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Ruthenium-Catalyzed Addition of Carbon–Hydrogen Bonds in Aromatic Ketones to Olefins. The Effect of Various Substituents at the Aromatic Ring

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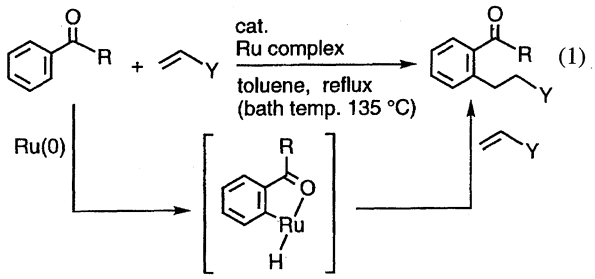
To obtain further insight into the new ruthenium-catalyzed reaction of carbon–hydrogen bonds in aromatic ketones with olefins, the effect of various substituents at the aromatic ring is examined. Reaction of *o*-methylacetophenone with triethoxyvinylsilane (**2**) in the presence of $[Ru(H)_2(CO)(PPh_3)_3]$ (**3**)as the catalyst gave the 1 : 1 addition product in quantitative yield. Similarly, the ketone having an *o*-CF_3 group gave the coupling product **9** in 92% yield. However, *ortho* substituents such as OMe, F, and CN, seem to react with and kill the catalyst so that no efficient reaction was attained. In the cases of the reactions of *p*-methoxy- and *p*-fluoroacetophenones with **2**, the corresponding 1 : 2 addition products were obtained as the major products. In the cases of *m*-substituted acetophenones, two different C–H bonds at the *ortho* positions are available. The C–C bond formation preferentially occurred at the sterically less congested positions. Exceptions are the reactions of *m*-methoxy- and *m*-fluoroacetophenones, in which the C–C bond formation took place preferentially at the more congested position. This may be due to the coordination of oxygen or fluorine atom to ruthenium. The factors controlling these selectivities are discussed.

We have reported addition of carbon–hydrogen bonds in aromatic ketones to olefins with the aid of ruthenium complexes as the catalysts (Eq. 1).[1] We extended this new catalytic reaction to various types of compounds.[2—17] Aromatic ketones react with a large numbers of olefins[1—4,7] and internal acetylenes[6] to give the corresponding 1 : 1 addition compounds. The C–H/olefin coupling reaction is not only limited to aromatic C–H bonds, but can be extended to olefinic C–H bonds. The olefinic C–H/olefin coupling reaction of cyclic enones with olefins took place in the presence of the same type of ruthenium complex as the catalyst.[5] The C–H bonds in aromatic esters also undergo C–H/olefin coupling reaction catalytically with the aid of the ruthenium complex.[8,18] In this case, the esters which have an electron-withdrawing group on the aromatic ring reacts with olefins smoothly. In place of carbonyl compounds, aromatic imines also undergo C–H/olefin coupling reaction in the presence of ruthenium carbonyl as the catalyst.[9] The C–H/olefin coupling reaction can be applied to the intramolecular cyclization reactions. The cyclization of 1-(2-pyridyl)-1,*n*-dienes was catalyzed by rhodium complexes to give the corresponding 5- and 6-membered carbocycles.[10,11] We also reported that C–H/CO/olefin coupling reactions with the aid of ruthenium or rhodium carbonyl complex.[13—17] All these reactions are believed to proceed in a chelation-assisted way, leading to a metallacycle intermediate.[1—17]



(1)

Several new type of catalytic reactions involving the chelation-assisted carbon–hydrogen bonds cleavage have been studied also by others.[19—23] These results indicate that the methodology of chelation-assisted carbon–hydrogen bonds cleavage is powerful. Thus the catalytic reactions have become as a new tool for a carbon–carbon bond forming reaction in organic synthesis.

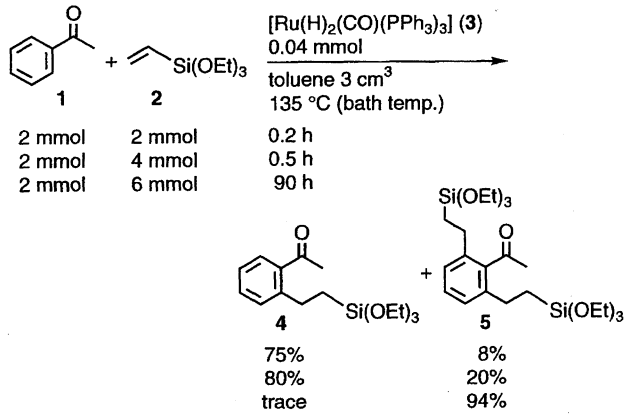
As the representative, typical reaction, the catalytic coupling of aromatic ketones with olefins (Eq. 1) should be explored further in various aspects. For example, the reaction is unique as the synthetic reaction since no conventional methods can bring about alkylation exclusively *ortho* to the electron-withdrawing group as in Eq. 1. Because the transformation is very useful in synthesis and also because the catalytic reaction is intrinsically interesting, we have studied and already reported structure-reactivity patterns of aromatic ketones and olefins.[4] Now, we have studied the catalytic reaction of aromatic ketones having various substituents. This

paper reports the functional group compatibility of the new catalytic reaction and unique secondary directing effects of the substituents[7] in substituted aromatic ketones.

Results and Discussion

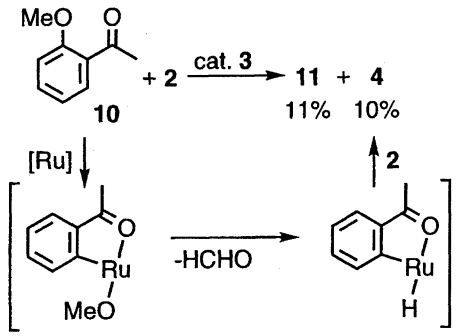
We were pleased to find that the ruthenium-catalyzed C–H/olefin coupling with aromatic ketones having a variety of substituents took place smoothly. General features of the reactions are as follows. Reactions of various *o*-, *m*-, and *p*-substituted acetophenones with triethoxyvinylsilane gave the corresponding 1 : 1 and/or 1 : 2 addition product(s) in excellent yield(s). Di- and trisubstituted acetophenones also reacted with triethoxyvinylsilane to afford the coupling products. The functional group compatibility is quite high. The present C–H/olefin coupling reactions are tolerant of both electron-donating and electron-withdrawing groups. In the reactions of acetophenones in which two *ortho* positions are not equivalent because of a *m*-substituent, the site selectivities are affected by the steric crowdness of the *m*-substituent of acetophenones. In some cases, unusual effects of the substituents for directing the ruthenium closer to the more congested C–H bonds were observed. Details of these results will be described below.

