 (s, 0.96 H), 2.32 (s, 2.04 H)], 2.10−2.30 (m, 4 H), 1.37−1.50 (m, 2 H),1.20−1.37 (m, 5 H), 0.87 (t, $J$ = 7.2 Hz, 3 H); MS *m*/*z* 225 ($M^+$ + 1, 69.06), 181 (100); IR (neat) 1708, 1296, 1091 $cm^{-1}$. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.54; H, 9.34.

**(C) 1-(Ethoxycarbonyl)-2-(2′-phenylethylidene)cyclopropyl Methyl Ketone (1c):** The reaction of 2-diazo-3-oxobutyric acid ethyl ester **7a** (3.97 g, 25 mmol) with buta-2,3-dienylbenzene (13.22 g, 102 mmol) and $Rh_2(OAc)_4$ (22 mg + 22 mg + 14 mg, 0.13 mmol) afforded 3.58 g (56%) of **1c**: liquid; mixture of *Z*/*E* isomers, ratio = 1:1; $^1H$ NMR

***Scheme 11.*** Pd(PPh$_3$)$_4$-Catalyzed Cyclization of **1j**−**k**




***Scheme 12.*** Mechanism for Pd(PPh$_3$)$_4$-Catalyzed Cyclization of **1**




(300 MHz, $CDCl_3$) $\delta$ 7.10−7.40 (m, 5 H), [6.05−6.15 (m, 0.5 H), 5.95−6.05 (m, 0.5 H)], 4.20 (m, 2 H), 3.50−3.65 (m, 2 H), [2.34 (s, 1.5 H), 2.33 (s, 1.5 H)], 2.05−2.30 (m, 2 H), 1.18−1.40 (m, 3 H); MS *m*/*z* 258 ($M^+$, 3.66), 91(100); IR (neat) 1720, 1708, 1603, 1296, 1091 $cm^{-1}$. HRMS cacld for $C_{16}H_{18}O_3$: 258.12560. Found: 258.12630.

**(D) 1-(Ethoxycarbonyl)-2-((*4′*-*tert*-butyldimethylsilyloxyl)butylidene)cyclopropyl Methyl Ketone (1d):** The reaction of 2-diazo-3-oxobutyric acid ethyl ester **7a** (1.32 g, 8.5 mmol) with 6-(*tert*-butyldimethylsilyloxyl)hexa-1,2-diene (5.30 g, 25 mmol) and $Rh_2(OAc)_4$ (20 mg + 20 mg, 0.09 mmol) afforded 1.17 g (41%) of **1d**: liquid; mixture of *Z*/*E* isomers, ratio = 3.4:1; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ [5.90−6.00 (m, 0.78 H), 5.80−5.90 (m, 0.22 H)], 4.10−4.30 (m, 2 H), 3.60 (t, $J$ = 6.3 Hz, 2 H), [2.33 and 2.31 (s, 3 H)], 2.10−2.42 (m, 4 H), 1.52−1.82 (m, 2 H), 1.25 (t, $J$ = 7.5 Hz, 3 H), [0.87 and 0.84 (s, 9 H)], 0.03 (s, 6 H); MS *m*/*z* 341 ($M^+$ + 1, 0.90), 325 ($M^+$ − $CH_3$, 0.82), 43 (100); IR (neat) 1723, 1709, 1295, 1257, 1093 $cm^{-1}$. HRMS calcd for $C_{17}H_{29}O_4Si$ [$M^+$ − $CH_3$]: 325.18351. Found 325.18780.

**(E) 1-Acetyl-2-(octylidene)cyclopropyl Methyl Ketone (1e):** The reaction of 3-diazopenta-2,4-dione **7b** (2.78 g, 18 mmol) with deca-1,2-diene (14.16 g, 103 mmol) and $Rh_2(OAc)_4$ (22 mg + 22 mg, 0.1 mmol) afforded 1.20 g (28%) of **1e**: liquid; mixture of *Z*/*E* isomers, ratio = 2.5:1; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ [5.90−5.97 (m, 0.71 H), 5.80−5.90 (m, 0.29 H)], 2.10−2.27 (m, 4 H), [2.16 (s, 1.74 H), 2.13 (s, 4.26 H)], 1.36−1.50 (m, 2 H), 1.19−1.36 (m, 8 H), 0.80−0.90 (m, 3 H). MS *m*/*z* 236 ($M^+$, 1.78), 43 (100); IR (neat) 1709, 1695, 1654 $cm^{-1}$. HRMS calcd for $C_{15}H_{24}O_2$: 236.17764. Found: 236.18220.

**(F) 1-(Benzenesulfonyl)-2-(octylidene)cyclopropyl Methyl Ketone (*E*-1f):** The reaction of 1-(benzenesulfonyl)-1-diazopropan-2-one **7c** (4.49 g, 20 mmol) with deca-1,2-diene (27.29 g, 200 mmol) and $Rh_2(OAc)_4$ (22 mg, 0.05 mmol) afforded 2.56 g (38%) of ***E*-1f** as an oil, and only one isomer was formed. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.95−8.00 (m, 2 H), 7.48−7.66 (m, 3 H), 6.05−6.15 (m, 1 H), 2.60−2.70 (m, 1 H), 2.25−2.35 (m, 3 H), 2.06 (s, 3 H), 1.40−1.60 (m, 2 H), 1.19−1.40 (m, 8 H), 0.87 (t, $J$ = 6.6 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 196.8, 139.2, 133.6, 129.1, 128.6, 125.1, 118.3, 53.5, 31.6, 31.3, 29.0, 28.9, 28.2, 26.2, 22.5, 17.5, 14.0; MS *m*/*z* 334 ($M^+$, 4.45), 43 (100); IR (neat) 1706, 1586, 1320, 1157 $cm^{-1}$. HRMS calcd for $C_{19}H_{26}O_3S$: 334.16026. Found: 334.16405. The stereochemistry of this product was determined by the $^1$H−$^1$H NOESY spectra (400 MHz).

**(G) 1-(Benzenesulfonyl)-2-(pentylidene)cyclopropyl Methyl Ketone (*E*-1g):** The reaction of 1-(benzenesulfonyl)-1-diazopropan-2-one **7c** (2.26 g, 10 mmol) with hepta-1,2-diene (12.05 g, 125 mmol) and $Rh_2(OAc)_4$ (24 mg + 16 mg, 0.09 mmol) afforded 0.75 g (26%) of ***E*-1g** as an oil, and only one isomer was formed. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.94−8.00 (m, 2 H), 7.48−7.66 (m, 3 H), 6.05−6.15 (m, 1 H), 2.60−2.70 (m, 1 H), 2.25−2.35 (m, 3 H), 2.06 (s, 3 H), 1.43−1.55 (m, 2 H), 1.30−1.43 (m, 2 H), 0.91 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 196.8, 139.3, 133.6, 129.1, 128.7, 125.1, 118.4, 53.6, 31.0, 30.4, 26.4, 22.2, 17.5, 13.8; MS *m*/*z* 292 ($M^+$, 1.8), 43 (100); IR (neat) 1705, 1585, 1319, 1158 $cm^{-1}$. Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.72; H, 6.89. Found: C, 65.53; H, 6.88.

**(H) 1-(Ethoxycarbonyl)-2-(octylidene)cyclopropyl Phenyl Ketone (1h):** The reaction of 2-diazo-3-oxo-3-phenylpropionic acid ethyl ester **7e** (3.27 g, 15 mmol) with deca-1,2-diene (17.89 g, 130 mmol) and $Rh_2(OAc)_4$ (22 mg, 0.05 mmol) afforded 1.94 g (40%) of **1h** with 13.16 g (95 mmol) of deca-1,2-diene recovered. **1h**: liquid; mixture of *Z*/*E* isomers; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.90−8.00 (m, 2 H), 7.40−7.60 (m, 3 H), 5.95−6.07 (m, 1 H), 3.97−4.18 (m, 2 H), 2.07−2.43 (m, 4 H), 1.37−1.55 (m, 2 H), 1.15−1.37 (m, 8 H), 1.01 (t, $J$ = 7.5 Hz, 3 H), 0.87 (t, $J$ = 6.3 Hz, 3 H); MS *m*/*z* 328 ($M^+$, 7.73), 43 (100); IR (neat) 1732, 1685, 1599, 1259, 1121 $cm^{-1}$. Anal. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59. Found: C, 76.81; H, 8.59.

**(I) 1-(Ethoxycarbonyl)-2,2-(cyclohexylidene)cyclopropyl Methyl Ketone (1j):** The reaction of 2-diazo-3-oxobutyric acid ethyl ester **7a** (3.11 g, 20 mmol) with vinylidenecyclohexane (9.51 g, 88 mmol) and $Rh_2(OAc)_4$ (28 mg + 20 mg, 0.11 mmol) afforded 2.71 g (57%) of **1j**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.19 (q, $J$ = 7.2 Hz, 2 H), 2.25 (s, 3 H), 2.17−2.40 (m, 4 H), 2.10−2.17 (m, 2 H), 1.40−1.70 (m, 6 H), 1.25 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 201.1, 169.1, 131.0, 114.9, 60.9, 39.9, 33.0, 32.8, 27.6, 27.2, 27.0, 25.9, 17.6, 13.8; MS *m*/*z* 236 ($M^+$, 2.37), 43 (100); IR (neat) 1733, 1705, 1293, 1104 $cm^{-1}$. HRMS calcd for $C_{14}H_{20}O_3$: 236.14125. Found: 236.14358.

**(J) 1-Acetyl-2-(cyclohexylidene)cyclopropyl Methyl Ketone (1k):** The reaction of 3-diazopenta-2,4-dione **7b** (2.52 g, 20 mmol) with vinylidenecyclohexane (6.20 g, 57 mmol) and $Rh_2(OAc)_4$ (9 mg + 12 mg, 0.05 mmol) afforded 0.92 g (22%) of **1k**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.18−2.25 (m, 2 H), 2.10−2.18 (m, 2 H), 2.05−2.10 (m, 8 H), 1.40−1.60 (m, 6 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 202.7, 131.2, 115.4, 48.0, 33.3, 33.0, 27.2, 27.1, 26.9, 25.8, 16.8; MS *m*/*z* 206 ($M^+$, 4.07), 43 (100); IR (neat) 1691, 1358, 1282 $cm^{-1}$. HRMS calcd for $C_{13}H_{18}O_2$: 206.13068. Found: 206.13239.

**(K) 1-(Benzenesulfonyl)-2-(chloromethylene)cyclopropyl Methyl Ketone (*E*-1l):** The reaction of 2-diazo-3-oxobutyric acid ester **7c** (3.36 g, 15 mmol) with 1-chloropropa-1,2-diene (9.11 g, 122 mmol) and $Rh_2(OAc)_4$ (50 mg + 30 mg + 18 mg, 0.22 mmol) afforded 0.41 g (10%) of ***E*-1l**: solid, mp 71−72 °C (petroleum ether/ether); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.90−7.97 (m, 2 H), 7.50−7.70 (m, 3 H), 6.70 (t, $J$ = 3.0 Hz, 1 H), 2.71 (dd, $J$ = 10.8 Hz, 3.0 Hz, 1 H), 2.40 (dd, $J$ = 10.8, 3.0 Hz, 1 H), 2.19 (s, 3 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 195.0, 138.2, 134.2, 129.1, 129.0, 120.8, 114.9, 56.1, 27.0, 18.0; MS *m*/*z* 273 ($M^+$ + 1 ($^{37}$Cl), 1.38), 271 ($M^+$ + 1 ($^{35}$Cl), 4.17), 43 (100); IR (neat) 1762, 1712, 1321, 1157 $cm^{-1}$. Anal. Calcd for $C_{12}H_{11}O_3SCl$: C, 53.24; H, 4.10. Found: C, 53.17; H, 4.03.

**General Procedure for the Synthesis of Methylenecyclopropyl Ketones:**[19] To an oven-dried three-necked round-bottom flask charged with a solution of methylenecyclopropyllithium (1 equiv) (prepared from the reaction of 1.2 equiv of methylenecyclopropane with 1 equiv of *n*-BuLi) was added a solution of *N*,*N*-dimethyl amide (1.2 equiv) in THF dropwise at −78 °C under Ar. After being stirred for 2 h, the mixture was poured into water, extracted with ether, and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether/$Et_2O$ = 100:1) to afford the corresponding product.

**(A) Methylenecyclopropyl Phenyl Ketone (1n):**[31] The reaction of *N*,*N*-dimethylbenzamide (6.6 g, 44 mmol) with methylenecyclopropyllithium (35 mmol) afforded 4.93 g (89%) of **1n**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.00−8.08 (m, 2 H), 7.40−7.63 (m, 3 H), 5.48−5.52 (m, 1 H), 5.40−5.45 (m, 1 H), 3.20−3.30 (m, 1 H), 2.10−2.19 (m, 1 H), 1.70−1.80 (m, 1 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 196.6, 137.4,

(31) Thomas, E. W.; Szmuszkovicz, J. R. *J. Org. Chem.* **1990**, *55*, 6054.

132.9, 132.7, 128.5, 128.2, 103.2, 22.9, 11.7; MS *m*/*z* 158 ($M^+$, 63.99), 157 (100); IR (neat) 1674, 1597, 1580 $cm^{-1}$.

