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Hydrosilanes are not always a reducing reagent: a ruthenium-catalyzed introduction of primary alkyl groups to electron-rich aromatic rings using esters as a source of the alkyl groups

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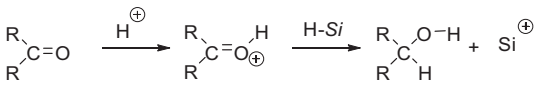
ABSTRACT

A triruthenium cluster, (μ_3, η^2, η^3, η^5-acenaphthylene)$Ru_3(CO)_7$ effectively catalyzes primary-alkylation reaction of electron-rich aromatic rings using a combination of hydrosilane and ester as a source of the primary-alkyl group. The reaction involves electrophilic substitution of arenes by carbocationic species stabilized by a neighboring alkoxy or siloxy group generated during the reduction of esters giving alkylated arenes after reductive removal of the alkoxy or siloxy group at the benzylic position.

1. Introduction

Hydrosilanes are important precursor of various organosilanes via catalytic hydrosilylation of alkenes and alkynes.[1] Hydrosilanes are also useful for reducing reagents of ketones, aldehydes, and imines.[2] Since they are less reactive than alumino- and borohydrides, a promoter, such as Brønsted acids,[2] Lewis acids,[3] fluoride anion,[4] and transition metal catalysts[5] is necessary to carry out the hydride reduction. The reduction proceeds through cationic intermediates; in the acidic media, the carbonyl function of ketones or aldehydes is activated by a proton or a Lewis acid; this places a positive charge on oxygen and makes the carbonyl group more electrophilic. Subsequent nucleophilic addition of a hydride from the hydrosilane to form the corresponding alcohols (Scheme 1).



Scheme 1. The ionic mechanism for acid-catalyzed hydrosilane reduction of ketones.

The ionic mechanism explains the reduction of aralkyl ketone to aralkanes by combination of Et_3SiH and CF_3CO_2H. The aralkyl ketone is first converted to the benzylic alcohols, which is followed by benzyl cation formation and subsequent hydride reduction to give the aralkanes.[2,3] As a closely related reaction, alkyl halides, alcohols, and ethers are reduced by Et_3SiH to alkanes by hydrosilanes via a carbocationic intermediate in the presence of a strong Lewis acid, e.g., $B(C_6F_5)_3$.[6] Interestingly, the ionic mechanism suggests that the carbocationic intermediate is not only trapped by the hydride but also carbonucleophiles.[7] This possibility is realized in special cases where stable carbocationic intermediates are formed or highly reactive nucleophiles are used.

Recent progress of InX_3 chemistry showed that Freidel–Crafts benzylation or reductive allylation with allyl trimethylsilanes were possible by the reaction of ketones with Me_2ClSiH in the presence of InX_3.[7,8] Very recently, Sakai and co-workers extends the protocol to the reaction of benzoic acids with hydrosilanes in the presence of arenes led to Friedel–Crafts benzylation.[8b] In the InX_3-promoted reactions, various arenes can be used for the Freidel–Crafts reaction, but only the reactions through benzyl cations are possible. In contrast, Augustine and co-workers reported that various aldehydes behave as alkylating reagents for electron-rich aromatic rings by treatment with hydrosilanes in CF_3CO_2H.[9]

Transition metal-catalyzed hydrosilylation of carbonyl compounds is generally explained by oxidative addition of a Si–H bond of the hydrosilane to a transition metal species, which is followed

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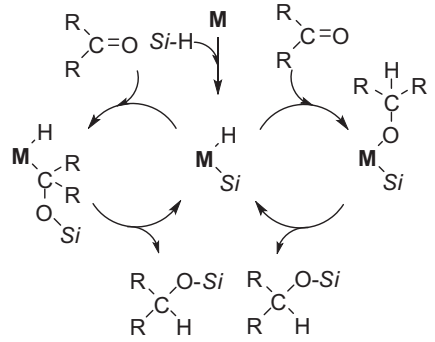
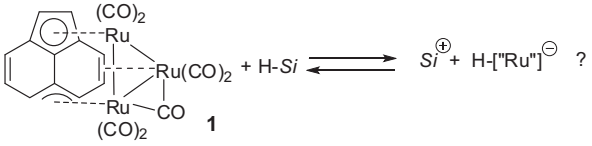
by insertion of a C=O bond to either M–Si or M–H bond. Reductive elimination of silyl ethers regenerates an active metal species for activation of another hydrosilane molecule to establish the catalytic cycle (Scheme 2).[1] Various transition metal compounds are investigated as the catalyst, and mechanistic studies of the metal-catalyzed hydrosilylation generally exclude the cationic intermediates except recent studies on the hydrosilylation of ketones using cationic iridium or ruthenium catalysts.[1,10]