Reaction of *o*-Substituted Acetophenones with Triethoxyvinylsilane. Before going into the substituted acetophenones, it may be appropriate to present the results of unsubstituted acetophenone. We previously reported that the reaction of acetophenone (**1**) with an equimolar amount of triethoxyvinylsilane (**2**) gave the corresponding 1 : 1 and 1 : 2 coupling products in 75% and 8% yields based on **1**, respectively[1,3,4] (Eq. 2). The yields were based on the starting ketone. When 2 molar amounts of **2** were used, the ketone **1** was completely consumed and the coupling products **4** and **5** were obtained in 80 and 20% yield, respectively. Under more forcing conditions (i.e., the use of 3 molar amounts of **2** and refluxing for 90 h), the 1 : 2 coupling product was obtained exclusively. Throughout the experiments described below, triethoxyvinylsilane (**2**) was used as the olefin because of its high reactivity, the easiness for handling, and the usefulness of the products.

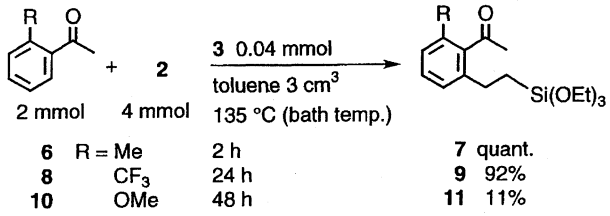


(2)

The C–H/olefin coupling reactions of *o*-substituted acetophenones were carried out under the same conditions to give the corresponding 1 : 1 addition products (Eq. 3). Reaction of *o*-methylacetophenone (**6**) with triethoxyvinylsilane (**2**) in the presence of **3** as the catalyst afforded the corresponding coupling product **7** in a quantitative yield. In the case of CF_3 group on the aromatic ring, the corresponding coupling product was obtained in 92% yield. Interestingly, however, *o*-fluoro and *o*-cyano groups completely suppressed the C–H/olefin coupling reactions. When the *ortho* substituent was a methoxy group, the expected product **11** was obtained in only 11% yield and unexpectedly the coupling product **4** was formed. The product **4** might have been formed via demethoxylation followed by β-hydride elimination (Scheme 1).[22,24] This result suggests that the C–O bond is also easily cleaved by a low-valent ruthenium. It is likely that the fluoro and the cyano substituents have reacted with ruthenium through the similar pathways shown in Scheme 1, but yielding inactive ruthenium complexes.



Scheme 1. Proposed pathway of demethoxylation.

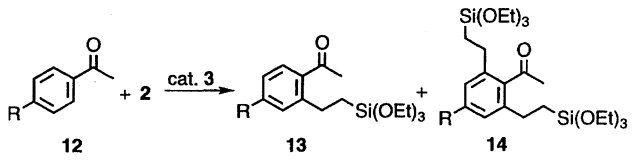


(3)

Reaction of *p*-Substituted Acetophenones with 2. In *p*-substituted acetophenones, there are two equivalent C–H bonds at the *ortho* positions to the carbonyl group. The ratio of the 1 : 1 and 1 : 2 addition products changes depending on the electronic nature of the substituent at *p*-position in the acetophenones. Selected results of the catalytic reaction of *p*-substituted acetophenones with **2** are listed in Table 1.

Various acetophenones are applicable to the present catalytic C–H/olefin coupling reaction. A notable exception is *p*-dimethylaminoacetophenone (**12a**), which will be discussed later. When *p*-methylacetophenone (**12b**) was used, the corresponding 1 : 1 and 1 : 2 addition products (**13b** and **14b**, respectively) were obtained in 69 and 31% yields, respectively (Run 2). In the reaction of the acetophenone having a good electron-donating group (methoxy group), the 1 : 2 addition product became predominant. As we have demonstrated previously, a considerable amount of the 1 : 2 addition product is formed without dissociation of the 1 : 1

Table 1. Catalytic Reaction of *p*-Substituted Acetophenones with **2**[a]



12 **13** **14**

Run	Substrate		Time	Products and Yields/%[b]	
	R	**12**	h	**13**	**14**
1	NMe_2	**a**	24	No reaction	
2	Me	**b**	0.5	69	31
3	OMe	**c**	0.5	7	93
4	NEtC(O)Me	**d**	7	93	0
5	F	**e**	0.5	9	91
6	CO_2Et	**f**	4	69	31
7	CF_3	**g**	24	63	17
8	CN	**h**	5	88	0

a) Reaction conditions: acetophenones (2 mmol), **2** (4 mmol), $[Ru(H)_2(CO)(PPh_3)_3]$ (**3**) (0.04 mmol), toluene (3 cm^3), 135 °C (oil bath temperature). b) GC yields.

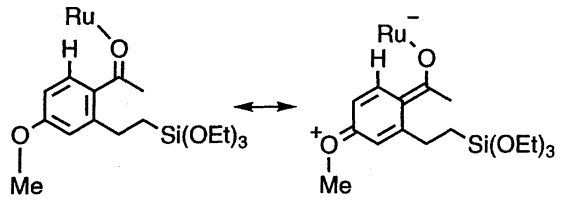


Fig. 1. Resonance form of proposed intermediate.

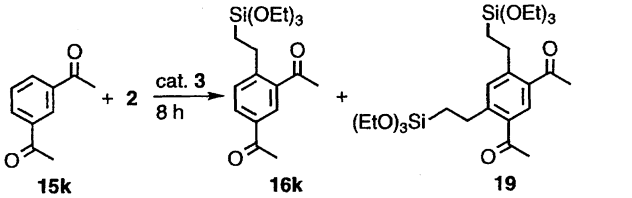
adduct from the ruthenium center, the binding of carbonyl oxygen to the metal being kept throughout.[2] As to the formation of **14**, considerable portions of the second C–H/olefin coupling step should also proceed without dissociation. This result may stem from a contribution of the resonance form as shown in Fig. 1. Thus, in the case of **12c**, the bonding between the ketone carbonyl oxygen and the ruthenium center becomes stronger than that of the parent acetophenone due to the π-electron-donation by the methoxy group.

Interestingly, however, a strong electron-donating substituent, i.e., dimethylamino group in **12a**, completely suppress the present coupling reaction. This complete deactivation of the catalyst is not due to strong, direct coordination of amino nitrogen to the ruthenium, since the reaction of *m*-dimethylaminoacetophenone gave the corresponding coupling product in high yield (vide infra). It is likely that the carbonyl oxygen in **12a** coordinates too strongly (similar to Fig. 1) for the catalytic reaction to turn over.

The present catalytic reaction is tolerant of the amido group. The reaction of *p*-(*N*-acetyl-*N*-ethylamino)acetophenone (**12d**) with **2** gave **13d** as a sole product even after a prolonged reaction period (7 h). Similar complete selectively to 1 : 1 adduct was also observed in the case of *p*-CN compound **12h**. These electron-withdrawing groups may suppress the coordination of carbonyl oxygen for further coupling. The reaction of *p*-fluoroacetophenone (**12e**) gave the corresponding 1 : 2 coupling product **14e** (91% yield) as the major isomer along with the 1 : 1 coupling product **13e** (9% yield). The selectivity is the same as that in the reaction of **12c**, even though each substituent has the opposite electronegativities. This suggests that the lone pair electrons in 2p orbitals of oxygen and fluorine atoms played important roles (Fig. 1).