**(B) Methylenecyclopropyl 4-Methylphenyl Ketone (1o):** The reaction of 25 mL of methylenecyclopropyllithium (0.78 M, 20 mmol) with *N*,*N*-dimethyl-4-methylbenzamide (4.5 g, 28 mmol) afforded 3.0 g (89%) of **1o**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.87 (d, $J$ = 8.1 Hz, 2 H), 7.22 (d, $J$ = 8.1 Hz, 2 H), 5.40−5.45 (m, 1 H), 5.32−5.38 (m, 1 H), 3.14−3.26 (m, 1 H), 2.35 (s, 3 H), 2.00−2.12 (m, 1 H), 1.60−1.75 (m, 1 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 196.2, 143.7, 134.9, 132.8, 129.2, 128.4, 103.2, 22.7, 21.5, 11.6; MS *m*/*z* 172 ($M^+$, 88.39), 119 (100); IR (neat) 1671, 1609 $cm^{-1}$. Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.64; H, 6.82.

**(C) Methylenecyclopropyl 4-Methoxylphenyl Ketone (1p):** The reaction of methylenecyclopropyllithium (30 mmol) with *N*,*N*-dimethyl-4-methoxylbenzamide (5.4 g, 30 mmol) afforded 4.9 g (87%) of **1p**: solid, mp 33−34 °C (hexanes/ether); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 8.02 (m, 2 H), 6.96 (m, 2 H), 5.46−5.52 (m, 1 H), 5.38−5.45 (m, 1 H), 3.88 (s, 3 H), 3.16−3.28 (m, 1 H), 2.05−2.18 (m, 1 H), 1.60−1.80 (m, 1 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 195.1, 163.3, 132.8, 130.4, 130.3, 113.6, 103.1, 55.3, 22.3, 11.5; MS *m*/*z* 188 ($M^+$, 61.44), 135 (100); IR (neat) 1666, 1603, 1344, 1221 $cm^{-1}$. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.58; H, 6.54.

**(D) Methylenecyclopropyl 4-Fluorophenyl Ketone (1q):** The reaction of methylenecyclopropyllithium with *N*,*N*-dimethyl 4-fluorobenzamide (5.0 g, 30 mmol) afforded 3.1 g (88%) of **1q**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.95−8.05 (m, 2 H), 7.05−7.15 (m, 2 H), 5.42−5.50 (m, 1 H), 5.35−5.40 (m, 1 H), 3.15−3.24 (m, 1 H), 2.05−2.15 (m, 1 H), 1.65−1.78 (m, 1 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 194.9, 167.2, 163.9, 133.8 (d, $^3J_{F-C}$ = 3.2 Hz), 132.5, 130.8 (d, $^2J_{F-C}$ = 9.5 Hz), 115.5 (d, $^1J_{F-C}$ = 21.9 Hz), 103.3, 22.7, 11.7; $^{19}F$ NMR (282 MHz, $CDCl_3$) $\delta$ −105.8; MS *m*/*z* 176 ($M^+$, 63.85), 123 (100); IR (neat) 1675, 1602, 1340 $cm^{-1}$. Anal. Calcd for $C_{11}H_9FO$: C, 74.99; H, 5.15. Found: C, 75.18; H, 5.35.

**(E) Methylenecyclopropyl 4-Chlorophenyl Ketone (1r):** The reaction of 40 mL of methylenecyclopropyllithium (0.70 M, 28 mmol) with *N*,*N*-dimethyl 4-chlorobenzamide (7.3 g, 40 mmol) afforded 5.1 g (95%) of **1r**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.97 (d, $J$ = 8.4 Hz, 2 H), 7.47 (d, $J$ = 8.4 Hz, 2 H), 5.49−5.53 (m, 1 H), 5.40−5.44 (m, 1 H), 3.16−3.28 (m, 1 H), 2.10−2.20 (m, 1 H), 1.70−1.83 (m, 1 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 195.5, 139.4, 135.7, 132.5, 129.7, 128.8, 103.5, 22.8, 12.0; MS *m*/*z* 194 ($M^+$ ($^{37}Cl$), 9.65), 192 ($M^+$ ($^{35}Cl$), 30.80), 139 (100); IR (neat) 1675, 1590 $cm^{-1}$. Anal. Calcd for $C_{11}H_9ClO$: C, 68.58; H, 4.71. Found: C, 68.56; H, 4.92.

**(F) Methylenecyclopropyl 4-Bromophenyl Ketone (1s):** The reaction of 25 mL of methylenecyclopropyllithium (0.78 M, 20 mmol) with *N*,*N*-dimethyl 4-bromobenzamide (5.70 g, 25 mmol) afforded 3.31 g (70%) of **1s**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.88 (d, $J$ = 8.4 Hz, 2 H), 7.62 (d, $J$ = 8.4 Hz, 2 H), 5.48−5.53 (m, 1 H), 5.40−5.45 (m, 1 H), 3.18−3.26 (m, 1 H), 2.08−2.20 (m, 1 H), 1.70−1.82 (m, 1 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 195.7, 136.1, 132.5, 131.8, 129.8, 128.1, 103.6, 22.8, 12.0; MS *m*/*z* 238 ($M^+$ ($^{81}Br$), 59.76), 236 ($M^+$ ($^{79}Br$), 60.10), 129 (100); IR (neat) 1675, 1586 $cm^{-1}$. Anal. Calcd for $C_{11}H_9BrO$: C, 55.72; H, 3.83. Found: C, 55.79; H, 4.02.

**(G) Methylenecyclopropyl 4-Iodophenyl Ketone (1t):** The reaction of 30 mL of methylenecyclopropyllithium (0.70 M, 21 mmol) with *N*,*N*-dimethyl 4-iodobenzamide (8.25 g, 30 mmol) afforded 4.49 g (73%) of **1t**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.83 (d, $J$ = 8.7 Hz, 2 H), 7.71 (d, $J$ = 8.7 Hz, 2 H), 5.45−5.52 (m, 1 H), 5.38−5.42 (m, 1 H), 3.15−3.25 (m, 1 H), 2.08−2.18 (m, 1 H), 1.70−1.80 (m, 1 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 196.0, 137.85, 136.7, 132.5, 129.7, 103.6, 101.0, 22.8, 12.1; MS *m*/*z* 284 ($M^+$, 100); IR (neat) 1671, 1581 $cm^{-1}$. Anal. Calcd for $C_{11}H_9IO$: C, 46.51; H, 3.19. Found: C, 46.32; H, 3.16.

**(H) Methylenecyclopropyl 1-Naphthyl Ketone (1u):** The reaction of 25 mL of methylenecyclopropyllithium (0.78 M, 20 mmol) with *N*,*N*-dimethyl 1-naphthoyl amide (4.98 g, 40 mmol) afforded 3.1 g (77%) of **1u**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 8.51 (d, $J$ = 8.4 Hz, 1 H), 7.92 (d, $J$ = 7.2 Hz, 2 H), 7.82 (d, $J$ = 8.1 Hz, 1 H), 7.40−7.60 (m, 3 H), 5.50−5.55 (m, 2 H), 3.10−3.20 (m, 1 H), 2.10−2.22 (m, 1 H), 1.77 (t, $J$ = 8.1 Hz, 1 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 200.7, 136.3, 133.7, 133.1, 132.3, 129.9, 128.3, 127.9, 127.7, 126.4, 125.6, 124.4, 103.4, 26.7, 12.7; MS *m*/*z* 208 ($M^+$, 56.09), 127 (100); IR (neat) 1669, 1509 $cm^{-1}$. Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.29; H, 5.85.

**(I) Methylenecyclopropyl 2-Furyl Ketone (1v):** The reaction of 25 mL of methylenecyclopropyllithium (0.78 M, 20 mmol) with *N*,*N*-dimethyl 2-furoyl amide (3.48 g, 25 mmol) afforded 2.27 g (79%) of **1v**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.53−7.57 (m, 1 H), 7.15−7.20 (m, 1 H), 6.40−6.55 (m, 1 H), 5.40−5.45 (m, 1 H), 5.30−5.40 (m, 1 H), 3.06−3.15 (m, 1 H), 1.95−2.04 (m, 1 H), 1.62−1.72 (m, 1 H);$^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 185.6, 152.6, 146.3, 132.3, 117.0, 112.0, 103.4, 22.2, 12.1; MS *m*/*z* 148 ($M^+$, 58.89), 95 (100); IR (neat) 1666, 1569 $cm^{-1}$. Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.86; H, 5.50.

**(J) Methylenecyclopropyl Phenylethyl Ketone (1w):** The reaction of 25 mL of methylenecyclopropyllithium (0.78 M, 20 mmol) with N,N-dimethyl phenylpropionamide (3.540 g, 20 mmol) afforded 2.07 g (57%) of **1w**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.10−7.40 (m, 5 H), 5.45−5.55 (m, 1 H), 5.30−5.45 (m, 1 H), 2.80−3.03 (m, 2 H), 2.65−2.80 (m, 2 H), 2.47−2.60 (m, 1 H), 1.75−1.90 (m, 1 H), 1.55−1.70 (m, 1 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 206.7, 140.8, 131.4, 128.3, 128.2, 125.9, 104.1, 42.1, 29.8, 26.6, 12.1; MS *m*/*z* 186 ($M^+$, 11.31), 91(100); IR (neat) 1699, 1604 $cm^{-1}$. Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.71; H, 7.46.

**(K) Methylenecyclopropyl 4-Methoxylphenylethyl Ketone (1x):** The reaction of 25 mL of methylenecyclopropyllithium (0.78 M, 20 mmol) with N,N-dimethyl 4-methoxylphenylpropionamide (4.14 g, 20 mmol) afforded 1.94 g (46%) of **1x**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.09 (d, $J$ = 8.4 Hz, 2 H), 6.82 (d, $J$ = 8.7 Hz, 2 H), 5.45−5.50 (m, 1 H), 5.35−5.40 (m, 1 H), 3.77 (s, 3 H), 2.80−2.90 (m, 2 H), 2.63−2.73 (m, 2 H), 2.47−2.57 (m, 1 H), 1.75−1.85 (m, 1 H), 1.58−1.70 (m, 1 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 206.9, 157.8, 132.9, 131.5, 129.1, 113.7, 104.1, 55.1, 42.4, 29.0, 26.7, 12.1; MS *m*/*z* 216 ($M^+$, 14.31), 121(100); IR (neat) 1699, 1612, 1247 $cm^{-1}$. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75, H, 7.46. Found: C, 77.64, H, 7.36.

**(L) Methylenecyclopropyl 3-Benzoxypropyl Ketone (1y):** The reaction of methylenecyclopropyllithium (19.2 mL, 0.78 M, 15 mmol) with *N*,*N*-dimethyl 3-benzoxypropionamide (4.42 g, 20 mmol) afforded 3.00 g (87%) of **1y**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.10−7.38 (m, 5 H), 5.40−5.45 (m, 1 H), 5.28−5.34 (m, 1 H), 4.41 (s, 2 H), 3.41 (t, $J$ = 6.1 Hz, 2 H), 2.40−2.52 (m, 3 H), 1.70−1.90 (m, 3 H), 1.50−1.64 (m, 1 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 207.4, 138.3, 131.7, 128.3, 127.5, 127.5, 103.9, 72.7, 69.1, 37.5, 26.5, 23.8, 12.2; MS *m*/*z* 199 (0.96), 91(100); IR (neat) 1700, 1104 $cm^{-1}$. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.76; H, 7.80.

**(M) 2-(Nonylidene)cyclopropyl Phenyl Ketone (1m).** The reaction of nonanylidenecyclopropyllithium (prepared from 3.65 g, 22 mmol with BuLi (20 mL, 1.6 M, 32 mmol)) with *N*,*N*-dimethyl benzamide (3.725 g, 25 mmol) afforded 2.91 g (54%) of **1m**: liquid, mixture of *Z*/*E* isomers, ratio = 1.8:1; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.90−8.10 (m, 2 H), 7.40−7.65 (m, 3 H), 5.77−5.90 (m, 1 H), [3.26−3.33 (m, 0.36 H), 3.20−3.26 (m, 0.64)], 2.17−2.27 (m, 1 H), 2.00−2.17 (m, 2 H), 1.65−1.82 (m, 1 H), 1.40−1.50 (m, 2 H), 1.03−1.40 (m, 10 H), 0.80−1.00 (m, 3 H); MS *m*/*z* 270 ($M^+$, 2.55), 171(100); IR (neat) 1677, 1214 $cm^{-1}$. Anal. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.53; H, 9.29.

**Typical Procedure for $PdCl_2(CH_3CN)_2$-Catalyzed Cycloisomerization (Procedure A). (A) 2-Methyl-3-(ethoxycarbonyl)-6-(*n*-heptyl)-4*H*-pyran (2a):** $PdCl_2(MeCN)_2$ (6 mg, 5 mol %) was added to a solution of **1a** (133 mg, 0.50 mmol) in 2 mL of acetone under the atmosphere of argon. The mixture was then stirred at rt for 15 min. Evaporation and chromatography on silica gel (petroleum ether/ether

100:1) under Ar afforded 106 mg (80%) of pure **2a** as an air-sensitive liquid. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.75 (t, $J$ = 3.6 Hz, 1 H), 4.10 (q, $J$ = 6.9 Hz, 2 H), 2.80−2.85 (m, 2 H), 2.17 (t, $J$ = 1.2 Hz, 3 H), 2.02 (t, $J$ = 7.2 Hz, 2 H), 1.37−1.50 (m, 2 H), 1.20−1.35 (m, 8 H), 1.22 (t, $J$ = 6.9 Hz, 3 H), 0.87 (t, $J$ = 6.6 Hz, 3 H); $^{13}$C NMR (75.4 Hz, $CDCl_3$): $\delta$ 168.2, 161.0, 150.2, 100.3, 97.3, 59.8, 32.6, 31.8, 29.0, 28.9, 26.4, 22.6, 21.9, 19.1, 14.3, 14.1; MS *m*/*z* 266 ($M^+$, 7.89), 43 (100); IR (neat) 1720, 1637, 1265, 1164 cm$^{-1}$. HRMS calcd for $C_{16}H_{26}O_3$: 266.18819. Found 266.1857.