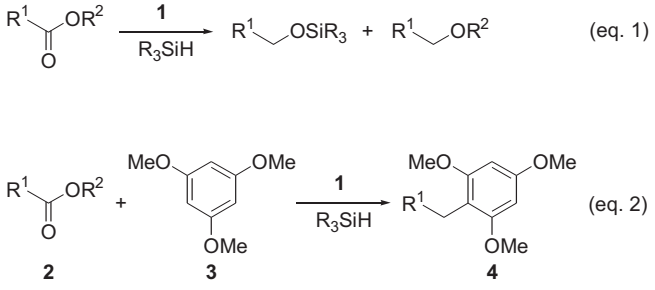
Scheme 2. Catalytic cycles of transition metal-catalyzed hydrosilylation of ketones.

We have recently found that a triruthenium cluster **1** is a highly efficient catalyst for hydrosilylation of carbonyl compounds.[11] Utility of **1** is seen in successful reduction of carboxylic acids, esters, and amides, which is hardly achieved with conventional catalysts and trialkylsilanes. In the course of the studies, we were aware that outcome of the reaction might suggest the involvement of cationic intermediates as shown in Scheme 3, though there is no compound having acidic or Lewis acidic property to activate Si–H bond.



Scheme 3. Possible generation of ionic species in the hydrosilane reduction catalyzed by a ruthenium cluster **1**.

Typical related examples are ring-opening polymerization of cyclic ethers,[11a] addition polymerization of vinyl ethers[12] and deprotection of *tert*-butyl esters and Boc,[13] which are induced by hydrosilanes activated by **1** under similar conditions to the reduction of carbonyl compounds. If the cationic intermediates are involved in the hydrosilane reduction of carbonyl compounds with **1**(Scheme 4, Eq. 1), it would be trapped by carbonucleophiles. In this paper, we wish to report that this working hypothesis actually works well in primary-alkylation of electron-rich aromatics shown in Scheme 4, Eq. 2, in which reductively generated 'RCH_2-' group



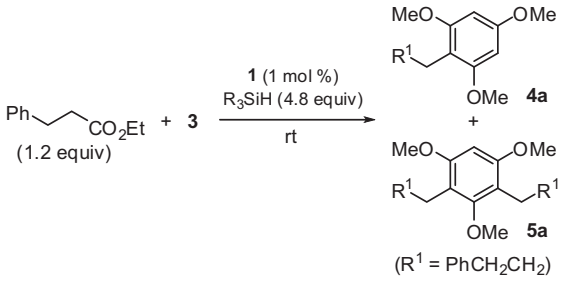
Scheme 4. Ruthenium-catalyzed reduction (Eq. 1) and reductive alkylation (Eq. 2) of esters by hydrosilanes.

from esters is introduced to the aromatic ring by treatment with hydrosilanes and a catalytic amount of **1**.

2. Results and discussion

As reported earlier, treatment of esters, $R^1CO_2R^2$, with hydrosilanes in the presence of 1 mol % of **1** at rt gives the corresponding alkyl or silyl ethers in good yields (Scheme 4, Eq. 1).[11b,f] The new finding is that an aromatic compound, 1,3,5-trimethoxybenzene (**3**), added to the reaction mixture, is substituted by a primary-alkyl group, R^1CH_2, on the aromatic ring as shown in Scheme 4, Eq. 2. The reactions of ethyl dihydrocinnamate with several hydrosilanes are summarized in Table 1. A mixture of **3** and ethyl dihydrocinnamate (1.2 equiv to **3**) was treated with several hydrosilanes (4.8 equiv to **3**) in the presence of **1** (1 mol %) at rt. In the absence of solvents, the reactions with $EtMe_2SiH$, 1,1,3,3-tetramethyldisiloxane (TMDS), or $PhMe_2SiH$ were complete in a few hours to give the corresponding alkylated product **4a** in good yields (runs 1–3). The reaction with sterically more crowded Et_3SiH was slower (run 4). The reaction without solvents is important for selective formation of the monoalkylated product. In diluted tetrahydropyran solutions, longer reaction time was required to obtain the product in moderate to good yields, and concomitant formation of the dialkylated product **5a** was observed (runs 5 and 6).