We have recently reported that aromatic esters having an electron-withdrawing group react with olefins to give the coupling products with the aid of **3**.[8] In the reaction of ketone **12f**, which can also be regarded as an ester having an electron-withdrawing group (acetyl group), it seemed interesting to know which *ortho* C–H bond would add to an olefin. This reaction yielded **13f** and **14f**[25] in 69 and 31% yields, respectively. This result indicates that the C–H bond at the position *ortho* to the acetyl group is more reactive than that at the position *ortho* to the ester group under these reaction conditions. It is noteworthy that, in most cases studied, the desired coupling products are obtained in high total yields.

Reactions of *m*-Substituted Acetophenones with 2. *m*-Substituted acetophenones **15** have two different reaction sites at the positions *ortho* to the acetyl group. We studied the substituents effect on the position of the C–H bond to be cleaved. Selected results are shown in Table 2 and Eq. 4.

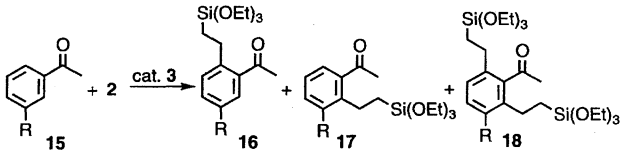


15k 2 mmol 4 mmol **16k** 30% **19** 62% (isolated)

(4)

It was interesting to observe that the reaction of *m*-dimethylaminoacetophenone (**15a**) took place smoothly to give the

Table 2. Catalytic Reaction of *m*-Substituted Acetophenones with **2**[a]



15 **16** **17** **18**

Run	Substrate		Time	Products and Yields/%[b]		
	R	**15**	h	**16**	**17**	**18**
1	NMe_2	**a**	8	85	0	0
2	Me	**b**	3	93	3	0
3	OMe	**c**	0.5	10	83	7
4	NEtC(O)Me	**d**	8	96	0	0
5	F	**e**	4	3	77	11
6	CO_2Et	**f**	4	91	0	0
7	CF_3	**g**	24	82	0	0
8	CN	**h**	0.5	71	26	3
9	OC(O)Me	**i**	5	11	29	0
10	OCF_3	**j**	2	56	26	17

a) Reaction conditions: acetophenones (2 mmol), **2** (4 mmol), $[Ru(H)_2(CO)(PPh_3)_3]$ (**3**) (0.04 mmol), toluene (3 cm^3), 135 °C (oil bath temperature). b) GC yields.

coupling product **16a** in 85% yield as an exclusive product. This is in sharp contrast to the result of the *p*-isomer **12a**, for which no reaction took place. The *m*-dimethylamino group does not make the carbonyl oxygen too basic, as in Fig. 1. In the case of the reaction of *m*-methylacetophenone (**15b**) with **2**, the C–C bond formation predominantly occurred at the less hindered *ortho* position. The similar site selectivities were also observed in Runs 4, 6, and 7. Steric crowdness around the *o*-position between two substituents might have prevented the ruthenium from coming closer to the C–H bond at this position.

On the other hand, interestingly, when *m*-methoxyacetophenone (**15c**) was subjected to this reaction, the C–C bond formation preferentially occurred at a more congested position. The C–H bond at the sterically less favorable position is cleaved. This unusual site selectivity might stem from electronic interaction between the ruthenium and lone pair electrons of the methoxy oxygen. This observation suggests that the methoxy group has behaved as the secondary directing group in addition to the acetyl group.

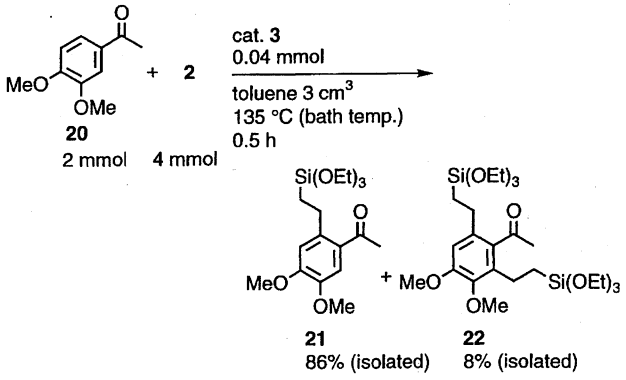
The similar phenomena were also reported by several groups[26–28] in a stoichiometric reaction of [(alkyl)$Mn(CO)_5$] with **15c**, resulting in a predominant cyclometalation at the more crowded position. Kaesz and co-workers proposed that the some polar interaction between the manganese and the methoxy group controlled the reaction site.[26] Liebeskind and co-workers also reported the similar unusual site selectivity. Nicholson and co-workers proposed that the electronic preference controlled the manganation position.[27] They concluded that an electronegative substituent in the absence of steric effects directed the manganation position.[28] Although there is no clear explanation with respect to this unusual site selectivity, we suppose that an interaction between the lone pair electrons of the methoxy oxygen and the ruthenium atom is the key of the site selectivity, based on the following results. In the reaction of *m*-acetoxyacetophenone (**15i**) in which the electron density on the lone pair of the oxygen was reduced comparing with that of methoxy group, the selectivity to the more congested position slightly decreased. In addition, in the case of *m*-(trifluoromethoxy)acetophenone (**15j**), the reaction resulted in the C–C bond formation at the less congested position, in spite of the fact that the van der Waals radius of the trifluoromethyl group is almost the same as that of the methoxy group. Obviously, a trifluoromethoxy group is less electron-donating than a methoxy group.

Fluorine substituent also directs the ruthenium to the more congested position. The van der Waals radius of the fluorine atom is almost same to that of a hydrogen atom.[29] Thus, it is likely that lone pair electrons of the fluorine directed the metal to the adjacent position.[30] A similar type of coordination ability of fluorine atom has been fairly well documented.[31] It is worthy to note that not only lone pair electrons as described above but also π-electrons of a nitrile group have seemingly directed the ruthenium to the sterically less favorable position, although these results may be also explained as due to the small size of the nitrile group (Run 8).

Yamazaki and Sonogashira reported a $Rh_4(CO)_{16}$-catalyzed reaction of mono-substituted benzenes (toluene, anisole, and fluorobenzene) with diphenylketene or diphenylacetylene.[30] Interestingly enough in these reactions, when anisole and fluorobenzene were used as the substrate, the C–C bond formation preferentially occurred at the position *ortho* to the substituents. The researchers suggested that the reason of this selectivity was an inductive effect of the electronegative atoms in anisole and fluorobenzene. In our cases, the inductive effects of the substituents seem to be neglected because the introduction of the electron-withdrawing group on the ether oxygen as in **15i** and **15j**, which increased the electron-withdrawing ability of the oxygen, decreased the selectivity of the adjacent position toward the substituent (Run 3 vs. Runs 9 and 10).

Ketone and ester carbonyl groups can bring the ruthenium close to their *ortho* C–H bond. Interestingly, however, the additional ketone and ester carbonyl groups did not help bringing the ruthenium closer to the more congested position (Run 6 and Eq. 4). We think that steric hindrance suppresses the C–C bond formation at a sterically unfavorable position.