**2-Methyl-3-(ethoxycarbonyl)-5-deutero-6-(*n*-heptyl)-4*H*-pyran (19):** Following procedure A, the reaction of **18** (120 mg, 0.45 mmol) and $PdCl_2(MeCN)_2$ (5 mg, 0.02 mmol) in 2 mL of acetone afforded 91 mg (76%) of **19**: liquid; $^1$H NMR (300 MHz, $d_6$-acetone) $\delta$ 4.77 (t, $J$ = 3.6 Hz, 0.20 H), 4.13 (q, $J$ = 7.2 Hz, 2 H), 2.80−2.90 (m, 2 H), 2.17−2.23 (m, 3 H), 2.04 (td, $J$ = 7.2, 1.2 Hz, 2 H), 1.40−1.53 (m, 2 H), 1.20−1.40 (m, 8 H), 1.24 (t, $J$ = 7.2 Hz, 3 H), 0.83−0.93 (m, 3 H); $^{13}$C NMR (75.4 Hz, $d_6$-acetone) $\delta$ 168.0, 161.1, 151.0, 101.2 (t, $J$ = 5.6 Hz), 98.2, 60.4, 33.1, 32.5, 29.8, 29.6, 27.1, 23.3, 22.6, 19.1, 14.6, 14.4; MS *m*/*z* 267 ($M^+$, 0.88), 43 (100); IR (neat) 1721, 1638, 1265, 1165 cm$^{-1}$. HRMS calcd for $C_{16}H_{25}DO_3$: 267.19447. Found 267.19418.

**Hydroboration−Oxidation Reaction of 2a (Procedure B). Synthesis of *trans*-2-Heptyl-3-hydroxy-5-(ethyloxycarbonyl)-6-methyl-3,4-dihydro-2*H*-pyran (9a):** A mixture of **1a** (266 mg, 1.0 mmol) and $PdCl_2(CH_3CN)_2$ (13 mg, 0.05 mmol) in 3 mL of $CH_2Cl_2$ was stirred for 5 min at rt to afford the crude product **1a** (procedure A). After removal of the sovlent, 5 mL of dry THF was added to the reaction tube, which was followed by the addition of 0.1 mL of 10 M $BH_3$·$SMe_2$ at 0 °C. After the mixture was stirred for 1 h at rt, 0.5 mL of 3 N NaOH and 0.5 mL of 30% $H_2O_2$ were added at 0 °C and the mixture was stirred overnight at rt. After the usual workup, the residue was purified via column chromatography on silica gel to afford 166 mg (59%) of **9a** (procedure B): solid; mp 41−42 °C ($Et_2O$/hexanes); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.15 (q, $J$ = 7.2 Hz, 2 H), 3.73−3.85 (m, 2 H), 2.45−2.63 (m, 1 H), 2.27−2.38 (m, 1 H), 2.28 (s, 3 H), 1.65−1.80 (bs, 1 H), 1.45−1.65 (m, 4 H), 1.20−1.45 (m, 8 H), 1.28 (t, $J$ = 7.1 Hz, 3 H), 0.88 (t, $J$ = 7.0 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 168.2, 163.5, 98.2, 79.6, 65.7, 59.8, 31.8, 31.2, 29.4, 29.2, 28.9, 25.2, 22.6, 20.0, 14.4, 14.1; MS *m*/*z* 284 ($M^+$, 6.62), 43 (100); IR (KBr) 3480, 1682, 1610, 1229, 1095 cm$^{-1}$. Anal. Calcd for $C_{16}H_{28}O_3$: C, 67.57; H, 9.92. Found: C, 67.59; H, 9.91.

**Hydrogenation Reaction of 2a (Procedure C). Synthesis of 2-Heptyl-5-(ethoxycarbonyl)-6-methyl-3,4-dihydro-2*H*-pyran (10a):** Following procedure A, the reaction of **1a** (170 mg, 0.64 mmol) and $PdCl_2(CH_3CN)_2$ (8 mg, 0.3 mmol) in 2.5 mL of $CH_2Cl_2$ afforded the crude product **2a**. Then 50 mg of 10% of Pd−C and 10 mL of methanol were added. The mixture was stirred for 17 h at 50 °C under 10 atm of $H_2$. After the usual workup, the reaction afforded 104 mg (60%) of **10a** (procedure C): liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.13 (q, $J$ = 7.2 Hz, 2 H), 3.72−3.82 (m, 1 H), 2.30−2.44 (m, 1 H), 2.10−2.28 (m, 1 H), 2.20 (s, 3 H), 1.80−1.90 (m, 1 H), 1.56−1.70 (m, 1 H), 1.37−1.56 (m, 3 H), 1.20−1.37 (m, 9 H), 1.25 (t, $J$ = 6.9 Hz, 3 H), 0.86 (t, $J$ = 6.6 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 168.8, 164.8, 100.8, 76.5, 59.5, 34.8, 31.8, 29.5, 29.2, 26.7, 25.2, 22.6, 21.4, 20.4, 14.4, 14.1; MS *m*/*z* 268 ($M^+$, 24.80), 97 (100); IR (neat) 1708, 1623, 1271, 1086 cm$^{-1}$. HRMS cacld for $C_{16}H_{28}O_3$: 268.20385. Found: 268.19920.

**(B) 2-Methyl-3-(ethoxycarbonyl)-6-(*n*-butyl)-4*H*-pyran (2b):** Following procedure A, the reaction of **1b** (112 mg, 0.5 mmol) and $PdCl_2(MeCN)_2$ (5 mg, 0.02 mmol) in 2 mL of acetone afforded 84 mg (75%) of **2b**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.62−4.68 (m, 1 H), 4.14 (q, $J$ = 6.9 Hz, 2 H), 2.80−2.88 (m, 2 H), 2.20 (t, $J$ = 1.2 Hz, 3 H), 2.00 (t, $J$ = 6.9 Hz, 2 H), 1.20−1.48 (m, 4 H), 1.25 (t, $J$ = 6.9 Hz, 3 H), 0.88 (t, $J$ = 6.9 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $d_6$-acetone): $\delta$ 168.0, 161.1, 151.0, 101.2, 98.2, 60.3, 32.9, 29.3, 22.7, 22.6, 19.1, 14.6, 14.1; MS *m*/*z* 224 ($M^+$, 3.96), 43 (100); IR (neat) 1720, 1637, 1268, 1072 cm$^{-1}$. HRMS calcd for $C_{13}H_{20}O_3$: 224.14124. Found: 224.13774.

**Hydroboration−Oxidation Reaction of 2b. Synthesis of *trans*-2-Butyl-3-hydroxy-5-(ethyloxycarbonyl)-6-methyl-3,4-dihydro-2*H*-pyran (9b):** Following procedure A, the reaction of **1b** (224 mg, 1.0 mmol) and $PdCl_2(CH_3CN)_2$ (13 mg, 0.05 mmol) in 3 mL of $CH_2Cl_2$ afforded the crude product **2b**. Following procedure B, the reaction of **2b**, $BH_3$·$Et_2O$ (0.80 mmol/mL) (1 mL, 0.80 mmol), THF (5 mL), NaOH (3 M) (0.5 mL, 1.5 mmol), and $H_2O_2$ (30%) (0.5 mL) afforded 136 mg (59%) of **9b** as solid, mp 65−66 °C (ether/hexanes). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.15 (q, $J$ = 7.2 Hz, 2 H), 3.70−3.88 (m, 2 H), 2.55−2.65 (m, 1 H), 2.20−2.38 (m, 1 H), 2.25 (s, 3 H), 1.77−1.84 (bs, 1 H), 1.43−1.70 (m, 3 H), 1.20−1.43 (m, 3 H), 1.27 (t, $J$ = 7.2 Hz, 3 H), 0.91 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 168.2, 163.5, 98.2, 79.6, 65.7, 59.8, 30.9, 28.9, 27.4, 22.6, 20.0, 14.4, 14.0; MS *m*/*z* 242 ($M^+$, 10.71), 43 (100); IR (KBr) 3466, 1690, 1619, 1236, 1067 cm$^{-1}$. Anal. Calcd for $C_{13}H_{22}O_3$: C, 64.44; H, 9.15. Found: C, 64.38; H, 9.15.

**Hydrogenation Reaction of 2b. Synthesis of 2-Butyl-5-(ethyloxycarbonyl)-6-methyl-3,4-dihydro-2*H*-pyran (10b):** Following procedure A, the reaction of **1b** (224 mg, 1.0 mmol) and $PdCl_2(CH_3CN)_2$ (13 mg, 0.05 mmol) in 2 mL of $CH_2Cl_2$ afforded the crude product **2b**. Then following procedure C, the reaction of **2b**, 50 mg of 10% of Pd−C in 10 mL of methanol under 10 atm of $H_2$ at 50 °C afforded 112 mg (50%) of **10b** as a liquid. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.13 (q, $J$ = 7.2 Hz, 2 H), 3.72−3.85 (m, 1 H), 2.30−2.44 (m, 1 H), 2.10−2.28 (m, 1 H), 2.20 (s, 3 H), 1.78−1.90 (m, 1 H), 1.56−1.73 (m, 1 H), 1.20−1.56 (m, 6 H), 1.25 (t, $J$ = 7.2 Hz, 3 H), 0.90 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 168.8, 164.8, 100.8, 76.5, 59.4, 34.5, 27.3, 26.6, 22.6, 21.4, 20.4, 14.4, 14.0; MS *m*/*z* 226 ($M^+$, 17.02), 97 (100); IR (neat) 1707, 1623, 1272, 1087 cm$^{-1}$. HRMS calcd for $C_{13}H_{22}O_3$: 226.15690. Found: 226.15489.

**(C) 2-Methyl-3-(ethoxycarbonyl)-6-benzyl-4*H*-pyran (2c):** Following procedure A, the reaction of **1c** (150 mg, 0.58 mmol) and $PdCl_2(MeCN)_2$ (5 mg, 0.02 mmol) in 2 mL of $CH_2Cl_2$ afforded 120 mg (80%) of **2c**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.12−7.30 (m, 5 H), 4.60−4.68 (m, 1 H), 4.08 (q, $J$ = 7.2 Hz, 2 H), 3.26 (s, 2 H), 2.78−2.82 (m, 2 H), 2.12 (t, $J$ = 0.9 Hz, 3 H), 1.19 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 168.0, 160.9, 149.2, 137.2, 128.9, 128.3, 126.5, 100.4, 99.3, 59.9, 39.1, 22.0, 19.1, 14.3; MS *m*/*z* 258 ($M^+$, 4.27), 229 (100); IR (neat) 1720, 1638 cm$^{-1}$. HRMS calcd for $C_{16}H_{18}O_3$: 258.12559. Found: 258.13650.

**Hydroboration−Oxidation Reaction of 2c. Synthesis of *trans*-2-Benzyl-3-hydroxy-5-(ethyloxycarbonyl)-6-methyl-3,4-dihydro-2*H*-pyran (9c):** Following procedure A, the reaction of **1c** (258 mg, 1.0 mmol) and $PdCl_2(CH_3CN)_2$ (7.8 mg, 0.03 mmol) in 2 mL of $CH_2Cl_2$ afforded the crude product **2c**. Following procedure B, the reaction of **2c**, $BH_3$·$SMe_2$ (10 M) (0.8 mL,0.80 mmol), NaOH (3 M) (0.5 mL, 1.5 mmol), and $H_2O_2$ (30%) (0.5 mL) in 5 mL of THF afforded 149 mg (54%) of **9c** as solid, mp 70−71 °C ($Et_2O$/hexanes). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.15−7.40 (m, 5 H), 4.15 (q, $J$ = 7.5 Hz, 2 H), 4.02−4.10 (m, 1 H), 3.75 (q, $J$ = 5.7 Hz, 1 H), 2.80−3.00 (m, 2 H), 2.66 (ddd, $J$ = 16.5, 5.1 and 1.2 Hz, 1 H), 2.28−2.40 (m, 1 H), 2.23 (s, 3 H), 1.92 (bs, 1 H), 1.28 (t, $J$ = 7.5 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 168.1, 163.4, 136.99, 129.42, 128.4, 126.6, 98.5, 80.0, 64.9, 59.9, 37.4, 29.1, 19.9, 14.6; MS *m*/*z* 276 ($M^+$, 3.54), 146 (100); IR (KBr) 3464, 1684, 1623, 1230 cm$^{-1}$. Anal. Calcd for $C_{16}H_{20}O_3$: C, 69.55; H, 7.29. Found: C, 69.61; H, 7.32.