Table 1
Alkylation of 1,3,5-trimethoxybenzene (**3**) by the reaction with ethyl dihydrocinnamate and hydrosilanes

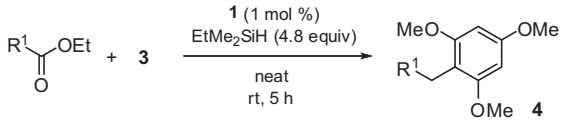


Run	R_3SiH	Concn	Time (h)	Yield	
				4a (%)	**5a** (%)
1	$EtMe_2SiH$	Neat	1	95	0
2	TMDS	Neat	0.5	79	0
3	$PhMe_2SiH$	Neat	2	94	0
4	Et_3SiH	Neat	24	98	0
5	$EtMe_2SiH$	5 M[a]	3	63[b]	37[b]
6	$EtMe_2SiH$	1 M[a]	24	51[b]	49[b]

[a] The reaction was carried out in tetrahydropyran (THP).
[b] Determined by ^1H NMR.

The results changing the esters are shown in Table 2. The reactions were carried out using $EtMe_2SiH$ as the hydrosilane. Treatment of **3** with the ester (1.2 equiv to **3**) and $EtMe_2SiH$ (4.8 equiv to **3**) at rt resulted in selective formation of the monoalkylating product **4a**–**i**. Although the reaction time of 5 h is long enough for giving the product listed in Table 2 in high yields, steric hindrance around the C=O group of the ester somewhat lowered the yield of the product as shown in runs 7 and 8. Lower reactivity was significantly observed when ethyl pivaloate was used as the ester; no reaction took place under the same conditions as above. Alkoxy moiety of the ester did not affect the rate and the yield of the product; the ethylation of **3** with EtOAc, *i*-PrOAc, PhOAc, or $MeOCH_2CH_2OAc$ smoothly took place to give **4b** quantitatively. The esters containing a halogen atom in the molecule reacted with **3** to give the product with the halogen group remaining intact (runs 3 and 4). The reaction of ethyl benzoate required longer reaction time

Table 2
Monoalkylation of 1,3,5-trimethoxybenzene (**3**) by ethyl alkanoate and $EtMe_2SiH$

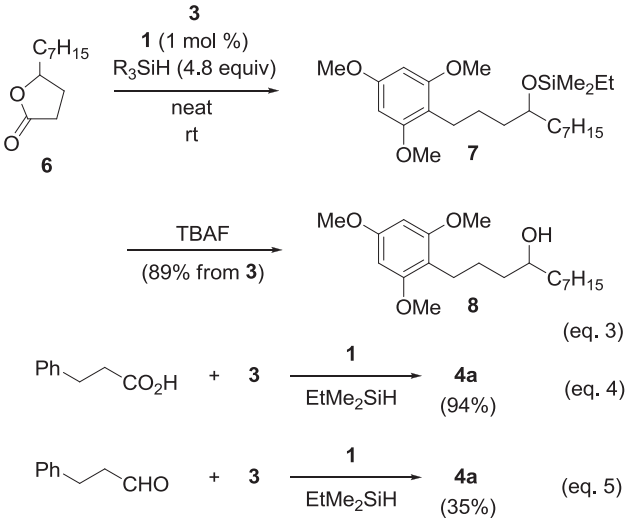


Run	R^1	Product	Yield (%)
1	$PhCH_2CH_2$	**4a**	95
2	Me	**4b**	99
3	$ClCH_2CH_2$	**4c**	96
4	$BrCH_2CH_2$	**4d**	95
5	*i*-Bu	**4e**	98
6	*i*-Pr	**4f**	99
7	Cyclopentyl	**4g**	88
8	Cyclohexyl	**4h**	76
9	Ph	**4i**	66[a]

[a] The reaction was performed with ethyl benzoate (4 equiv) and the hydrosilane (16 equiv).

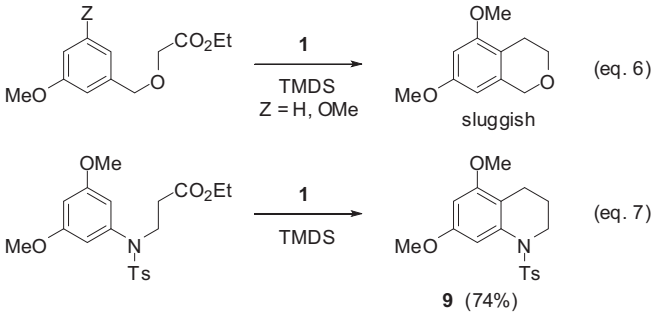
(48 h); the yield of the product was moderate even in the presence of excess amounts of the ester and $EtMe_2SiH$ (run 9).