Directing Effect of the Ether Oxygen. To substantiate further the directing ability of the ether oxygen, we carried out the reaction of *m*, *p*-dimethoxyacetophenone (**20**) with **2** (Eq. 5). The coupling reaction exclusively occurred at the sterically less crowed position (*o'*-position). No sterically unfavorable coupling product, i.e., *o*,*m*,*p*-trisubstituted aceophenone, could be detected by GCMS. While we could not determine whether **22** was formed via **21** or not, the reaction site completely moved to the opposite *ortho* position. This result was somewhat unexpected, judging from the result of the reaction of *m*-methoxyacetophenone. This opposite site selectivity seems to be caused by a so-called buttressing effect between the methoxy groups.[32,33] However, this steric hindrance is not so serious. The reaction of *m*,*m'*,*p*-trimethoxyacetophenone (**23**) gave the corresponding coupling product **24** in quite high yield (Eq. 6).[33] The low reactivity might be also caused by the buttressing effect. Actually, the reaction of *m*,*m'*-dimethoxyacetophenone (**25**), which does not have any steric interaction between the methoxy groups, completed within 1.5 h, affording the 1 : 1 addition product **26** in 96% yield (Eq. 7).



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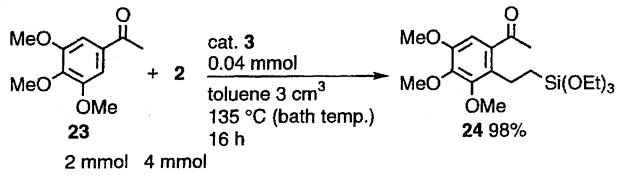

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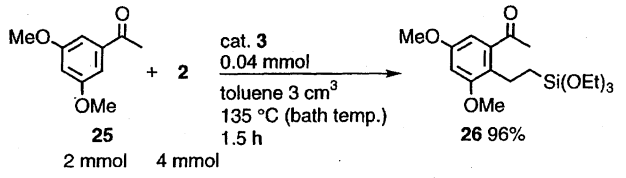
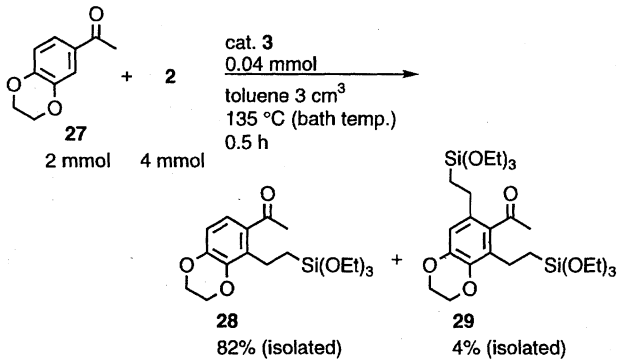


(7)

The ketone **27** was selected for a study with respect to the effect of the conformation of the substituent on the site selectivity. In the case of **27**, the reaction site became at a more crowded position probably because the free conformational rotation around C–O–C bonds is not possible, due to the ethylene bridge and thus the lone pair electrons point towards desired directions (Eq. 8). In place of the ethylene bridge, when methylene tether was used, products **31**, **32**, and **33** were obtained in 63, 14, and 18% yields, respectively (Eq. 9). The formation of **31** as the major product indicates again the importance of the interaction between the ether oxygen and the ruthenium atom. Therefore, the low selectivity of reaction of Eq. 9 may stem from the decrease of an interaction between the lone pair electron and the ruthenium.



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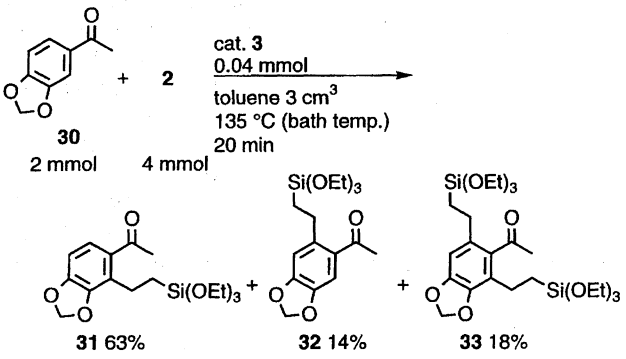
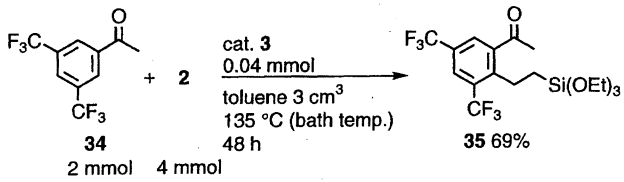


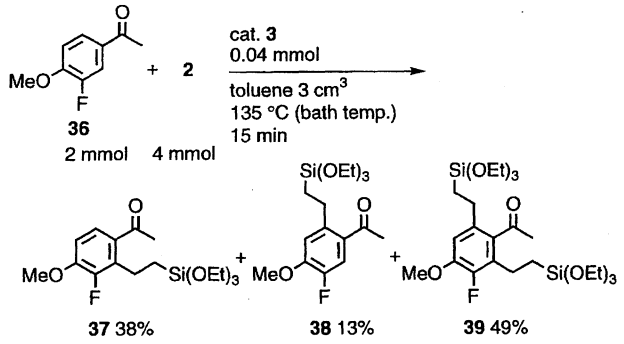
(9)

Reactions of Disubstituted Acetophenones. Even when a highly electron-deficient acetophenone **34** having two CF_3 groups was employed in the reaction, the desired coupling product **35** was obtained in a good yield (Eq. 10). This result is noteworthy. In the case of the reaction of *m*-CF_3 compound **15g** (Run 7 in Table 2), the C–C bond is formed only at the position remote from CF_3 group to give **16g**. But in the present case of **34**, the C–C bond formation is forced to take place at the position adjacent to CF_3 (**35**). This result indicates that the C–C bond formation overcomes the steric problem if there is no sterically favorable C–H bond.



(10)

As mentioned above, the presence of the methoxy group at the *p*-position seems to facilitate the second C–H/olefin coupling (Fig. 1). A similar effect of the methoxy group was observed in the reaction of *m*-fluoro-*p*-methoxyacetophenone (**36**) with **2**. Although the reaction of *m*-fluoroacetophenone (**15e**) preferentially afforded the 1 : 1 addition product **17e** (Run 5 in Table 2), the reaction shown in Eq. 11 yielded the corresponding 1 : 2 addition product **39** mainly, even at the early stage of the reaction period. This acceleration of 1 : 2 adduct formation can be ascribed to the enhancement of donor ability of carbonyl oxygen by the *p*-methoxy group, as shown in Fig. 1.