**Hydrogenation Reaction of 2c. Synthesis of 2-Benzyl-5-(ethyloxycarbonyl)-6-methyl-3,4-dihydro-2*H*-pyran (10c):** Following procedure A, the reaction of **1c** (100 mg, 0.38 mmol) and $PdCl_2(CH_3CN)_2$ (13 mg, 0.05 mmol) in 2 mL of $CH_2Cl_2$ afforded the crude product **2c**. Following procedure C, the reaction of **2c** and 50 mg of 10% of Pd−C in 10 mL of methanol under 10 atm of $H_2$ at 50 °C afforded 54 mg (54%) of **10c**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.18−7.36 (m, 5 H), 4.14 (q, $J$ = 6.9 Hz, 2 H), 3.95−4.08 (m, 1 H), 3.02 (dd, $J$ = 13.2, 6.6 Hz, 1 H), 2.79 (dd, $J$ = 13.8, 6.6 Hz, 1 H), 2.36−2.44 (m, 1 H), 2.23 (s, 3 H), 2.10−2.25 (m, 1 H), 1.80−1.90 (m, 1 H), 1.40−

1.58 (m, 1 H), 1.27 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 168.6, 164.5, 137.5, 129.5, 128.3, 126.5, 101.0, 77.0, 59.5, 41.1, 25.8, 21.2, 20.4, 14.4; MS *m*/*z* 260 ($M^+$, 0.63), 130 (100); ESI-MS 283.2 ($M + Na^+$); IR (neat) 1704, 1624, 1271, 1076 cm$^{-1}$. HRMS calcd for $C_{16}H_{20}O_3$ Na: 283.13040. Found: 283.13047.

**(D) 2-Methyl-3-(ethoxycarbonyl)-6-(3′-*tert*-butyldimethylsilyloxypropyl)-4*H*-pyran (2d):** Following procedure A, the reaction of **1d** (130 mg, 0.38 mmol) and $PdCl_2(MeCN)_2$ (5 mg, 0.02 mmol) in 3 mL of benzene afforded 110 mg (85%) of **2d**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.68 (t, $J = 3.3$ Hz, 1 H), 4.14 (q, $J = 7.2$ Hz, 2 H), 3.61(t, $J = 5.7$ Hz, 2 H), 2.80−2.86 (m, 2 H), 2.20 (s, 3 H), 2.08 (t, $J = 7.2$ Hz, 2 H), 1.60−1.70 (m, 2 H), 1.26 (t, $J = 7.2$ Hz, 3 H), 0.88 (s, 9 H), 0.03 (s, 6 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 168.1, 160.9, 149.7, 100.3, 97.7, 62.1, 59.8, 29.5, 29.0, 25.9, 21.9, 19.1, 18.3, 14.3, −5.4; MS *m*/*z* 340 ($M^+$, 1.68), 75 (100); IR (neat) 1720, 1638 cm$^{-1}$. HRMS calcd for $C_{18}H_{32}O_4Si$: 340.20699. Found: 340.20632.

**Hydroboration−Oxidation Reaction of 2d. Synthesis of *trans*-2-(3′-*tert*-Butyldimethylsilanyloxypropyl)-3-hydroxy-5-(ethyloxycarbonyl)-6-methyl-3,4-dihydro-2*H*-pyran (9d):** Following procedure A, the reaction of **1d** (150 mg, 0.44 mmol) and $PdCl_2(CH_3CN)_2$ (5 mg, 0.02 mmol) in 2 mL of $CH_2Cl_2$ afforded the crude product **2d**. Then following procedure B, the reaction of **2d**, $BH_3{\cdot}SMe_2$ (10 M) (1 mL, 1 mmol), NaOH (3 M) (1 mL, 3 mmol), and $H_2O_2$ (30%) (1 mL) in 5 mL of THF afforded 58 mg (37%) of **9d**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.14 (q, $J = 7.5$ Hz, 2 H), 3.68−3.85 (m, 2 H), 3.64 (t, $J = 5.1$ Hz, 2 H), 2.55−2.65 (m, 1 H), 2.24−2.38 (m, 1 H), 2.23 (s, 3 H), 1.66−1.80 (m, 2 H), 1.60−1.66 (m, 1 H), 1.54−1.64 (m, 2 H), 1.27 (t, $J = 7.2$ Hz, 3 H), 0.88 (s, 9 H), 0.05 (s, 6 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 168.2, 163.6, 98.5, 79.5, 65.7, 62.9, 59.8, 29.3, 28.0, 27.4, 25.9, 19.9, 18.3, 14.3, −5.3; ESI-MS 381.3 [$M + Na^+$]; IR (neat) 3404, 1708, 1689, 1625, 1230, 1096 cm$^{-1}$. HRMS for $C_{18}H_{34}O_5SiNa$: 381.20677. Found: 381.20531.

**(E) 2-Methyl-3-acetyl-6-(*n*-heptyl)-4*H*-pyran (2e):** Following procedure A, the reaction of **1e** (134 mg, 0.57 mmol) and $PdCl_2(MeCN)_2$ (10 mg, 0.04 mmol) in 2.5 mL of acetone afforded 80 mg (60%) of **2e**: liquid; $^1$H NMR (300 MHz, $d_6$-acetone) $\delta$ 4.81 (t, $J = 3.6$ Hz, 1 H), 2.92−3.00 (m, 2 H), 2.14 (s, 3 H), 2.12 (t, $J = 1.2$ Hz, 3 H), 2.04 (td, $J = 6.9$ Hz, 1.2 Hz, 2 H), 1.40−1.52 (m, 2 H), 1.20−1.40 (m, 8 H), 0.88 (t, $J = 6.9$ Hz, 3 H); $^{13}$C NMR (75.4 MHz, $d_6$-acetone) $\delta$ 198.8, 159.6, 151.2, 109.4, 98.4, 33.3, 32.7, 29.9, 29.8, 29.7, 27.2, 23.6, 23.4, 19.8, 14.5; MS *m*/*z* 236 ($M^+$, 46.60), 43(100); IR (neat) 1716, 1682, 1595 cm$^{-1}$. HRMS calcd for $C_{15}H_{24}O_2$: 236.17763. Found: 237.17411.

**(F) 2-Methyl-3-(benzenesulfonyl)-6-heptyl-4*H*-pyran (2f):** Following procedure A, the reaction of **1f** (158 mg, 0.47 mol) and $PdCl_2(MeCN)_2$ (7 mg, 0.027 mmol) in 4 mL of benzene afforded 89 mg (56%) of **2f**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.83−7.90 (m, 2 H), 7.50−7.65 (m, 3 H), 4.63 (t, $J = 3.6$ Hz, 1 H), 2.85−2.95 (m, 2 H), 2.30 (s, 3 H), 1.96 (t, $J = 2.7$ Hz, 2 H), 1.32−1.50 (m, 2 H), 1.18−1.32 (m, 8 H), 0.86 (t, $J = 6.9$ Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 158.7, 150.4, 141.2, 133.0, 129.0, 127.0, 110.1, 96.4, 32.3, 31.7, 29.0, 28.9, 26.2, 22.6, 22.2, 18.1, 14.1; MS *m*/*z* 334 ($M^+$, 32.11), 192 (100); IR (neat) 1715, 1637, 1305, 1149, 725 cm$^{-1}$. HRMS calcd for $C_{19}H_{26}O_3S$: 334.16026. Found: 334.16283.

**Hydroboration−Oxidation Reaction of 2f. Synthesis of *trans*-2-Heptyl-3-hydroxy-5-(phenylsulfonyl)-6-methyl-3,4-dihydro-2*H*-pyran (9f):** Following procedure A, the reaction of **1f** (334 mg, 1 mmol) and $PdCl_2(CH_3CN)_2$ (6.5 mg, 0.03 mmol) in 2 mL of $CH_2Cl_2$ afforded the crude product **2f**. Then following procedure B, the reaction of **2f**, $BH_3{\cdot}SMe_2$ (10 M) (0.6 mL,0.80 mmol), NaOH (3 M) (0.6 mL, 1.5 mmol), and $H_2O_2$ (30%) (0.6 mL) in 4 mL of THF afforded 194 mg (55%) of **9f**: solid; mp 92−93 °C ($CH_2Cl_2$/hexanes); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.75−8.00 (m, 2 H), 7.40−7.65 (m, 3 H), 3.70−3.85 (m, 2 H), 2.55−2.70 (m, 1 H), 2.25−2.40 (m, 1 H), 2.28 (s, 3 H), 1.93 (d, $J = 5.4$ Hz, 1 H), 1.15−1.75 (m, 12 H), 0.87 (t, $J = 6.9$ Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 161.59, 142.13, 132.72, 129.08, 126.66, 107.69, 80.00, 65.37, 31.73, 31.03, 29.43, 29.33, 29.09, 25.03, 22.61, 18.90, 14.09; MS *m*/*z* 352 ($M^+$, 4.52), 211 (100); IR (KBr) 3496, 1630, 1297 cm$^{-1}$; Anal. Calcd for $C_{19}H_{28}SO_4$: C, 64.74; H, 8.01. Found C, 64.71; H, 8.01.

**(G) 2-Methyl-3-(benzenesulfonyl)-6-(*n*-butyl)-4*H*-pyran (2g):** Following procedure A, the reaction of **1g** (120 mg, 0.41 mmol) and $PdCl_2(MeCN)_2$ (5 mg, 0.02 mmol) in 2 mL of acetone afforded 109 mg (91%) of **2g**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.80−7.90 (m, 2 H), 7.45−7.60 (m, 3 H), 4.60−4.66 (m, 1 H), 2.84−2.90 (m, 2 H), 2.29 (t, $J = 1.2$ Hz, 3 H), 1.96 (t, $J = 6.9$ Hz, 2 H), 1.20−1.42 (m, 4 H), 0.86 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (75.4 MHz., $CDCl_3$) $\delta$ 158.6, 150.3, 141.1, 132.9, 129.0, 126.9, 110.1, 96.4, 32.0, 28.3, 22.2, 22.0, 18.0, 13.7; MS *m*/*z* 292 ($M^+$, 20.36), 150 (100); IR (neat) 1715, 1638, 1306, 1149 cm$^{-1}$. HRMS calcd for $C_{16}H_{20}O_3S$: 292.11332. Found: 292.11486.

**Hydroboration−Oxidation Reaction of 2g. Synthesis of 2-Butyl-3-hydroxy-5-(phenylsulfonyl)-6-methyl-3,4-dihydro-2*H*-pyran (9g):** Following procedure A, the reaction of **1g** (292 mg, 1 mmol) and $PdCl_2(CH_3CN)_2$ (6.5 mg, 0.03 mmol) in 2 mL of $CH_2Cl_2$ afforded the crude product **2g**. Then following procedure B, the reaction of **2g**, $BH_3{\cdot}SMe_2$ (10 M) (0.8 mL, 0.80 mmol), NaOH (3 M) (0.5 mL, 1.5 mmol), and $H_2O_2$ (30%) (0.5 mL) in 5 mL of THF afforded 198 mg (64%) of **9g**: solid; mp 88−89 °C ($CH_2Cl_2$/hexanes); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.80−7.90 (m, 2 H), 7.45−7.60 (m, 3 H), 3.70−3.85 (m, 2 H), 2.55−2.70 (m, 1 H), 2.25−2.40 (m, 1 H), 2.29 (s, 3 H), 1.70−1.85 (bs, 1 H), 1.20−1.70 (m, 6 H), 0.88 (t, $J = 6.6$ Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 161.7, 142.1, 132.7, 129.1, 126.6, 107.6, 80.0, 65.3, 30.7, 29.4, 27.1, 22.4, 18.9, 13.9; MS *m*/*z* 310 ($M^+$, 8.98), 43 (100); IR (KBr) 3499, 1628, 1296, 1157, 724 cm$^{-1}$; Anal. Calcd for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14. Found C, 62.03; H, 6.85.

**(H) 2-Phenyl-3-(ethoxycarbonyl)-6-heptyl-4*H*-pyran (2h):** Following procedure A, the reaction of **1h** (85 mg, 0.26 mol) and $PdCl_2(MeCN)_2$ (4 mg, 0.015 mmol) in 3 mL of benzene afforded 82 mg (96%) of **2h**: air-sensitive solid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.30−7.40 (m, 5H), 4.76 (t, $J = 3.4$ Hz, 1 H), 3.95 (q, $J = 7.2$ Hz, 2 H), 3.05 (d, $J = 3.4$ Hz, 2 H), 2.07 (t, $J = 7.2$ Hz, 2 H), 1.40−1.55 (m, 2 H), 1.17−1.40 (m, 8 H), 0.93 (t, $J = 7.2$ Hz, 3 H), 0.88 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 168.1, 159.1, 151.1, 135.8, 129.0, 128.2, 127.7, 102.1, 96.9, 59.9, 32.6, 31.7, 29.0, 28.9, 26.4, 22.7, 22.6, 14.1, 13.6; MS *m*/*z* 328 ($M^+$, 7.52), 299 (100); IR (neat) 1717, 1290, 1260 cm$^{-1}$. HRMS calcd for $C_{21}H_{28}O_3$: 328.20385. Found: 328.20476.

**(I) 2-Methyl-3-(ethoxycarbonyl)-1-oxa-spiro[5,5]undeca-2,4-diene (8j):** Following procedure A, the reaction of **1j** (128 mg, 0.54 mol) and $PdCl_2(MeCN)_2$ (8 mg, 0.03 mmol) in 3 mL of benzene afforded 123 mg (96%) of **8j**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.32 (d, $J = 9.9$ Hz, 1 H), 5.16 (d, $J = 9.9$ Hz, 1 H), 4.16 (q, $J = 6.9$ Hz, 2 H), 2.28 (s, 3 H), 1.78−1.90 (m, 2 H), 1.30−1.77 (m, 8 H), 1.27 (t, $J = 6.9$ Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 166.5, 165.9, 120.2, 120.2, 103.6, 78.9, 59.7, 35.8, 25.2, 21.1, 20.1, 14.3; MS *m*/*z* 236 ($M^+$, 32.01), 193 (100); IR (neat) 1710, 1636, 1581, 1269, 1103 cm$^{-1}$. HRMS calcd for $C_{14}H_{20}O_3$: 236.14125. Found: 236.14293.