The scheme opened further possibilities for modification of the reactions. Lactones, carboxylic acids, and aldehydes are also useful for an alkylating reagent for **3**. In typical examples, the lactone **6** was converted to the alcohol **8** as shown in Scheme 5, Eq. 3. NMR analysis of the primary product indicated formation of the silyl ether **7**, which was treated with TBAF to give the alcohol **8** in 89% yield from **3**. Dihydrocinnamic acid is also useful for the production of **4** (Scheme 5, Eq. 4). Since the ruthenium cluster **1** is a powerful catalyst for dehydrogenative silylation of carboxylic acids to silyl esters, the alkylation proceeds through the silyl ester as the intermediate.[11a] Despite the low yield of the product, dihydrocinnamaldehyde also gives **4** under similar conditions (Scheme 5, Eq. 5).



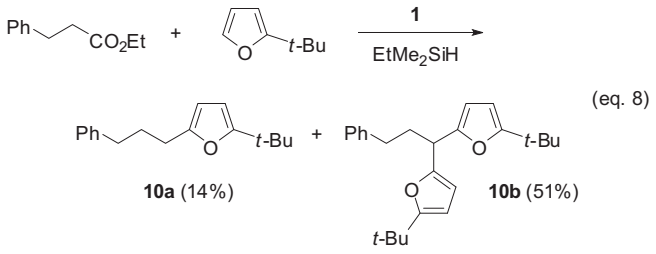
Scheme 5. The reaction of **3** with a lactone, carboxylic acid, and aldehyde.

Intramolecular version of this aromatic alkylation is attractive for novel access to bicyclic aromatic compounds. Although attempted preparation of a dihydrochromane and a dihydroisochromane shown in Eq. 6 of Scheme 6 is hampered due to the fact that the reduction of ester is faster than the cyclization, the reaction shown in Eq. 7 gave a trihydroquinoline derivative in 74% yield probably due to a significant steric bias of *N*-tosyl group. The result indicates potential of intramolecular reaction when the appropriate substrate design is performed.



Scheme 6. Intramolecular reaction.

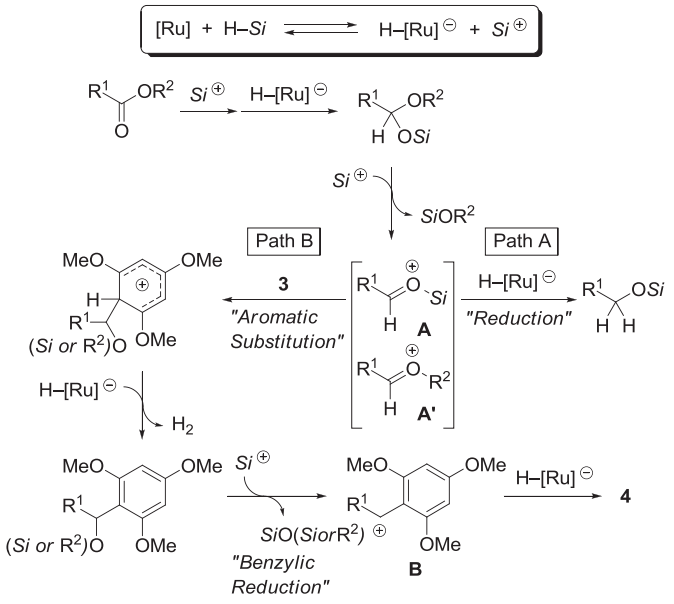
Above results demonstrates that the ruthenium-catalyzed reaction with hydrosilane leads to primary-alkylation of 1,3,5-trimethoxybenzene with various esters. This is an advantage of this reaction, because it is well known that Friedel–Crafts aromatic substitution is a good method for introduction of *tert*- or *sec*-alkyl groups to the aromatic ring, but not good for that of CH_2R groups.[14] In contrast, the arenes, which can be used in this reaction are limited to electron-rich aromatics, and reduction of esters predominantly takes place in the case where nucleophilicity of the arene is not strong enough to trap the intermediary cationic species. Two side reactions are observed; one is the reaction of two molecules of the ester with one molecule of the arene to form dialkylated products (2:1 reaction), whereas another is that of one molecule of the ester with two molecules of the arene (1:2 reaction). The 2:1 reaction is typically seen in the case where the aromatic ring is sterically less crowded, whereas the 1:2 reaction is observed in the reaction of electron-rich aromatics. Thus, attempted alkylation of anisole, 1,2-dimethoxybenzene, and 1,4-dimethoxybenzene resulted in reduction of esters. The reaction of 1,3-dimethoxybenzene was sluggish due to the predominance of 2:1 reaction. The reaction of 2-*tert*-butylfuran gave a mixture of the 1:1 and 1:2 product as shown in Scheme 7. Sakai and co-workers reported benzylation of several aromatic compounds in the indium-promoted reactions of benzoic acids with hydrosilanes.[8b] Although benzyl cationic intermediate formed by the ruthenium-catalyzed reaction of benzoates with hydrosilanes may promote the benzylation of a variety of arenes; however, attempted reaction of anisole with ethyl benzoate was failed due to the slow reaction of benzoates with hydrosilanes as described above.