(11)

Conclusion

The *ortho* C–H bond in acetophenone derivatives can be cleaved and added to an olefin such as a vinylsilane in the presence of $[Ru(H)_2(CO)(PPh_3)_3]$ as the catalyst. The methodology is quite useful in organic synthesis because of the high selectivity of the alkylating position and the high functional group compatibility. Both electron-donating and electron-withdrawing groups on the aromatic ring of acetophenones can be used in the catalytic reaction, resulting in the formation of the corresponding C–H/olefin coupling product in high yield. The reaction site is directed by the ketone carbonyl. The electron-donating group except for dimethylamino group at *p*-position of acetophenones seems to enforce the interaction between the ketone carbonyl and the ruthenium atom in the catalyst. Interesting directing abilities

of the methoxy and fluoro groups which have lone pair electrons at the *m*-position were observed. The site selectivity of the more congested position decreased with decreasing the electron density on the ether oxygen. We hope these results of various substituted acetophenones will provide the bases for designing useful synthetic transformation.

Experimental

General Information. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JNM-EX270 spectrometer operating at 270 and 67.5 MHz, respectively. The chemical shift of ^{1}H NMR and ^{13}C NMR signals are quoted relative to internal $CHCl_3$ (δ=7.26 and 77.0) or tetramethylsilane. ^{1}H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, c=complex), coupling constant (Hz), relative intensity, and interpretation. ^{13}C NMR data are reported as follows: chemical shift in ppm (δ) and interpretation. IR spectra were measured on a Hitachi 270-50 infrared spectrometer. The GCMS analysis were measured on a Shimadzu GCMS-QP 1000 or a Shimadzu GCMS-QP 5000 gas chromatography mass spectrometer.

GC Analysis. The conditions used for the GC analysis were as follows: Shimadzu GC-14A (equipped with CBP-20 25 m×0.2 mm); temperature program, 70 °C (0 min)→10 °C min^{-1}→230 °C (30 min); injection temperature, 270 °C; detector temperature, 270 °C. The high-polarity capillary column (Shimadzu CBP-20) is suitable for quantification of the coupling products and the starting acetophenones using GC.

Solvents and Materials. Toluene was distilled under nitrogen from CaH_2. Triethoxyvinylsilane (**2**) was distilled from CaH_2 under reduced pressure. *p*-Dimethylaminoacetophenone (**12a**),[34] *m*-dimethylaminoacetophenone (**15a**),[34] *p*-acetyl-*N*-ethylacetanilide (**12d**),[35] *m*-acetyl-*N*-ethylacetanilide (**15d**),[35] and ethyl *m*-acetylbenzoate (**15f**)[36] were prepared by modified methods from the literature. Other acetophenones used in this study are commercially available. $[Ru(H)_2(CO)(PPh_3)_3]$ (**3**) was prepared by the literature method.[4,37]

A Typical Procedure for the Reaction of Substituted Acetophenones with Triethoxyvinylsilane (2). A 10-cm^3, two necked, round-bottomed flask equipped with a reflux condenser, a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum, was flushed with dry nitrogen, and then the apparatus was flame-dried under a flow of dry nitrogen. In the flask was placed **3** (37 mg, 0.040 mmol) under a flow of nitrogen. To the flask were added 3 cm^3 of toluene, a substituted acetophenone (2.0 mmol), **2** (760 mg, 4.0 mmol), and hexadecane (an internal standard for GC). The mixture was heated under vigorous reflux (at 135 °C, oil bath temperature) with stirring. The reaction was monitored by GC. After heating for an appropriate period, the mixture was allowed to cool to room temperature, and toluene and unreacted **2** were removed by rotary evaporation (40 °C/5 mmHg, 1 mmHg=133.322 Pa). A dark-brown concentrate was passed through a short column of silica gel (9 cm length×3 cm i.d.) with hexane. The product was isolated by bulb-to-bulb distillation.

2-Methyl-6-[2-(triethoxysilyl)ethyl]acetophenone (7). Bp=130 °C/2 mmHg. ^{1}H NMR δ=0.91—0.97 (c, 2 H, $SiCH_2$), 1.23 (t, J=7.08 Hz, 9 H, CH_3), 2.24 (s, 3 H, $ArCH_3$), 2.49 (s, 3 H, $C(O)CH_3$), 2.57—2.63 (c, 2 H, CH_2), 3.82 (q, J=7.08 Hz, 6 H, OCH_2), 7.00—7.32 (m, 3 H); ^{13}C NMR δ=13.01 ($SiCH_2$), 18.23 (CH_3), 19.06 ($ArCH_3$), 26.23 (CH_2), 32.46 ($C(O)CH_3$), 58.37 (OCH_2), 126.06, 127.73, 128.62, 132.01, 139.34, 141.83 (Ar), 208.30 (C=O); IR (neat) ν 1702 s cm^{-1}; MS *m/z* (% rel intensity) 324 (M^+; 1), 135 (100). Found: C, 63.11; H, 8.70%. Calcd for $C_{17}H_{28}F_3O_4Si$: C, 62.93H, 8.70%.

2- Trifluoromethyl- 6- [2- (triethoxysilyl)ethyl]acetophenone (9). Bp=170 °C/1 mmHg. ^{1}H NMR δ=0.91—0.97 (c, 2 H, $SiCH_2$), 1.23 (t, J=7.02 Hz, 9 H, CH_3), 2.55 (s, 3 H, $C(O)CH_3$), 2.62—2.68 (c, 2 H, CH_2), 3.82 (q, J=7.02 Hz, 6 H, OCH_2), 7.39—7.50 (m, 3 H); ^{13}C NMR δ=12.96 ($SiCH_2$), 18.22 (CH_3), 26.11 (CH_2), 32.40 ($C(O)CH_3$), 58.33 (OCH_2), 123.72 (q, J_{C-F}=4.9 Hz, Ar), 123.86 (q, J_{C-F}=271.7 Hz, CF_3), 125.79 (q, J_{C-F}=31.5 Hz), 128.86, 132.69, 139.62, 140.93 (Ar), 204.41 (C=O); IR (neat) ν 1710 s cm^{-1}; MS *m/z* (% rel intensity) 378 (M^+; 12), 181 (100), 178 (58), 163 (52), 119 (62), 79 (75). Found: C, 53.76; H, 6.34%. Calcd for $C_{17}H_{25}F_3O_4Si$: C, 53.95; H,6.66%.

2- Methoxy- 6- [2- (triethoxysilyl)ethyl]acetophenone (11). The product **11** could not be isolated as an analytically pure from. Bp=120 °C/2 mmHg. ^{1}H NMR δ=0.90—0.96 (c, 2 H, $SiCH_2$), 1.22 (t, J=7.02 Hz, 9 H, CH_3), 2.49 (s, 3 H, $C(O)CH_3$), 2.56—2.63 (c, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 3.81 (q, J=7.02 Hz, 6 H, OCH_2), 6.74 (d, J=7.83 Hz, 1 H), 6.85 (d, J=7.83 Hz, 1 H), 7.23 (t, J=7.83 Hz, 1 H); ^{13}C NMR δ=13.01 ($SiCH_2$), 18.24 (CH_3), 26.02 (CH_2), 32.38 ($C(O)CH_3$), 55.55 (OCH_3), 58.35 (OCH_2), 108.21, 121.35, 122.12, 129.90, 142.35, 155.94 (Ar), 205.53 (C=O); MS *m/z* (% rel intensity) 340 (M^+; 8), 294 (100), 279 (76), 160 (65). HRMS Found: *m/z* 340.1703. Calcd for $C_{17}H_{28}O_5Si$: M, 340.1707.