**(J) 2-Methyl-3-(benzenesulfonyl)-5-chloro-4*H*-pyran (20l):** Following procedure A, the reaction of **1l** (135 mg, 0.5 mmol) and $PdCl_2(MeCN)_2$ (13 mg, 0.05 mmol) in 2 mL of benzene afforded 103 mg (76%) of **20l**: solid; mp 103−105 °C (*n*-hexane/ether); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.83−7.90 (m, 2 H), 7.50−7.68 (m, 3 H), 6.45 (t, $J = 1.5$ Hz, 1 H), 3.14 (s, 3 H), 2.31 (bs, 2 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 157.3, 140.4, 136.0, 133.5, 129.3, 127.1, 113.6, 110.3, 28.8, 17.4; MS *m*/*z* 272 ($M^+$ ($^{37}$Cl), 9.49), 270 ($M^+$ ($^{35}$Cl), 24.65), 128 (100); IR (KBr) 1699, 1637, 1206, 1143 cm$^{-1}$. HRMS calcd for $C_{12}H_{11}O_3SCl$: 270.00837. Found: 270.00919. Anal. Calcd for $C_{12}H_{11}O_3SCl$: C, 53.24; H, 4.10. Found: C, 53.36; H, 4.14.

**(K) 2-Phenyl-6-(*n*-octyl)-4*H*-pyran (2m):** Following procedure A, the reaction of **1m** (135 mg, 0.05 mmol) and $PdCl_2(MeCN)_2$ (6.5 mg, 0.025 mmol) in 1 mL of benzene afforded 94 mg (70%) of **2m**: liquid; $^1$H NMR (300 MHz, $d_6$-acetone) $\delta$ 7.54−7.68 (m, 2 H), 7.24−7.40

(m, 3 H), 5.40−5.48 (m, 1 H), 4.60−4.68 (m, 1 H), 2.80−2.90 (m, 2 H), 2.15(t, $J$ = 7.2 Hz, 2 H), 1.50−1.68 (m, 2 H), 1.22−1.44 (m, 10 H), 0.87 (t, $J$ = 6.9 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 151.9, 149.1, 134.9, 128.1, 127.9, 124.2, 96.5, 94.7, 33.5, 31.8, 31.6, 29.1, 29.1, 26.7, 22.7, 21.4, 14.1; MS *m*/*z* 270 ($M^+$, 3.03), 105 (100); IR (neat): 1706, 1654, 754 cm$^{-1}$. HRMS calcd for $C_{19}H_{26}O$: 270.19837. Found: 270.19765.

**Typical Procedure for NaI-Catalyzed Cycloisomerization (Procedure D). (A) 3-Octylidene-4-(ethoxycarbonyl)-5-methyl-2,3-dihydrofuran (3a):** A solution of **1a** (134 mg, 0.5 mmol) and NaI (4 mg, 0.027 mmol, 5 mol %) in 4 mL of acetone was refluxed for 11 h. Evaporation and flash chromatography on silica gel afforded 106 mg (79%) of **3a** (procedure D): liquid; mixture of *Z*/*E* isomers, ratio = 2.3:1; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.75−5.84 (m, 1 H), [4.93−5.01 (m, 1.4 H); 4.87−4.93 (m, 0.6 H)], [4.23 (q, $J$ = 7.2 Hz, 0.6 H); 4.22 (q, $J$ = 7.2 Hz, 1.4 H)], [2.28 (s, 2.1 H); 2.19 (s, 0.9 H)], [2.10−2.22 (m, 0.6 H); 1.82−1.95 (m, 1.4 H)], 1.20−1.43 (m, 10 H), 1.34 (t, $J$ = 7.2 Hz, 3 H), 0.87 (t, $J$ = 6.6 Hz, 3 H); MS *m*/*z* 266 ($M^+$, 77.83), 168 (100); IR (neat) 1704, 1613, 1172, 1085 cm$^{-1}$. HRMS calcd for $C_{16}H_{26}O_3$: 266.18819. Found: 266.18844.

**(B) 3-Pentylidene-4-(ethoxycarbonyl)-5-methyl-2,3-dihydrofuran (3b):** Following procedure D, the reaction of **1b** (112 mg, 0.5 mmol) and NaI (4 mg, 0.027 mmol) in 2 mL of acetone afforded 51 mg (46%) of **3b**: liquid; mixture of *Z*/*E* isomers, ratio = 3:1; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.75−5.85 (m, 1 H), [4.94−5.10 (m, 1.5 H); 4.90−4.94 (m, 0.5 H)], 4.17−4.40 (m, 2 H), [2.29 (s, 2.3 H); 2.19 (s, 0.7 H)], [2.10−2.20 (m, 0.5 H); 1.80−1.95 (m, 1.5 H)], 1.20−1.50 (m, 4 H), 1.33 (t, $J$ = 7.2 Hz, 3 H), 0.90 (q, $J$ = 6.9 Hz, 3 H); MS *m*/*z* 224 ($M^+$, 100); IR (neat) 1713, 1608, 1255, 1099 cm$^{-1}$. HRMS calcd for $C_{13}H_{20}O_3$: 224.14124. Found: 224.14282.

**(C) 3-((2′-Phenyl)ethylidene)-4-(ethoxycarbonyl)-5-methyl-2,3-dihydrofuran (3c):** Following procedure D, the reaction of **1c** (123 mg, 0.5 mmol) and NaI (4 mg, 0.027 mmol) in 2 mL of acetone afforded 95 mg (80%) of **3c**: liquid; mixture of *Z*/*E* isomers, ratio = 1.5:1; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.15−7.35 (m, 5 H), [6.05−6.15 (m, 0.6 H); 5.13−5.20 (m, 0.4 H)], [5.03−5.08 (m, 1.3 H); 4.96−5.01 (m, 0.7 H)], 4.25 (q, $J$ = 7.5 Hz, 2 H), [3.60−3.68 (m, 0.7 H); 3.30 (d, $J$ = 7.8 Hz, 1.3 H)], [2.34 (s, 1.9 H); 2.27 (s, 1.1 H)], [1.33 (t, $J$ = 7.5 Hz, 1.8 H); 1.29 (t, $J$ = 7.5 Hz, 1.2 H)]; MS *m*/*z* 258 ($M^+$, 72.01), 137 (100); IR (neat) 1700, 1606, 1299, 1100 cm$^{-1}$; HRMS calcd for $C_{16}H_{18}O_3$: 258.12559. Found: 258.12661.

**(D) 3-Octylidene-4-acetyl-5-methyl-2,3-dihydrofuran (3e):** Following procedure D, the reaction of **1e** (120 mg, 0.5 mmol) and NaI (4 mg, 0.027 mmol) in 2 mL of acetone afforded 95 mg (79%) of ***E*-3e** and ***Z*-3e**: mixture of *Z*/*E* isomers, ratio = 1.9:1. ***E*-3e**: liquid; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 4.70−4.80 (m, 1 H), 4.54 (dd, $J$ = 4.8 Hz, 2.1 Hz, 2 H), 2.00−2.18 (m, 2 H), 2.06 (s, 3 H), 1.82 (s, 3 H), 1.10−1.40 (m, 10 H), 0.89 (t, $J$ = 7.5 H, 3 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 194.55, 171.32, 135.77, 118.28, 115.02, 76.54, 32.25, 30.63, 30.54, 30.26, 29.68, 23.07, 14.69, 14.37; MS *m*/*z* 236 ($M^+$, 14.79), 138 (100); IR (neat) 1669, 1410 cm$^{-1}$. HRMS calcd for $C_{15}H_{24}O_2$: 236.17763. Found: 236.17520. ***Z*-3e**: liquid, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.62−5.72 (m, 1 H), 4.80−4.86 (m, 2 H), 2.24 (s, 3 H), 2.20 (s, 3 H), 1.76−1.84 (m, 2 H), 1.24−1.38 (m, 2 H), 1.10−1.24 (m, 8 H), 0.77 (t, $J$ = 7.0 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 194.09, 174.86, 135.30, 115.99, 115.79, 73.99, 31.71, 30.94, 30.02, 29.25, 29.24, 29.10, 22.54, 16.36, 13.98; MS *m*/*z* 236 ($M^+$, 7.39), 43 (100); IR (neat) 1775, 1695, 1671, 1362 cm$^{-1}$. HRMS calcd for $C_{15}H_{24}O_2$: 236.17763. Found: 236.18120.

**(E) 3(*E*)-Pentylidene-4-(benzenesulfonyl)-5-methyl-2,3-dihydrofuran (*E*-3g):** Following procedure D, the reaction of **1g** (145 mg, 0.5 mmol) and NaI (4 mg, 0.027 mmol) in 2 mL of acetone afforded 113 mg (78%) of ***E*-3g**: solid; mp 54−56 °C (petroleum ether/ether). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.85−7.92 (m, 2 H), 7.45−7.65 (m, 3 H), 5.47−5.58 (m, 1 H), 4.90−4.95 (m, 2 H), 2.39 (s, 3 H), 1.77−1.87 (m, 2 H), 1.10−1.36 (m, 4 H), 0.82 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 172.8, 142.2, 132.8, 132.0, 128.8, 126.4, 115.6, 114.0, 73.9, 31.1, 29.4, 22.1, 14.5, 13.9; MS *m*/*z* 292 ($M^+$, 42.32), 108 (100.00); IR (KBr) 1598, 1303, 1150 cm$^{-1}$. HRMS calcd for $C_{16}H_{20}O_3S$: 292.11332. Found: 292.11430. Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.72; H, 6.89. Found: C, 65.70; H, 6.78.

**(F) 3-Octylidene-4-(ethoxycarbonyl)-5-phenyl-2,3-dihydrofuran (3h):** Following procedure D, the reaction of **1h** (164 mg, 0.5 mmol) and NaI (10 mg, 0.06 mmol) in 2 mL of acetone afforded 135 mg (79%) of **3h**: liquid; mixture of *Z*/*E* isomers, ratio = 3.3:1; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.55−7.68 (m, 2 H), 7.30−7.47 (m, 3 H), 5.86−5.97 (m, 1 H), [5.11−5.17 (m, 1.54 H); 5.06−5.11 (m, 0.46 H)], [4.24 (q, $J$ = 7.5 Hz, 0.46 H); 4.18 (q, $J$ = 7.5 Hz, 1.54 H)], [2.02−2.17 (m, 0.46 H); 1.92−2.02 (m, 1.54 H)], 1.20−1.53 (m, 10 H), 1.18 (t, $J$ = 7.5 Hz, 3 H), 0.82−0.95 (m, 3 H); MS *m*/*z* 328 ($M^+$, 34.66), 230 (100); IR (neat) 1706, 1591, 1379, 1096 cm$^{-1}$. HRMS calcd for $C_{21}H_{28}O_3$: 328.20385. Found: 328.20240.

**(7) 3-Cyclohexylidene-4-acetyl-5-methyl-2,3-dihydrofuran (3k):** Following procedure D, the reaction of **1k** (106 mg, 0.5 mmol) and NaI (5 mg, 0.033 mmol) in 2 mL of acetone afforded 62 mg (58%) of **3k**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.93 (s, 2H), 2.20 (s, 3 H), 2.01 (s, 3 H), 1.87−2.00 (m, 4 H), 1.40−1.55 (m, 6 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 197.8, 168.7, 127.5, 125.0, 118.1, 74.7, 32.4, 32.2, 30.3, 27.3, 27.0, 26.0, 14.1; MS *m*/*z* 206 ($M^+$, 42.61), 43 (100); IR (neat) 1672, 1594 cm$^{-1}$. HRMS calcd for $C_{13}H_{18}O_2$: 206.13068. Found: 206.13107.

**Typical Procedure for $PdCl_2(CH_3CN)_2$ and NaI-Catalyzed Cycloisomerization (Procedure E). (A) 2-Methyl-3-(ethoxycarbonyl)-4-(*n*-heptyl)furan (4a):** A solution of **1a** (356 mg, 1.3 mmol), NaI (400 mg, 2.6 mmol), and $PdCl_2(CH_3CN)_2$ (17 mg, 0.65 mmol) in 5 mL of acetone was refluxed for 10 h. Evaporation and flash chromatography on silica gel afforded 265 mg (74%) of **4a** (procedure E). A solution of **1a** (139 mg, 0.5 mmol) and sodium iodide (77 mg, 0.5 mmol) in 1 mL of acetone was stirred under reflux for 24 h. Evaporation and chromatography on silica gel (petroleum ether/ether 100:1) afforded 104 mg (75%) of **4a** (procedure D): liquid; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 6.85 (s, 1 H), 4.06 (q, $J$ = 7.2 Hz, 2 H), 2.65 (t, $J$ = 7.5 Hz, 2 H), 2.40 (s, 3 H), 1.50−1.63 (m, 2 H), 1.15−1.40 (m, 10 H), 1.01 (t, $J$ = 7.2 Hz, 3 H), 0.87 (t, $J$ = 7. 2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 164.2, 160.1, 137.7, 126.9, 113.6, 59.7, 32.3, 30.2, 30.1, 30.0, 29.8, 25.3. 23.1, 14.41, 14.36, 14.34; MS *m*/*z* 266 ($M^+$, 1.14), 168 (100); IR (neat) 1716, 1607, 1559, 1301, 1099 cm$^{-1}$. HRMS calcd for $C_{16}H_{26}O_3$: 266.18819. Found: 266.18641.