Scheme 7. Reaction with 2-*tert*-butylfuran.

Possible mechanisms are illustrated in Scheme 8. As reported previously, polymerization of vinyl ethers is initiated by combination of hydrosilanes and a catalytic amount of **1** under similar conditions to those used for the aromatic alkylation presented in this paper. Although the mechanism of hydride abstraction by **1** from hydrosilanes is not clear at present, one of the reasonable explanations is as follows: the catalyst activates an Si–H bond of R_3SiH to result in heterolytic cleavage producing R_3Si^+ species. Addition of the formed silyl cation to CH_2=CHOR to give a carbocation stabilized by the neighboring OR group, $R_3SiCH_2CH^+OR$,

which reacts with another molecule of CH_2=CHOR to initiate the addition polymerization.[12] When similar mechanisms are applied to the reaction presented in this paper, a sequence of the reactions involving activation of C=O or C–O bonds by R_3Si^+ followed by attack of the ruthenium hydride results in formation of the intermediates **A** and **A′** from the ester used. As shown in path A, the hydride attack to the intermediate **A** accomplishes the reduction of esters. In the meantime, the cationic intermediates **A** and **A′** have lifetime enough to trap an electron-rich aromatic compound **3**, leading to the aromatic substitution (Path B).[15] The resulting benzyl silyl ether undergoes the above described R_3Si^+ activation/hydride reduction sequence to form the final product **4**. A possible side reaction is further alkylation of **4** giving rise to the 2:1 reaction. Another possible side reaction is trapping of the benzyl cation **B** by aromatic compounds leading to the 1:2 reaction. This has never been observed in the reactions of **3**; two OMe groups at the *ortho* positions sterically presumably prevent the access of the second molecule of **3** to the cationic intermediate **B**. However, the 1:2 reaction actually takes place in the reactions of sterically less crowded *tert*-butylfuran and 1,3-dimethoxybenzene.



Scheme 8. Possible mechanisms.

Despite the limitation of aromatic compounds, the results clearly demonstrate that combination of hydrosilanes, esters, and the ruthenium cluster provides a good method for introduction of primary-alkyl group to the electron-rich aromatic ring and the same catalyst system realizes the C–C bond forming reaction. In a series of our works, we have been showing that hydrosilanes activated by **1** not only behave as an efficient reducing reagent for carbonyl compounds but also contributed to achievement of other organic transformations, such as dehydration[13a] and deprotection.[13b] The possible mechanisms suggest that appropriate design of the reaction considering the intermediary cationic species would give a clue for developing further novel organic transformations, in which we are currently investigating.

3. Experimental section

3.1. General methods

All reactions were carried out under a nitrogen or argon atmosphere. ^{1}H and ^{13}C NMR spectra were measured on JEOL GSX-270 (270 MHz) and ECA-600 (600 MHz) spectrometers. Chemical shifts (δ values) were given in parts per million relative to the solvent signal (7.26 ppm for $CDCl_3$). Chemical shifts for ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard (δ=77.1). HRMS analysis was performed at the Analytical Center in Institute for Materials Chemistry and Engineering, Kyushu University. IR spectra were measured on JASCO FT/IR-550 and 4200 spectrometers. Analytical thin-layer chromatography (TLC) was performed on glass plates and aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F_{254}, layer thickness 0.25 and 0.2 mm, respectively). Visualization was accomplished by UV light (254 nm), anisaldehyde, and phosphomolybdic acid. (μ_3, η^2, η^3, η^5-acenaphthylene)$Ru_3(CO)_7$(**1**) was prepared by our method.[11]