4-Methyl-2-[2-(triethoxysilyl)ethyl]acetophenone (13b) and 4- Methyl- 2, 6- bis[2- (triethoxysilyl)ethyl]acetophenone (14b). **13b**: Bp=160 °C/4 mmHg. ^{1}H NMR δ=0.94—1.00 (c, 2 H, $SiCH_2$), 1.25 (t, J=7.02 Hz, 9 H, CH_2CH_3), 2.36 (s, 3 H, CH_3), 2.56 (s, 3 H, $C(O)CH_3$), 2.92—2.98 (c, 2 H, CH_2), 3.86 (q, J=7.02 Hz, 6 H, OCH_2), 7.05 (d, J=7.83 Hz, 1 H), 7.10 (s, 1 H), 7.58 (d, J=7.83 Hz, 1 H); ^{13}C NMR δ=12.79 ($SiCH_2$), 18.26 (CH_2CH_3), 21.35 (CH_3), 27.42 (CH_2), 29.54 ($C(O)CH_3$), 58.30 (OCH_2), 126.25, 129.82, 131.50, 134.28, 142.11, 145.44 (Ar), 201.12 (C=O); IR (neat) ν 1686 s cm^{-1}; MS *m/z* (% rel intensity) 278 (M^+ − EtOH; 70), 135 (100), 79 (53). Found: C, 62.62; H, 8.87%. Calcd for $C_{17}H_{28}O_4Si$: C, 62.93; H, 8.70%.

14b: Bp=180 °C/4 mmHg. ^{1}H NMR δ=0.89—0.96 (c, 4 H, $SiCH_2$), 1.22 (t, J=7.02 Hz, 18 H, CH_2CH_3), 2.30 (s, 3 H, CH_3), 2.48 (s, 3 H, $C(O)CH_3$), 2.52—2.59 (c, 4 H, CH_2), 3.81 (q, J=7.02 Hz, 12 H, OCH_2), 6.90 (s, 2 H); ^{13}C NMR δ=13.03 ($SiCH_2$), 18.28 (CH_2CH_3), 21.21 (CH_3), 26.20 (CH_2), 33.10 ($C(O)CH_3$), 58.38 (OCH_2), 126.85, 138.47, 138.51, 139.37 (Ar), 208.18 (C=O); IR (neat) ν 1696 m cm^{-1}; MS *m/z* (% rel intensity) 514 (M^+; 1), 453 (59), 163 (85), 119 (73), 79 (100). Found: C, 58.08; H, 8.90%. Calcd for $C_{25}H_{46}O_7Si_2$: C, 58.33; H, 9.01%.

4-Methoxy-2-[2-(triethoxysilyl)ethyl]acetophenone (13c) and 4-Methoxy-2,6-bis[2-(triethoxysilyl)ethyl]acetophenone (14c). **13c**: Bp=160 °C/4 mmHg. ^{1}H NMR δ=0.95—1.02 (c, 2 H, $SiCH_2$), 1.25 (t, J=7.02 Hz, 9 H, CH_3), 2.55 (s, 3 H, $C(O)CH_3$), 2.99—3.05 (c, 2 H, CH_2), 3.84 (s, 3 H, OCH_3), 3.87 (q, J=7.02 Hz, 6 H, OCH_2), 6.74 (dd, J=8.10, 2.70 Hz, 1 H), 6.81 (d, J=2.70 Hz, 1 H), 7.72 (d, J=8.10 Hz, 1 H); ^{13}C NMR δ=12.50 ($SiCH_2$), 18.25 (CH_3), 28.06 (CH_2), 29.22 ($C(O)CH_3$), 55.23 (OCH_3), 58.31 (OCH_2), 110.52, 116.06, 129.41, 132.51, 148.74, 162.03 (Ar), 199.41 (C=O); IR (neat) ν 1678 s cm^{-1}; MS *m/z* (% rel intensity) 340 (M^+; 1), 294 (100), 279 (59). Found: C, 59.72; H, 8.36%. Calcd for $C_{17}H_{28}O_5Si$: C, 59.97; H, 8.29%.

14c: Bp=210 °C/4 mmHg. ^{1}H NMR δ=0.90—0.97 (c, 4 H, $SiCH_2$), 1.23 (t, J=7.02 Hz, 18 H, CH_3), 2.48 (s, 3 H, $C(O)CH_3$), 2.54—2.61 (c, 4 H, CH_2), 3.79 (s, 3 H, OCH_3), 3.82 (q, J=7.02 Hz, 12 H, OCH_2), 6.62 (s, 2 H); ^{13}C NMR δ=12.87 ($SiCH_2$),

18.24 (CH_3), 26.49 (CH_2), 33.19 (C(O)CH_3), 55.11 (OCH_3), 58.38 (OCH_2), 111.50, 134.11, 141.44, 159.75 (Ar), 208.07 (C=O); IR (neat) ν 1694 s cm^{-1}; MS *m/z* (% rel intensity) 530 (M^+; 1), 469 (100), 163 (88), 119 (55), 79 (54). Found: C, 56.27; H, 8.87%. Calcd for $C_{25}H_{46}O_8Si_2$: C, 56.57; H, 8.74%.

4-Acetyl-3-[2-(triethoxysilyl)ethyl]-*N*-ethylacetanilide (13d). Bp=140 °C/2 mmHg. ^{1}H NMR δ=0.92—0.98 (c, 2 H, $SiCH_2$), 1.11 (t, J=7.09 Hz, 3 H, NCH_2CH_3), 1.24 (t, J=7.06 Hz, 9 H, CH_3), 1.87 (s, 3 H, NC(O)CH_3), 2.60 (s, 3 H, C(O)CH_3), 2.93—2.99 (c, 2 H, CH_2), 3.75 (q, J=7.09 Hz, 2 H, NCH_2), 3.85 (q, J=7.06 Hz, 6 H, OCH_2), 7.05 (dd, J=8.02, 2.08 Hz, 1 H), 7.10 (d, J=2.08 Hz, 1 H), 7.67 (d, J=8.02 Hz, 1 H); ^{13}C NMR δ=12.80 ($SiCH_2$), 13.16 (NCH_2CH_3), 18.28 (CH_3), 22.81 (NC(O)CH_3), 27.24 (CH_2), 29.85 (C(O)CH_3), 43.90 (NCH_2), 58.42 (OCH_2), 125.18, 130.01, 130.35, 136.82, 145.39, 146.92 (Ar), 169.58 (NC=O), 201.10 (C=O); IR (neat) ν 1667 s cm^{-1}; MS *m/z* (% rel intensity) 395 (M^+; 3), 70 (100). Found: C, 60.61; H, 8.38; N, 3.56%. Calcd for $C_{20}H_{33}NO_5Si$: C, 60.73; H, 8.41; N, 3.54%.