**(B) 2-Methyl-3-(ethoxycarbonyl)-4-*n*-pentylfuran (4b):** Following procedure E, the reaction of **1b** (178 mg, 0.8 mmol), NaI (150 mg, 1 mmol), and $PdCl_2(CH_3CN)_2$ (4 mg, 0.015 mmol) in 2.5 mL of acetone afforded 132 mg (74%) of **4b**. Following procedure D, the reaction of **1b** (108 mg, 0.5 mmol) and NaI (76 mg, 0.5 mmol) in 4 mL acetone afforded 99 mg (92%) of **4b**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.99 (s, 1 H), 4.26 (q, $J$ = 7.2 Hz, 2 H), 2.54 (t, $J$ = 7.5 Hz, 2 H), 2.51 (s, 3 H), 1.44−1.60 (m, 2 H), 1.22−1.38 (m, 4 H), 1.33 (t, $J$ = 7.2 Hz, 3 H), 0.87 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 164.6, 160.1, 137.2, 126.2, 112.8, 59.7, 31.7, 29.2, 24.7, 22.5, 14.3, 14.2, 14.0; MS *m*/*z* 224 ($M^+$, 17.47), 168 (100); IR (neat) 1716, 1607, 1561, 1099 cm$^{-1}$. HRMS calcd for $C_{13}H_{20}O_3$: 224.14125. Found: 224.13990.

**(C) 2-Methyl-3-(ethoxycarbonyl)-4-(2′-phenylethyl)furan (4c):** Following procedure E, the reaction of **1c** (129 mg, 0.5 mmol), NaI (150 mg, 1 mmol), and $PdCl_2(CH_3CN)_2$ (7 mg, 0.027 mmol) in 2 mL of acetone afforded 101 mg (78%) of **4c**. A solution of **1c** (130 mg, 0.5 mmol) and NaI (4 mg, 0.025 mmol) in 2 mL of acetone was stirred under reflux for 2.5 h until the reaction was finished. Then 3 mL of 3 M HCl was added to the mixture. The reaction was monitored by TLC. Usual workup, evaporation, and chromatography on silica gel afforded 103 mg (79%) of **4c** (procedure F): liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.18−7.35 (m, 5 H), 7.01 (s, 1 H), 4.34 (q, $J$ = 7.2 Hz, 2 H), 2.85−2.95 (m, 4 H), 2.57 (s, 3 H), 1.39 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 164.5, 160.22, 141.9, 137.6, 128.4, 128.2, 125.8, 125.3,

112.8, 59.9, 36.0, 26.6, 14.44, 14.36; MS *m*/*z* 258 ($M^+$, 17.57), 139 (100); IR (neat) 1713, 1605, 1561, 1099 $cm^{-1}$. HRMS calcd for $C_{16}H_{18}O_3$: 258.12560. Found: 258.12406.

**(4) 2-Methyl-3-(ethoxycarbonyl)-4-(4′-*tert*-butyldimethylsilyloxybutyl)furan (4d):** Following procedure E, the reaction of **1d** (148 mg, 0.4 mmol), NaI (150 mg, 1 mmol), and $PdCl_2(CH_3CN)_2$ (5 mg, 0.019 mmol) in 2 mL of acetone afforded 121 mg (82%) of **4d**. Following procedure D, the reaction of **1d** (83 mg, 0.24 mmol) and NaI (37 mg, 0.25 mmol) in 2 mL of acetone afforded 66 mg (80%) of **4d**: liquid; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 6.83 (s, 1 H), 4.06 (q, $J$ = 6.9 Hz, 2 H), 3.54 (t, $J$ = 6.0 Hz, 2 H), 2.66 (t, $J$ = 7.5 Hz, 2 H), 2.39 (s, 3 H), 1.50−1.70 (m, 4 H), 1.00 (t, $J$ = 7.2 Hz, 3 H), 0.95 (s, 9 H), 0.03 (s, 6 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 164.2, 160.2, 137.8, 126.6, 113.6, 63.2, 59.7, 33.1, 26.4, 26.2, 25.0, 18.5, 14.4, 14.3, −5.2; MS *m*/*z* 325 ($M^+ - CH_3$, 2.52), 283 (100); IR (neat) 1716, 1606, 1256, 1101 $cm^{-1}$. HRMS calcd for $C_{17}H_{29}O_4Si$ [$M^+ - CH_3$]: 325.18351. Found: 325.18268.

**(E) 2-Methyl-3-acyl-4-(*n*-octyl)furan (4e):** Following procedure E, the reaction of **1e** (127 mg, 0.5 mmol), NaI (150 mg, 1 mmol), and $PdCl_2(CH_3CN)_2$ (5 mg, 0.019 mmol) in 2 mL of acetone afforded 102 mg (80%) of **4e**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.76 (t, $J$ = 0.9 Hz, 1 H), 2.32 (td, $J$ = 6.9, 0.9 Hz, 2 H), 2.29 (s, 3 H), 2.17 (s, 3 H), 1.20−1.32 (m, 2 H), 0.92−1.16 (m, 10 H), 0.62 (t, $J$ = 6.6 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 194.8, 158.8, 137.4, 125.9, 122.0, 31.8, 30.8, 29.5, 29.4, 29.3, 29.2, 25.2, 22.6, 15.4, 14.0; MS *m*/*z* 236 ($M^+$, 17.71), 138 ($M^+ - C_7H_{14}$, 100); IR (neat) 1670, 1587, 1549 $cm^{-1}$. HRMS calcd for $C_{15}H_{24}O_2$: 236.17763. Found: 236.17648.

**(F) 2-Methyl-3-(benzenesulfonyl)-4-octylfuran (4f):** Following procedure E, the reaction of **1f** (164 mg, 0.5 mmol), NaI (148 mg, 1.0 mmol), and $PdCl_2(CH_3CN)_2$ (6.5 mg, 0.025 mmol) in 2 mL of acetone afforded 138 mg (84%) of a mixture of **4f** and **3f** (**4f:3f** = 1:9.6). Following procedure F, the reaction of **1f** (168 mg, 0.5 mmol) and NaI (4 mg, 0.025 mmol) in 2 mL of acetone afforded 158 mg (94%) of **4f**: oil; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.85−7.92 (m, 2 H), 7.47−7.62 (m, 3 H), 7.02 (s, 1 H), 2.63 (s, 3 H), 2.41 (t, $J$ = 7.5 Hz, 2 H), 1.32−1.48 (m, 2 H), 1.15−1.30 (m, 10 H), 0.87 (t, $J$ = 6.9 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 158.2, 142.8, 137.9, 132.9, 129.0, 126.6, 124.7, 121.0, 31.8, 29.3, 29.3, 29.2, 28.6, 23.6, 22.6, 14.1, 13.7; MS *m*/*z* 334 ($M^+$, 14.43), 236 (100); IR (neat) 1594, 1552, 1320, 1163 $cm^{-1}$. Anal. Calcd for $C_{19}H_{26}O_3S$: C, 68.23; H, 7.84. Found: C, 68.20; H, 8.04.

**(G) 2-Methyl-3-(benzensulfonyl)-4-pentylfuran (4g):** Following procedure E, the reaction of **1g** (143 mg, 0.5 mmol), NaI (150 mg, 1 mmol), and $PdCl_2(CH_3CN)_2$ (6.5 mg, 0.025 mmol) in 2 mL of acetone afforded 109 mg (76%) of a mixture of **4g** and **3g** (**4g:3g** = 3.2:1). Following procedure F, the reaction of **1g** (146 mg, 0.5 mmol) and NaI (4 mg, 0.025 mmol) in 2 mL of acetone afforded 76 mg (52%) of **4g**: solid, mp 60−62 °C (petroleum ether/ether); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.85−7.90 (m, 2 H), 7.45−7.62 (m, 3 H), 7.02 (s, 1 H), 2.64 (s, 3 H), 2.41 (t, $J$ = 7.5 Hz, 2 H), 1.35−1.50 (m, 2 H), 1.15−1.35 (m, 4 H), 0.85 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 158.2, 142.8, 137.9, 133.0, 129.1, 126.6, 124.7, 121.0, 31.5, 28.3, 23.6, 22.4, 14.0, 13.7; MS *m*/*z* 292 ($M^+$, 13.22), 236 (100); IR (KBr) 1599, 1558, 1321, 725 $cm^{-1}$. Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.72; H, 6.89. Found: C, 65.53; H, 6.49.

**(H) 2-Phenyl-3-(ethoxycarbonyl)-4-octylfuran (4h):** Following procedure E, the reaction of **1h** (164 mg, 0.5 mmol), NaI (150 mg, 1 mmol), and $PdCl_2(CH_3CN)_2$ (6.5 mg, 0.025 mmol) in 2 mL of acetone afforded 144 mg (88%) of a mixture of **4h** and **3h** (**4h:3h** = 1:5.5). Following procedure F, the reaction of **1h** (164 mg, 0.5 mmol) and NaI (8 mg, 0.05 mmol) in 2 mL of acetone afforded 111 mg (68%) of **4h**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.73−7.80 (m, 2 H), 7.30−7.45 (m, 3 H), 7.24 (s, 1 H), 4.29 (q, $J$ = 7.2 Hz, 2 H), 2.64 (t, $J$ = 7.2 Hz, 2 H), 1.55−1.65 (m, 2 H), 1.30 (t, $J$ = 7.2 Hz, 3 H), 1.20−1.45 (m, 10 H), 0.90 (t, $J$ = 6.9 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 164.5, 157.6, 138.7, 130.4, 128.9, 128.3, 127.9, 127.5, 113.6, 60.3, 31.9, 29.55, 29.54, 29.4, 29.3, 24.8, 22.7, 14.1, 14.0; MS *m*/*z* 328 ($M^+$, 28.47), 230 (100); IR (KBr) 1716, 1594, 1406 $cm^{-1}$. HRMS calcd for $C_{21}H_{28}O_3$: 328.20385. Found: 328.20578.

**(I) 2-Methyl-3-acetyl-4-cyclohexylfuran (4k):** Following procedure E, the reaction of **1k** (103 mg, 0.5 mmol), NaI (46 mg, 0.3 mmol), and $PdCl_2(CH_3CN)_2$ (10 mg, 0.039 mmol) in 4 mL of acetone afforded 76 mg (74%) of **4k**. Following procedure F, the reaction of **1k** (103 mg, 0.5 mmol) and NaI (75 mg, 0.5 mmol) in 1 mL of acetone afforded 51 mg (50%) of **4k**: solid; mp 55−57 °C (petroleum ether/ether); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.97 (s, 1 H), 2.75−2.90 (m, 1 H), 2.51 (s, 3 H), 2.41 (s, 3 H), 1.83−2.00 (m, 2 H), 1.62−1.80 (m, 3 H), 1.28−1.50 (m, 2 H), 1.03−1.25 (m, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 194.8, 158.3, 136.3, 132.2, 121.7, 34.3, 33.8, 30.8, 26.6, 26.2, 15.4; MS *m*/*z* 206 ($M^+$, 56.1), 43 (100); IR (KBr) 1656, 1538, 1406 $cm^{-1}$. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.45; H, 8.79.

**(J) 2-Phenyl-4-methylfuran (4n):**[32] Following procedure E, the reaction of **1n** (158 mg, 1.0 mmol), NaI (300 mg, 2 mmol), and $PdCl_2(CH_3CN)_2$ (13 mg, 0.05 mmol) in 2 mL of acetone afforded 127 mg (80%) of **4n**. Following procedure D, a solution of methylenecyclopropyl phenyl ketone **1n** (80 mg, 0.50 mol) and NaI (15 mg, 0.1 mmol, 0.2 equiv) in 2 mL of acetone afforded 72 mg (90%) of **4n**: liquid; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 7.67 (d, $J$ = 7.8 Hz, 2 H), 7.10−7.40 (m, 2 H), 7.00−7.06 (m, 1 H), 6.96 (s, 1 H), 6.27 (s, 1 H), 1.78 (s, 3 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 154.3, 139.1, 131.6, 128.9, 127.3, 123.9, 122.0, 108.0, 9.7; MS *m*/*z* 158 ($M^+$, 100.00); IR (neat) 1597, 1538, 1484, 1445, 914, 763 $cm^{-1}$.

**(K) 2-(4′-Methylphenyl)-4-methylfuran (4o):**[33] Following procedure E, the reaction of **1o** (172 mg, 1 mmol), NaI (300 mg, 2 mmol), and $PdCl_2(CH_3CN)_2$ (13 mg, 0.05 mmol) in 2 mL of acetone afforded 125 mg (73%) of **4o**. Following procedure D, the reaction of methylenecyclopropyl ketone **1o** (84 mg, 0.5 mmol) and NaI (15 mg, 0.1 mmol) in 2 mL of acetone afforded 48 mg (57%) of **4o**: solid; mp 55−56 °C;[34] $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 7.62 (d, $J$ = 7.2 Hz, 2 H), 6.97 (d, $J$ = 7.2 Hz, 2 H), 6.96 (s, 1 H), 6.25 (s, 1 H), 2.06 (s, 3 H), 1.78 (s, 3 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 154.57, 138.78, 136.97, 129.67, 129.04, 124.03, 121.99, 107.40, 21.17, 9.79; MS *m*/*z* 172 ($M^+$, 100.00); IR (KBr) 1605, 1543, 1490, 914, 805 $cm^{-1}$.