3.2. General procedure

The Ru catalyst **1** (0.005 mmol), ethyl 3-phenylpropanate (**2**) (0.6 mmol), and 1,3,5-trimethoxybenzene (**3**) (0.5 mmol) were sequentially added to a reaction tube equipped with a stirring bar and a septum under an argon atmosphere. Ethyldimethylsilane (2.4 mmol) was added by a syringe. After 5 h, the reaction was quenched with MeOH, and the volatiles were removed in vacuo. The residue was purified by chromatography (silica-gel) eluting with hexane/EtOAc to afford the product.

3.3. Spectral data of the products

*3.3.1. 1-(3-Phenylpropyl)-2,4,6-trimethoxybenzene (**4a**).* Mp 46.0 °C; IR (KBr) ν 2935, 2834, 1609, 1595, 1497, 1455, 1416, 1204, 1150, 1118, 1061, 949, 750, 700 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.79 (m, 2H), 2.59–2.68 (m, 4H), 3.78 (s, 6H), 3.80 (s, 3H), 6.13 (s, 2H), 7.10–7.33 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 22.6, 31.0, 36.0, 55.4, 55.7, 90.5, 111.5, 125.4, 128.1, 128.4, 143.2, 158.9, 159.2; HRMS (EI) calcd for $C_{18}H_{22}O_3$ 286.1569, found 286.1564.

*3.3.2. 1-Ethyl-2,4,6-trimethoxybenzene (**4b**)*[16]. IR (neat) ν 2960, 2937, 2835, 1609, 1497, 1455, 1417, 1314, 1225, 1204, 1148, 1057, 946, 810 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.04 (t, J=7.2 Hz, 3H), 2.58 (q, J=7.2 Hz, 2H), 3.799 (s, 6H), 3.803 (s, 3H), 6.14 (s, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 14.2, 16.0, 55.3, 55.7, 90.7, 113.4, 158.7, 159.1; HRMS (EI) calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1101.

*3.3.3. 1-(4-Chlorobutyl)-2,4,6-trimethoxybenzene (**4c**).* IR (neat) ν 2938, 1595, 1497, 1455, 1416, 1321, 1204, 1149, 1115, 060, 949, 811 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.58 (m, 2H), 1.77 (m, 2H), 2.58 (t, J=7.2 Hz, 2H), 3.56 (t, J=7.2 Hz, 2H), 3.79 (s, 6H), 3.80 (s, 3H), 6.12 (s, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 21.6, 26.7, 32.5, 45.4, 55.4, 55.7, 90.5, 111.0, 158.9, 159.3; HRMS (EI) calcd for $C_{13}H_{19}ClO_3$ 258.1023, found 258.1021.

*3.3.4. 1-(4-Bromobutyl)-2,4,6-trimethoxybenzene (**4d**).* IR (neat) ν 2937, 1595, 1497, 1455, 1204, 1148, 810 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.58 (m, 2H), 1.85 (m, 2H), 2.58 (t, J=7.5 Hz, 2H), 3.43 (t, J=7.2 Hz, 2H), 3.79 (s, 6H), 3.80 (s, 3H), 6.12 (s, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 21.4, 28.0, 32.7, 34.2, 55.4, 55.7, 90.5, 110.9, 158.9, 159.3; HRMS (EI) calcd for $C_{13}H_{19}BrO_3$ 302.0518, found 302.0515.

*3.3.5. 1-(3-Methylbutyl)-2,4,6-trimethoxybenzene (**4e**)*[17]. IR (neat) ν 2953, 2835, 1609, 1497, 1465, 1455, 1416, 1206, 1142, 1082, 1061, 950, 909, 810, 733 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 0.92 (d, J=6.8 Hz, 6H), 1.30 (m, 2H), 1.55 (sept, J=6.8 Hz, 1H), 2.54 (m, 2H), 3.79 (s, 6H), 3.80 (s, 3H), 6.13 (s, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 20.6, 22.7, 38.9, 55.3, 55.7, 90.6, 112.4, 158.8, 159.0; HRMS (EI) calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1568.