4-Fluoro-2-[2-(triethoxysilyl)ethyl]acetophenone (13e) and 4-Fluoro-2,6-bis[2-(triethoxysilyl)ethyl]acetophenone (14e). 13e: Bp=120 °C/2 mmHg. ^{1}H NMR δ=0.93—0.99 (c, 2 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 9 H, CH_3), 2.56 (s, 3 H, C(O)CH_3), 2.94—3.00 (c, 2 H, CH_2), 3.85 (q, J=7.02 Hz, 6 H, OCH_2), 6.92 (ddd, $J_{H-H'\ H-H'\ H-F}$=8.35, 2.57, 8.35 Hz, 1 H), 7.01 (dd, $J_{H-H'\ H-F}$= 2.57, 10.06 Hz, 1 H), 7.68 (dd, $J_{H-H'\ H-H}$=8.35, 5.60 Hz, 1 H); ^{13}C NMR δ=12.44 ($SiCH_2$), 18.24 (CH_3), 27.51 (CH_2), 29.62 (C(O)CH_3), 58.35 (OCH_2), 112.43 (d, J_{C-F}=20.7 Hz), 117.35 (d, J_{C-F}=20.6 Hz), 131.87 (d, J_{C-F}=8.5 Hz), 133.40 (d, J_{C-F}=3.7 Hz), 148.95 (d, J_{C-F}=7.3 Hz), 164.20 (d, J_{C-F}=251.1 Hz) (Ar), 200.04 (C=O); IR (neat) ν 1688 s cm^{-1}; MS *m/z* (% rel intensity) 282 (M^+ − EtOH; 32), 135 (51), 128 (100), 79 (85). Found: C, 58.27; H, 7.72%. Calcd for $C_{16}H_{25}FO_4Si$: C, 58.51; H, 7.67%.

14e: Bp=200 °C/2 mmHg. ^{1}H NMR δ=0.86—0.93 (c, 4 H, $SiCH_2$), 1.20 (t, J=7.02 Hz, 18 H, CH_3), 2.47 (s, 3 H, C(O)CH_3), 2.53—2.59 (c, 4 H, CH_2), 3.79 (q, J=7.02 Hz, 12 H, OCH_2), 6.77 (d, J_{H-F}=9.45 Hz, 2 H); ^{13}C NMR δ=12.55 ($SiCH_2$), 18.21 (CH_3), 26.20 (CH_2), 32.99 (C(O)CH_3), 58.38 (OCH_2), 112.76 (d, J_{C-F}=21.8 Hz), 137.16 (d, J_{C-F}=2.4 Hz), 142.12 (d, J_{C-F}=7.3 Hz), 162.73 (d, J_{C-F}=245.0 Hz) (Ar), 207.44 (C=O); IR (neat) ν 1699 s cm^{-1}; MS *m/z* (% rel intensity) 518 (M^+; 1), 457 (94), 163 (100), 119 (72), 79 (89). Found: C, 55.39; H, 8.41%. Calcd for $C_{24}H_{43}FO_7Si_2$: C, 55.57; H, 8.36%.

Ethyl 4-Acetyl-3-[2-(triethoxysilyl)ethyl]benzoate (13f) and Ethyl 4-Acetyl-3,5-bis[2-(triethoxysilyl)ethyl]benzoate (14f). 13f: Bp=180 °C/3 mmHg. ^{1}H NMR δ=0.94—1.00 (c, 2 H, $SiCH_2$), 1.23 (t, J=7.02 Hz, 9 H, CH_3), 1.40 (t, J=7.02 Hz, 3 H, $CO_2CH_2CH_3$), 2.58 (s, 3 H, C(O)CH_3), 2.90—2.97 (c, 2 H, CH_2), 3.84 (q, J=7.02 Hz, 6 H, OCH_2), 4.39 (q, J=7.02 Hz, 2 H, CO_2CH_2), 7.60 (d, J=8.10 Hz, 1 H), 7.89 (dd, J=8.10, 1.89 Hz, 1 H), 7.96 (d, J=1.89 Hz, 1 H); ^{13}C NMR δ=12.76 ($SiCH_2$), 14.28 ($CO_2CH_2CH_3$), 18.28 (CH_3), 27.02 (CH_2), 30.14 (C(O)CH_3), 58.40 (OCH_2), 61.26(CO_2CH_2), 126.78, 128.30, 131.50, 132.54, 141.63, 144.40 (Ar), 165.91 (CO_2), 202.10 (C=O); IR (neat) ν 1727 s, 1696 s cm^{-1}; MS *m/z* (% rel intensity) 382 (M^+; 0.4), 336 (100). Found: C, 59.36; H, 8.08%. Calcd for $C_{19}H_{30}O_6Si$: C, 59.66; H, 7.91%. A nuclear Overhauser enhancement study was undertaken to determine the structure of the product (**13f**). Irradiation of the acetyl methyl gave a 12.1% enhancement of the aromatic hydrogen and irradiation of the benzyl hydrogens gave a 1.3% enhancement of the acetyl methyl and a 17.6% enhancement of the aromatic hydrogens. The structure of product **13f** was assigned as shown (Chart 1):

14f: Bp=210 °C/2 mmHg. ^{1}H NMR δ=0.91—0.97 (c, 4 H, $SiCH_2$), 1.22 (t, J=6.91 Hz, 18 H, CH_3), 1.39 (t, J=7.16 Hz, 3 H, $CO_2CH_2CH_3$), 2.50 (s, 3 H, C(O)CH_3), 2.58—2.64 (c, 4 H, CH_2), 3.81 (q, J=6.91 Hz, 12 H, OCH_2), 4.37 (q, J=7.16 Hz, 2 H, CO_2CH_2), 7.77 (s, 2 H); ^{13}C NMR δ=12.81 ($SiCH_2$), 14.32 ($CO_2CH_2CH_3$), 18.26 (CH_3), 26.20 (CH_2), 32.71 (C(O)CH_3), 58.44 (OCH_2), 61.04 (CO_2CH_2), 127.37, 130.76, 139.68, 145.09 (Ar), 166.32 (CO_2), 207.49 (C=O); IR (neat) ν 1722 s, 1700 s cm^{-1}; MS *m/z* (% rel intensity) 572 (M^+; 1), 511 (96), 163 (72), 119 (89), 79 (100). Found: C, 56.62; H, 8.38%. Calcd for $C_{27}H_{48}O_9Si_2$: C, 56.61; H, 8.45%.

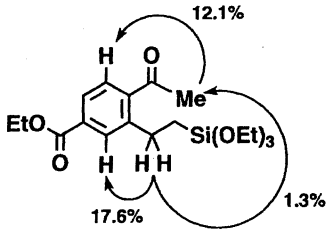


Chart 1.