**(L) 2-(4′-Methoxylphenyl)-4-methylfuran (4p):**[35] Following procedure E, the reaction of **1p** (188 mg, 1 mmol), NaI (300 mg, 2 mmol), and $PdCl_2(CH_3CN)_2$ (13 mg, 0.05 mmol) in 2 mL of acetone afforded 165 mg (88%) of **4p**. Following procedure D, the reaction of **1p** (54 mg, 0.3 mmol) and NaI (8 mg, 0.05 mmol) in 2 mL of acetone afforded 33 mg (61%) of **4p**: solid; mp 80−81 °C.[33] $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 7.56 (d, $J$ = 9.0 Hz, 2 H), 7.19 (s, 1 H), 6.90 (d, $J$ = 9.0 Hz, 2 H), 6.39 (s, 1 H), 3.81 (s, 3 H), 2.06 (s, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 158.7, 153.8, 138.0, 124.9, 124.1, 121.8, 113.9, 106.1, 55.1, 9.8; MS *m*/*z* 188 ($M^+$, 100.00); IR (KBr) 1620, 1497, 915, 834 $cm^{-1}$.

**(M) 2-(4′-Fluorophenyl)-4-methylfuran (4q):** Following procedure E, the reaction of **1q** (106 mg, 0.6 mmol), NaI (180 mg, 1.2 mmol), and $PdCl_2(CH_3CN)_2$ (7.8 mg, 0.03 mmol) in 1.2 mL of acetone afforded 89 mg (84%) of **4q**. Following procedure D, the reaction of **1q** (87 mg, 0.5 mmol) and NaI (15 mg, 0.1 mmol) in 2 mL of acetone afforded 66 mg (76%) of **4q**: solid; mp 47−48 °C; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 7.38 (dd, $J$ = 8.7 Hz, 5.4 Hz, 2 H), 6.91 (t, $J$ = 0.9 Hz, 1 H), 6.76 (t, $J$ = 9.0 Hz, 2 H), 6.10 (s, 1 H), 1.77 (d, $J$ = 0.9 Hz, 3 H); $^{19}$F NMR (282 MHz, $C_6D_6$) $\delta$ −114.9; $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 164.0, 160.8, 153.4, 139.1, 125.7 (d, $J$ = 7.2 Hz), 122.1, 115.8 (d, $J$ = 21.8 Hz), 107.7 (d, $J$ = 1.6 Hz), 9.7; MS *m*/*z* 176 ($M^+$, 100); IR (KBr) 1602, 1544, 1493, 917, 838, 808 $cm^{-1}$. Anal. Calcd for $C_{11}H_9FO$: C, 74.99; H, 5.15. Found: C, 74.68; H, 5.20.

**(N) 2-(4′-Chlorophenyl)-4-methylfuran (4r):**[34] Following procedure E, the reaction of **1r** (192.5 mg, 1 mmol), NaI (300 mg, 2 mmol), and

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$PdCl_2(CH_3CN)_2$ (13 mg, 0.025 mmol) in 2 mL of acetone afforded 132 mg (69%) of **4r**. Following procedure D, the reaction of **1r** (98 mg, 0.5 mmol) and NaI (15 mg, 0.1 mmol) in 2 mL of acetone afforded 70 mg (71%) of **4r**: solid; mp 86−87 °C;[32] $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.55 (d, $J$ = 9.0 Hz, 2 H), 7.32 (d, $J$ = 9.0 Hz, 2 H), 7.23 (q, $J$ = 1.2 Hz, 1 H), 6.51 (s, 1 H), 2.07 (d, $J$ = 1.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 153.1, 139.4, 133.0, 129.9, 129.1, 125.2, 122.2, 108.5, 9.7; MS *m*/*z* 192 ($M^+$, 100.00); IR (KBr) 1612, 1533, 1480, 916, 810 $cm^{-1}$.

**(O) 2-(4′-Bromophenyl)-4-methylfuran (4s):** Following procedure E, the reaction of **1s** (237 mg, 1 mmol), NaI (300 mg, 2 mmol), and $PdCl_2(CH_3CN)_2$ (13 mg, 0.025 mmol) in 2 mL of acetone afforded 180 mg (76%) of **4s**. Following procedure D, the reaction of **1s** (59 mg, 0.25 mmol) and NaI (7 mg, 0.05 mmol) in 2 mL of acetone afforded 48 mg (81%) of **4s**: solid; mp 95−96 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.49 (s, 4 H), 7.23 (t, $J$ = 1.3 Hz, 1 H), 6.53 (s, 1 H), 2.07 (d, $J$ = 1.3 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 153.1, 139.4, 132.1, 130.3, 125.4, 122.2, 121.2, 108.6, 9.7; MS *m*/*z* 238 ($M^+$ ($^{81}$Br), 54.05), 236 ($M^+$ ($^{79}$Br), 59.54), 128 (100.00); IR (KBr) 1608, 1533, 1476, 915, 809 $cm^{-1}$. Anal. Calcd for $C_{11}H_9BrO$: C, 55.72; H, 3.83. Found: C, 55.67; H, 3.99.

**(P) 2-(4′-Iodophenyl)-4-methylfuran (4t):** Following procedure E, the reaction of **1t** (294 mg, 1 mmol), NaI (300 mg, 2 mmol), and $PdCl_2(CH_3CN)_2$ (13 mg, 0.025 mmol) in 2 mL of acetone afforded 211 mg (69%) of **4t**. Following procedure D, the reaction of **1t** (139 mg, 0.5 mmol) and NaI (15 mg, 0.10 mmol) in 2 mL of acetone afforded 102 mg (73%) of **4t**: solid; mp 116−117 °C; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 7.44 (d, $J$ = 8.4 Hz, 2 H), 7.13 (d, $J$ = 8.4 Hz, 2 H), 6.90 (t, $J$ = 0.9 Hz, 1 H), 6.12 (s, 1 H), 1.76 (d, $J$ = 0.9 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 153.2, 139.5, 138.0, 130.8, 125.5, 122.2, 108.7, 92.5, 9.7; MS *m*/*z* 284 ($M^+$, 100.00); IR (KBr) 1529, 1398, 914, 807 $cm^{-1}$. Anal. Calcd for $C_{11}H_9IO$: C, 46.51; H, 3.19. Found: C, 46.73; H, 3.36.

**(Q) 2-(1′-Naphthyl)-4-methylfuran (4u):** Following procedure E, the reaction of **1u** (208 mg, 1 mmol), NaI (300 mg, 2 mmol), and $PdCl_2(CH_3CN)_2$ (13 mg, 0.025 mmol) in 2 mL of acetone afforded 173 mg (83%) of **4u**. Following procedure D, the reaction of **1u** (50 mg, 0.24 mmol) and NaI (8 mg, 0.05 mmol) in 2 mL of acetone afforded 49 mg (98%) of **4u**: liquid; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 8.60 (d, $J$ = 8.7 Hz, 1 H), 7.75 (dd, $J$ = 7.2, 1.5 Hz, 1 H), 7.63 (d, $J$ = 9.0 Hz, 1 H), 7.56 (d, $J$ = 8.1 Hz, 1 H), 7.20−7.40 (m, 3 H), 7.09 (t, $J$ = 0.9 Hz, 1 H), 6.40 (s, 1 H), 1.83 (d, $J$ = 0.9 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 153.8, 139.5, 134.5, 130.9, 129.4, 128.9, 128.7, 126.7, 126.3, 126.1, 126.1, 125.6, 121.8, 112.4, 9.8; MS *m*/*z* 208 ($M^+$, 100); IR (neat) 1589, 1509, 1390, 798, 773 $cm^{-1}$. HRMS calcd for $C_{15}H_{12}O$: 208.08882. Found: 208.09197.

**(R) 2-(2′-Furyl)-4-methylfuran (4v):**[36] Following procedure E, the reaction of **1v** (148 mg, 1 mmol), NaI (300 mg, 2 mmol), and $PdCl_2(CH_3CN)_2$ (13 mg, 0.025 mmol) in 2 mL of acetone afforded 104 mg (70%) of **4v**. Following procedure D, the reaction of **1v** (74 mg, 0.5 mmol) and NaI (14 mg, 0.09 mmol) in 2 mL of acetone afforded 58 mg (78%) of **4v**: liquid; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 7.00−7.03 (m, 1 H), 6.83−6.90 (m, 1 H), 6.51 (d, $J$ = 3.3 Hz, 1 H), 6.39 (s, 1 H), 6.07 (dd, $J$ = 3.3 Hz, 1.8 Hz, 1 H), 1.70 (s, 3 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 147.4, 147.1, 141.8, 138.8, 121.8, 111.6, 108.1, 105.2, 9.5; MS *m*/*z* 148 ($M^+$, 71.77), 91 (100); IR (neat) 1581, 1451, 1005 $cm^{-1}$. HRMS calcd for $C_9H_8O_2$: 148.05243. Found: 148.05316.

**(S) 2-Phenethyl-4-methylfuran (4w):** Following procedure E, the reaction of **1w** (290 mg, 1.55 mmol), NaI (300 mg, 2 mmol), and $PdCl_2(CH_3CN)_2$ (11 mg, 0.025 mmol) in 5 mL of acetone afforded 223 mg (77%) of **4w**: liquid; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.16−7.10 (m, 2 H), 7.08−7.00 (m, 3 H), 6.97 (d, $J$ = 1.1 Hz, 1 H), 5.74 (s, 1 H), 2.90−2.78 (m, 4 H), 1.87 (d, $J$ = 1.1 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 155.4, 141.3, 137.4, 128.35, 128.33, 126.0, 120.4, 108.0, 34.4, 30.0, 9.8; MS *m*/*z* 186 ($M^+$, 28.25), 95 (100); IR (neat) 1618, 1604, 1552, 1498 $cm^{-1}$; Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.76; H, 7.34.

**(T) 2-(4′-Methoxylphenylethyl)-4-methylfuran (4x):** Following procedure E, the reaction of **1x** (226 mg, 1 mmol), NaI (300 mg, 2 mmol), and $PdCl_2(CH_3CN)_2$ (11 mg, 0.025 mmol) in 2 mL of acetone afforded 138 mg (72%) of **4x**. Following procedure D, the reaction of **1x** (110 mg, 0.5 mmol) and NaI (74 mg, 0.5 mmol) in 2 mL of acetone afforded 74 mg (67%) of **4x**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.13 (d, $J$ = 8.4 Hz, 2 H), 7.12 (s, 1 H), 6.87 (d, $J$ = 8.1 Hz, 2 H), 5.89 (s, 1 H), 3.82 (s, 3 H), 2.80−3.00 (m, 4 H), 2.02 (s, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 157.8, 155.4, 137.3, 133.3, 129.2, 120.4, 113.7, 107.9, 55.1, 33.4, 30.2, 9.8; MS *m*/*z* 216 ($M^+$, 8.12), 121 (100); IR (neat) 1613, 1513, 1247, 910 $cm^{-1}$. HRMS calcd for $C_{14}H_{16}O_2$: 216.11503. Found: 216.11254.

**(U) 2-(3′-Benzoxypropyl)-4-methylfuran (4y):** Following procedure E, the reaction of **1y** (345 mg, 1.5 mmol), NaI (400 mg, 2.7 mmol), and $PdCl_2(CH_3CN)_2$ (13 mg, 0.025 mmol) in 4 mL of acetone afforded 230 mg (66%) of **4y**. Following procedure D, the reaction of **1y** (110 mg, 0.5 mmol) and NaI (15 mg, 0.11 mmol) in 2 mL of acetone afforded 26 mg (24%) of **4y**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.25−7.50 (m, 5 H), 7.10 (s, 1 H), 5.89 (s, 1 H), 4.55 (s, 2 H), 3.55 (t, $J$ = 6.3 Hz, 2 H), 2.73 (t, $J$ = 7.2 Hz, 2 H), 2.02 (s, 3 H), 1.90−2.05 (m, 2 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 155.6, 138.4, 137.3, 128.3, 127.6, 127.5, 120.3, 107.7, 72.8, 69.3, 28.1, 24.7, 9.8; MS *m*/*z* 230 ($M^+$, 21.75), 109 (100); IR (neat) 1619, 1553, 1454, 736 $cm^{-1}$. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.91; H, 7.68.

**Typical Procedure for Pd(0)-Catalyzed Cycloisomerization (Procedures G and H). (A) 2,4-Dimethyl-3-(ethoxycarbonyl)-5-heptylfuran (6a). Procedure G:** A solution of **1a** (66 mg, 0.25 mmol) and $Pd(PPh_3)_4$ (16 mg, 5 mol %) in 4 mL of $CH_3CN$ was stirred at 80 °C under Ar for 12 h. After the reaction was over, the solvent was evaporated, and 3 mL of THF and 3 mL of 3 M HCl were added to the residue. After complete aromatization as monitored by TLC, the solution was extracted with ethyl ether, and the organic layer was dried over $MgSO_4$. Filtration, evaporation, and flash chromatography on silica gel afforded 57 mg (84%) of **6a** as a liquid. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.26 (q, $J$ = 7.2 Hz, 2 H), 2.49 (t, $J$ = 6.6 Hz, 2 H), 2.49 (s, 3 H), 2.06 (s, 3 H), 1.47−1.62 (m, 2 H), 1.34 (t, $J$ = 7.2 Hz, 3 H), 1.20−1.40 (m, 8 H), 0.87 (t, $J$ = 6.9 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 165.1, 157.2, 149.9, 114.3, 113.6, 59.6, 31.8, 29.0, 28.5, 25.4, 22.6, 14.3, 14.2, 14.0, 9.8; MS *m*/*z* 266 ($M^+$, 31.69), 181 (100); IR (neat) 1714, 1585, 1286, 1091 $cm^{-1}$. HRMS calcd for $C_{16}H_{26}O_3$: 266.18820. Found: 266.18753.