*3.3.6. 1-(2-Methylpropyl)-2,4,6-trimethoxybenzene (**4f**)*[17]. IR (neat) ν 2954, 2835, 1610, 1497, 1464, 1416, 1218, 1204, 1142, 1078, 952,

811 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 0.85 (d, J=6.8 Hz, 6H), 1.81 (sept, J=6.8 Hz, 1H), 2.43 (d, J=7.2 Hz, 2H), 3.77 (s, 6H), 3.81 (s, 3H), 6.13 (s, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 22.6, 28.6, 31.4, 55.3, 55.6, 90.5, 111.2, 159.1, 159.2; HRMS (EI) calcd for $C_{13}H_{20}O_3$ 224.1412, found 224.1412.

*3.3.7. 1-(Cyclopentylmethyl)-2,4,6-trimethoxybenzene (**4g**).* IR (neat) ν 2949, 2864, 1610, 1496, 1455, 1416, 1318, 1204, 1153, 1110, 1062, 950, 811 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 1.16–1.29 (m, 2H), 1.41–1.52 (m, 2H), 1.53–1.69 (m, 4H), 2.05 (m, 1H), 2.55 (d, J=7.2 Hz, 2H), 3.78 (s, 6H), 3.80 (s, 3H), 6.13 (s, 2H); ^{13}C NMR (99.5 MHz, benzene-d_6) δ 25.4, 28.5, 32.8, 41.1, 54.8, 55.1, 90.9, 111.7, 159.5, 159.8; HRMS (EI) calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1571.

*3.3.8. 1-(Cyclohexylmethyl)-2,4,6-trimethoxybenzene (**4h**).* Mp 68.8 °C; IR (KBr) ν 2923, 2846, 1600, 1496, 1467, 1413, 1324, 1232, 1147, 1103, 1058, 952, 806 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 0.91–1.04 (m, 2H), 1.10–1.20 (m, 3H), 1.45 (m, 1H), 1.55–1.69 (m, 5H), 2.43 (d, J=7.2 Hz, 2H), 3.78 (s, 6H), 3.80 (s, 3H), 6.12 (s, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 26.6, 26.8, 30.1, 33.3, 38.1, 55.3, 55.7, 90.5, 110.8, 159.0, 159.2; HRMS (EI) calcd for $C_{16}H_{24}O_3$ 264.1725, found 264.1718.

*3.3.9. Benzyl-2,4,6-trimethoxybenzene (**4i**)[17].* IR (neat) ν 2959, 2835, 1596, 1495, 1454, 1416, 1321, 1207, 1151, 1120, 1060, 950, 816, 735 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 3.78 (s, 6H), 3.81 (s, 3H), 3.93 (s, 2H), 6.15 (s, 2H), 7.06–7.25 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 28.4, 55.4, 55.7, 90.7, 110.2, 125.3, 128.0, 128.5, 142.3, 158.9, 159.7; HRMS (EI) calcd for $C_{16}H_{18}O_3$ 258.1256, found 258.1253.

*3.3.10. 2-(4-Hydroxyundecyl)-1,3,5-trimethoxybenzene (**8**).* IR (NaCl) ν 3424, 2925, 2853, 1609, 1597, 1497, 1459, 1228, 1206, 1087, 806 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 6.13 (s, 2H), 3.80 (s, 3H), 3.79 (s, 6H), 3.70–3.60 (m, 1H), 2.57 (t, J=6.8 Hz, 2H), 1.66–1.20 (m, 19H), 0.88 (t, J=6.8 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 159.1, 158.7, 111.4, 90.4, 71.8, 55.6, 55.3, 37.3, 37.0, 31.8, 29.7, 29.3, 25.7, 25.4, 22.6, 22.1, 14.1; HRMS (EI) calcd for $C_{20}H_{34}O_4$ 0.338.2457, found 338.2458.

Reaction with carboxylic acid (Eq. 4): Following the general procedure, using 3-phenylpropionic acid (0.6 mmol), $EtMe_2SiH$ (3.0 mmol), Ru catalyst **1**(0.0025 mmol) for 8 h, yielded **4a** (94%).

Reaction with aldehyde (Eq. 5): Following the general procedure, using 3-phenylpropionaldehyde (0.6 mmol), $EtMe_2SiH$ (1.5 mmol), Ru catalyst **1**(0.0025 mmol) for 1 h, yielded **4a** (35%).

*3.3.11. 1,2,3,4-Tetrahydro-5,7-dimethoxy-1-(p-toluenesulfonyl)quinoline (**9**).* Following the general procedure, using ester shown in Eq. 9 (0.25 mmol), TMDS (2.0 mmol), Ru catalyst **1**(0.0025 mmol), benzene at 50 °C for 5 h, yielded the product **9** (62.3 mg, 74%), IR (neat) ν 2940, 2839, 1611, 1589, 1492, 1462, 1421, 1350, 1341, 1285, 1203, 1163, 1031, 942, 815, 772 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 1.49–1.59 (m, 2H), 2.35 (t, J=7.2 Hz, 2H), 2.38 (s, 3H), 3.75 (s, 3H), 3.77–3.81 (m, 2H), 3.81 (s, 3H), 6.26 (d, J=2.4 Hz, 1H), 7.05 (d, J=2.4 Hz, 1H), 7.20 (d, J=8.2 Hz, 2H), 7.54 (d, J=8.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 20.2, 20.4, 21.5, 46.5, 55.4, 55.5, 95.4, 100.6, 111.3, 127.1, 129.6, 137.2, 138.1, 143.5, 157.9, 158.2; HRMS (EI) calcd for $C_{18}H_{21}NrO_4S$ 347.1191, found 347.1191.

*3.3.12. Reaction with furan (**10**).* Following the general procedure, using ethyl 3-phenylpropionate (1.0 mmol), 2-*tert*-butylfuran (0.5 mmol), $EtMe_2SiH$ (4.0 mmol), Ru catalyst **1** (0.0025 mmol) at rt for 5 h, yielded the product (14% **10a**, 51% **10b**). Compound **10a**: ^1H NMR ($CDCl_3$, 395 MHz, rt) δ 7.33–7.24 (m, 2H), 7.23–7.16 (m, 3H), 5.88–5.80 (m, 2H), 2.67 (t, J=7.7 Hz, 2H), 2.62 (t, J=7.7 Hz, 2H), 1.96 (tt, J=7.7 Hz, 2H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.8 MHz, rt) δ 162.5, 153.9, 142.2, 128.5, 128.3, 125.7, 104.8, 101.9, 35.3, 32.5, 29.8, 29.1, 27.6; IR (NaCl) 3065, 3027, 2965, 2866, 2008, 1946, 1604, 1560, 1496, 1459, 1455, 1390, 1361, 1279, 1260, 1194, 1140, 1126, 1096, 1079, 1030, 1012, 948, 802, 781, 743, 700 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{22}O242.1671$, found 242.1671. Compound **10b**: ^1H NMR ($CDCl_3$, 395 MHz, rt) δ 7.33–7.25 (m, 2H), 7.22–7.14 (m, 3H), 5.90 (d, J=3.4 Hz, 2H), 5.85 (d, J=3.4 Hz, 2H), 4.01 (t, J=7.2 Hz, 1H), 2.62 (t, J=7.2 Hz, 2H), 2.27 (dt, J=7.2, 7.2 Hz, 2H), 1.27 (s, 18H); ^{13}C NMR ($CDCl_3$, 67.8 MHz, rt) δ 162.8, 153.4, 142.2, 128.5, 128.3, 125.8, 105.7, 102.0, 38.6, 35.2, 32.6, 29.1; IR (NaCl) 3028, 2965, 2931, 2905, 2867, 1604, 1557, 1496, 1476, 1458, 1362, 1279, 1261, 1227, 1194, 1127, 1031, 1014, 950, 785, 749, 699 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{32}O_2$ 364.2402, found 364.2405.

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Supplementary data

These data include experimental details, copies of ^1H and ^{13}C NMR spectra. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.08.033.

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15. As shown in Scheme 5, Eq. 5, aldehydes also behave as a reagent for the aromatic alkylation. When esters are used as the alkylating reagent, the aromatic alkylation is not seriously competitive with simple reduction of esters to silyl ethers. In contrast, the reduction to silyl ethers is a major reaction pathway in the reaction with aldehydes; this leads to the lower yield of **4a** in Eq. 5 (35%). As illustrated in Scheme 8, two intermediates **A** and **A′** possibly mediated the reductive alkylation with esters, while the reaction of aldehydes with the hydrosilane activated by **1** generates **A** as a single intermediate. It is important that **A** has two pathways, reduction (path A) and reductive alkylation (Path B), whereas **A′** is able to take only Path B. One of the explanation for the lower yield of **4a** from the aldehyde than that from the ester is absence of the reaction pathway to form **4a** through **A′**.
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