**(B) 2,4-Dimethyl-3-(ethoxycarbonyl)-5-butylfuran (6b):** Following procedure G, the reaction of **1b** (114 mg, 0.50 mmol) and $Pd(PPh_3)_4$ (26 mg, 0.023 mmol) in 4 mL of $CH_3CN$ afforded 89 mg (78%) of **6b**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.27 (q, $J$ = 7.2 Hz, 2 H), 2.50 (s, 3 H), 2.49 (t, $J$ = 7.5 Hz, 2 H), 2.06 (s, 3 H), 1.50−1.65 (m, 2 H), 1.34 (t, $J$ = 7.2 Hz, 3 H), 1.20−1.40 (m, 2 H), 0.91 (t, $J$ = 7.5 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 165.1, 157.2, 149.9, 114.3, 113.6, 59.6, 30.6, 25.1, 22.1, 14.3, 14.2, 13.7, 9.8; MS *m*/*z* 224 ($M^+$, 30.19), 181 (100); IR (neat) 1714, 1585, 1286, 1091 $cm^{-1}$. HRMS calcd for $C_{13}H_{20}O_3$: 224.14124. Found: 224.14031.

**(C) 2,4-Dimethyl-3-(ethoxycarbonyl)-5-(3-hydroxypropyl)furan (6d′):** Following procedure G, the reaction of **1d** (100 mg, 0.30 mmol) and $Pd(PPh_3)_4$ (33 mg, 0.029 mmol) in 4 mL of $CH_3CN$ afforded 41 mg (62%) of **6d′**: liquid; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.25 (q, $J$ = 7.2 Hz, 2 H), 3.62 (t, $J$ = 6.3 Hz, 2 H), 2.61 (t, $J$ =7.2 Hz, 2 H), 2.47 (s, 3 H), 2.05 (s, 3 H), 1.77−2.00 (m, 3 H), 1.32 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 165.0, 157.6, 148.9, 114.9, 113.7, 61.9, 59.7, 31.2, 21.7, 14.3, 14.2, 9.8; MS *m*/*z* 261 ($M^+$, 61.50), 181 (100); IR (neat) 3406, 1712, 1584, 1287, 1094 $cm^{-1}$. HRMS calcd for $C_{12}H_{18}O_4$: 226.12051. Found: 226.12370.

**(D) 2,4-Dimethyl-3-acetyl-5-heptylfuran (6e):** Following procedure G, the reaction of **1e** (114 mg, 0.48 mmol) and $Pd(PPh_3)_4$ (31 mg,

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0.027 mmol) in 4 mL of $CH_3CN$ afforded 86 mg (75%) of **6e**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.48 (s, 3 H), 2.47 (t, $J = 7.8$ Hz, 2 H), 2.37 (s, 3 H), 2.06 (s, 3 H), 1.45−1.60 (m, 2 H), 1.17−1.37 (m, 8 H), 0.85 (t, $J = 7.2$ Hz, 3 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 195.0, 156.3, 150.1, 122.8, 113.6, 31.7, 30.7, 29.0, 28.9, 28.4, 25.2, 22.6, 15.1, 14.0, 10.5; MS *m*/*z* 236 ($M^+$, 40.24), 151 (100); IR (neat) 1670, 1563, 1285 $cm^{-1}$. HRMS calcd for $C_{15}H_{24}O_2$: 236.17764. Found: 236.18043.

**(E) 2,4-Dimethyl-3-(benzenesulfonyl)-5-heptylfuran (6f):** Following procedure G, the reaction of **1f** (171 mg, 0.50 mmol) and $Pd(PPh_3)_4$ (33 mg, 0.029 mmol) in 4 mL of $CH_3CN$ afforded 104 mg (74%) of **6f**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.85−7.90 (m, 2 H), 7.45−7.60 (m, 3 H), 2.59 (s, 3 H), 2.42 (t, $J = 7.8$ Hz, 2 H), 1.92 (s, 3 H), 1.43−1.57 (m, 2 H), 1.15−1.30 (m, 8 H), 0.84 (t, $J = 6.6$ Hz, 3 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 155.4, 151.0, 142.8, 132.8, 129.0, 126.6, 121.3, 112.5, 31.6, 28.9, 28.8, 28.1, 25.4, 22.5, 14.0, 13.4, 8.7; MS *m*/*z* 334 ($M^+$, 18.55), 249 (100); IR (neat) 1630, 1568, 1319, 1159 $cm^{-1}$. HRMS calcd for $C_{19}H_{26}O_3S$: 334.16027. Found: 334.16121.

**(F) 2-Phenyl-3-(ethoxycarbonyl)-4-methyl-5-heptylfuran (6h):** Following procedure G, the reaction of **1h** (87 mg, 0.27 mmol) and $Pd(PPh_3)_4$ (31 mg, 0.027 mmol) in 4 mL of $CH_3CN$ afforded 67 mg (77%) of **6h**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.75−7.80 (m, 2 H), 7.30−7.45 (m, 3 H), 4.29 (q, $J = 7.2$ Hz, 2 H), 2.62 (t, $J = 7.2$ Hz, 2 H), 2.14 (s, 3 H), 1.57−1.73 (m, 2 H), 1.30 (t, $J = 7.2$ Hz, 3 H), 1.20−1.45 (m, 8 H), 0.89 (t, $J = 6.6$ Hz, 3 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 164.8, 154.9, 151.7, 130.6, 128.5, 128.1, 127.8, 116.0, 114.5, 60.2, 31.8, 29.0, 29.0, 28.4, 25.7, 22.6, 14.08, 14.07, 10.0; MS *m*/*z* 328 ($M^+$, 46.37), 243(100); IR (neat) 1716, 1557, 1290, 1108 $cm^{-1}$. Anal. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59. Found: C, 76.66; H, 8.53.

**(G) 2-Heptyl-3-methylene-4-(ethoxycarbonyl)-5-methyl-2,3-dihydrofuran (5a). Procedure H:** A solution of **1a** (134 mg, 0.50 mmol), 0.5 mL of $Et_3N$, and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) in 2 mL of $CH_3CN$ was stirred at 80 °C under Ar for 14.5 h. Evaporation and flash chromatography on silica gel (petroleum ether/$Et_2O$/$Et_3N$ = 20:1:0.1) afforded 120 mg (90%) of **5a**: liquid; $^1H$ NMR (300 MHz, $C_6D_6$) $\delta$ 5.93 (d, $J = 3.0$ Hz, 1 H), 4.80−4.90 (m, 1 H), 4.66 (d, $J = 3.0$ Hz, 1 H), 4.08 (q, $J = 7.2$ Hz, 2 H), 2.21 (s, 3 H), 1.45−1.65 (m, 2 H), 1.10−1.40 (m, 10 H), 0.99 (t, $J = 7.2$ Hz, 3 H), 0.96 (t, $J = 6.3$ Hz, 3 H); $^{13}C$ NMR (75.4 MHz, $C_6D_6$) $\delta$ 175.6, 164.6, 147.7, 107.2, 98.6, 87.0, 59.5, 36.8, 32.2, 29.8, 29.6, 24.6, 23.0, 15.6, 14.4, 14.3; MS *m*/*z* 266 ($M^+$, 45.75), 181 (100); IR (neat) 1711, 1610, 1288, 1093 $cm^{-1}$. HRMS calcd for $C_{16}H_{26}O_3$: 266.18819. Found: 266.18944.

**(H) 2-[(3′-*tert*-Butyldimethylsilyloxy)propyl]-3-methylene-4-(ethoxycarbonyl)-5-methyl-2,3-dihydrofuran (5d):** Following procedure H, the reaction of **1d** (171 mg, 0.50 mmol) and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) in 3 mL of $CH_3CN$ afforded 154 mg (90%) of **5d**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.41 (d, $J = 2.5$ Hz, 1 H), 5.02−5.10 (m, 1 H), 4.58 (d, $J = 2.5$ Hz, 1 H), 4.23 (q, $J = 7.5$ Hz, 2 H), 3.58−3.68 (m, 2 H), 2.30 (s, 3 H), 1.50−1.90 (m, 4 H), 1.32 (t, $J = 7.5$ Hz, 3 H), 0.88 (s, 9 H), 0.03 (s, 6 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 175.8, 165.1, 146.9, 106.5, 98.1, 86.6, 62.6, 59.6, 32.7, 27.3, 25.9, 18.3, 15.6, 14.3, 1.0, −5.4; MS *m*/*z* 340 ($M^+$, 2.51), 283 (100); IR (neat) 1706, 1610, 1205, 1097 $cm^{-1}$. HRMS calcd for $C_{18}H_{32}O_4Si$: 340.20699. Found: 340.20949.

**(I) 2-Heptyl-3-methylene-4-(benzenesulfonyl)-5-methyl-2,3-dihydrofuran (5f):** Following procedure H, the reaction of **1f** (138 mg, 0.41 mmol) and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) in 2 mL of $CH_3CN$ afforded 119 mg (86%) of **5f**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.85−7.90 (m, 2 H), 7.45−7.60 (m, 3 H), 5.20 (d, $J = 3.0$ Hz, 1 H), 4.97−5.07 (m, 1 H), 4.55 (d, $J = 2.7$ Hz, 1 H), 2.40 (s, 3 H), 1.45−1.75 (m, 2 H), 1.15−1.35 (m, 10 H), 0.85 (t, $J = 7.2$ Hz, 3 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 173.5, 144.3, 142.4, 132.8, 128.9, 126.3, 114.0, 98.4, 86.9, 36.0, 31.6, 29.2, 29.0, 23.6, 22.6, 14.6, 14.0; MS *m*/*z* 334 ($M^+$, 28.86), 249 (100); IR (neat) 1637, 1597, 1317, 1157 $cm^{-1}$. HRMS calcd for $C_{19}H_{26}O_3S$: 334.16026. Found: 334.16173.

**(J) 2-Heptyl-3-methylene-4-(ethoxycarbonyl)-5-phenyl-2,3-dihydrofuran (5h):** Following procedure H, the reaction of **1h** (163 mg, 0.5 mmol), $Et_3N$ (0.5 mL), and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) in 2 mL of $CH_3CN$ afforded 114 mg (70%) of **5h**: liquid; $^1H$ NMR (300 MHz, $C_6D_6$) $\delta$ 7.70−7.80 (m, 2 H), 7.03−7.10 (m, 3 H), 6.05 (d, $J = 3.0$ Hz, 1 H), 4.93−5.03 (m, 1 H), 4.77 (d, $J = 2.4$ Hz, 1 H), 3.99 (q, $J = 7.5$ Hz, 2 H), 1.50−1.70 (m, 3 H), 1.15−1.55 (m, 9 H), 0.87 (t, $J = 6.6$ Hz, 3 H), 0.84 (t, $J = 7.5$ Hz, 3 H); $^{13}C$ NMR (75.4 MHz, $C_6D_6$) $\delta$ 170.8, 164.2, 149.0, 131.4, 130.6, 129.7, 127.8, 107.7, 100.5, 86.4, 59.8, 37.0, 32.0, 29.9, 29.6, 24.6, 23.0, 14.3, 14.0; MS *m*/*z* 328 ($M^+$, 34.19), 243 (100); IR (neat) 1708, 1610, 1591, 1380, 1089 $cm^{-1}$. HRMS calcd for $C_{21}H_{28}O_3$: 328.21172. Found: 328.20778.

**(K) 2-Methyl-3-(ethoxycarbonyl)-4-methylene-1-oxa-spiro[4,5]-dec-2-ene (5j):** Following procedure H, the reaction of **1j** (116 mg, 0.50 mol) and $Pd(PPh_3)_4$ (31 mg, 0.027 mmol) in 4 mL of $CH_3CN$ afforded 102 mg (88%) of **5j**: liquid; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.35 (s, 1 H), 4.42 (s, 1 H), 4.21 (q, $J = 7.5$ Hz, 2 H), 2.31 (s, 3 H), 1.57−1.80 (m, 7 H), 1.10−1.43 (m, 3 H), 1.30 (t, $J = 7.5$ Hz, 3 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 174.0, 165.4, 152.2, 105.2, 97.3, 91.1, 59.4, 37.4, 24.8, 21.9, 15.8, 14.2; MS *m*/*z* 236 ($M^+$, 38.50), 181 (100.00); IR (neat) 1701, 1663, 1608, 1230, 1079 $cm^{-1}$. HRMS calcd for $C_{14}H_{20}O_3$: 236.14125. Found: 236.14468.

**(L) 2-Methyl-3-acetyl-4-methylene-1-oxa-spiro[4,5]dec-2-ene (5k):** Following procedure H, the reaction of **1k** (106 mg, 0.51 mol) and $Pd(PPh_3)_4$ (31 mg, 0.027 mmol) in 4 mL of $CH_3CN$ afforded 89 mg (84%) of **5k**: solid; mp 67−69 °C (petroleum ether/ether); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.25 (s, 1 H), 4.45 (s, 1 H), 2.31 (s, 6 H), 1.57−1.87 (m, 7 H), 1.18−1.40 (m, 3 H); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 194.5, 173.8, 152.8, 114.9, 97.7, 91.2, 37.4, 31.0, 24.8, 21.9, 16.8; MS *m*/*z* 206 ($M^+$, 56.66), 43(100); IR (KBr) 1636, 1571, 1229 $cm^{-1}$. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.67; H, 8.83.

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**Supporting Information Available:** Copies of $^1H$/$^{13}C$ NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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