4- Trifluoromethyl- 2- [2- (triethoxysilyl)ethyl]acetophenone (13g) and 4-Trifluoromethyl-2,6-bis[2-(triethoxysilyl)ethyl]acetophenone (14g). 13g: Bp=150 °C/1 mmHg. ^{1}H NMR δ=0.93—1.00 (c, 2 H, $SiCH_2$), 1.23 (t, J=7.02 Hz, 9 H, CH_3), 2.60 (s, 3 H, C(O)CH_3), 2.92—2.99 (c, 2 H, CH_2), 3.84 (q, J=7.02 Hz, 6 H, OCH_2), 7.51 (d, J=8.10 Hz, 1 H), 7.56 (s, 1 H), 7.65 (d, J=8.10 Hz, 1 H); ^{13}C NMR δ=12.78 ($SiCH_2$), 18.24 (CH_3), 27.10 (CH_2), 30.10 (C(O)CH_3), 58.42 (OCH_2), 122.56 (q, J_{C-F}=3.6 Hz, Ar), 123.64 (q, J_{C-F}=271.1 Hz, CF_3), 127.31 (q, J_{C-F}=3.6 Hz), 128.64, 132.68 (q, J_{C-F}=31.9 Hz), 141.02, 145.05 (Ar), 201.60 (C=O); IR (neat) ν 1694 s cm^{-1}; MS *m/z* (% rel intensity) 332 (M^+ − EtOH; 32), 178 (60), 79 (100). Found: C, 53.97; H, 6.69%. Calcd for $C_{17}H_{25}F_3O_4Si$: C, 53.95; H, 6.66%.

14g: Bp=200 °C/3 mmHg. ^{1}H NMR δ=0.90—0.97 (c, 4 H, $SiCH_2$), 1.23 (t, J=7.02 Hz, 18 H, CH_3), 2.52 (s, 3 H, C(O)CH_3), 2.60—2.67 (c, 4 H, CH_2), 3.82 (q, J=7.02 Hz, 12 H, OCH_2), 7.36 (s, 2 H); ^{13}C NMR δ=12.67 ($SiCH_2$), 18.24 (CH_3), 26.26 (CH_2), 32.67 (C(O)CH_3), 58.46 (OCH_2), 123.01 (q, J_{C-F}=3.6 Hz, Ar), 123.96 (q, J_{C-F}=270.5 Hz, CF_3), 130.87 (q, J_{C-F}=31.5 Hz), 140.27, 144.22 (Ar), 206.90 (C=O); IR (neat) ν 1704 s cm^{-1}; MS *m/z* (% rel intensity) 522 (M^+ − EtOH; 15), 507 (73), 163 (100), 119 (76), 79 (68). Found: C, 52.70; H, 7.62%. Calcd for $C_{25}H_{43}F_3O_7Si_2$: C, 52.79; H, 7.62%.

4-Acetyl-3-[2-(triethoxysilyl)ethyl]benzonitrile (13h). Bp= 200 °C/1 mmHg. ^{1}H NMR δ=0.91—0.97 (c, 2 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 9 H, CH_3), 2.59 (s, 3 H, C(O)CH_3), 2.89—2.95 (c, 2 H, CH_2), 3.84 (q, J=7.02 Hz, 6 H, OCH_2), 7.55 (dd, J=7.83, 1.35 Hz, 1 H), 7.61 (d, J=1.35 Hz, 1 H), 7.63 (d, J=7.83 Hz, 1 H); ^{13}C NMR δ=12.62 ($SiCH_2$), 18.22 (CH_3), 26.79 (CH_2), 30.01 (C(O)CH_3), 58.40 (OCH_2), 114.52 (Ar), 118.08 (CN), 128.55, 129.29, 134.03, 141.78, 145.12 (Ar), 201.20 (C=O); IR (neat) ν 2232 m, 1693 s cm^{-1}; MS *m/z* (% rel intensity) 335 (M^+; 5), 277 (100). Found: C, 60.90; H, 7.51; N, 4.11%. Calcd for $C_{17}H_{25}NO_4Si$: C, 60.87; H, 7.51; N, 4.18%.

5- Dimethylamino- 2- [2- (triethoxysilyl)ethyl]acetophenone (16a). A product **16a** was isolated by bulb-to-bulb distillation (200 °C/4 mmHg) in 72% yield (543 mg). ^{1}H NMR δ=0.91—0.97 (c, 2 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 9 H, CH_3), 2.56 (s, 3 H, C(O)CH_3), 2.78—2.85 (c, 2 H, CH_2), 2.94 (s, 6 H, $N(CH_3)_2$), 3.84 (q, J=7.02 Hz, 6 H, OCH_2), 6.79 (dd, J=8.64, 2.70 Hz, 1 H), 6.90 (d, J=2.70 Hz, 1 H), 7.15 (d, J=8.64 Hz, 1 H); ^{13}C NMR δ=13.17 ($SiCH_2$), 18.30 (CH_3), 26.11 (CH_2), 29.98 (C(O)CH_3), 40.76 (N-

($CH_3)_2$), 58.33 (OCH_2), 112.74, 115.89, 131.11, 132.18, 138.60, 148.54 (Ar), 203.05 (C=O); IR (neat) ν 1684 s, 1352 s cm^{-1}; MS *m/z* (% rel intensity) 353 (M^+; 19), 176 (100), 173 (79), 79 (52). Found: C, 60.92; H, 8.97; N, 4.12%. Calcd for $C_{18}H_{31}NO_4Si$: C, 61.15; H, 8.84; N, 3.96%.

5-Methyl-2-[2-(triethoxysilyl)ethyl]acetophenone (16b) and 3-Methyl-2-[2-(triethoxysilyl)ethyl]acetophenone (17b). A 97 : 3 mixture of isomers, **16b** and **17b**, was obtained by bulb-to-bulb distillation (150 °C/4 mmHg) in 83% total yield (531 mg). Spectral data were obtained from a mixture of **16c** and **17c**. The minor product **17b** was detected by GC and GCMS. In the ^1H NMR spectrum of the mixture of **16b** and **17b**, the signals arising from the minor isomer **17b** could not be observed. The presence of the isomer **17b** was confirmed by using GCMS and HRMS. ^1H NMR (major isomer **16b** δ=0.92—0.98 (c, 2 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 9 H, CH_3), 2.35 (s, 3 H, $ArCH_3$), 2.56 (s, 3 H, $C(O)CH_3$), 2.87—2.93 (c, 2 H, CH_2), 3.85 (q, J=7.02 Hz, 6 H, OCH_2), 7.19 (m, 2 H), 7.41 (s, 1 H); ^{13}C NMR (major isomer **16b**) δ=13.02 ($SiCH_2$), 18.28 (CH_3), 20.88 ($ArCH_3$), 26.82 (CH_2), 29.83 (C-(O)*C*H_3), 58.34 (OCH_2), 129.55, 130.51, 132.18, 135.14, 137.54, 141.76 (Ar), 202.22 (C=O); IR (neat) (mixture of **16b** and **17b**) ν 1689 s cm^{-1}; MS *m/z* (% rel intensity) (major isomer **16b**) 324 (M^+; 2), 278 (100), 135 (63); (minor isomer **17b**) 324 (M^+; 1), 278 (69), 135 (100). HRMS Found: (major isomer **16b**) *m/z* 324.1771; (minor isomer **17b**) *m/z* 324.1768. Calcd for $C_{17}H_{28}O_4Si$: M, 324.1757. Found (mixture of **16b** and **17b**): C, 62.93; H, 8.90%. Calcd for $C_{17}H_{28}O_4Si$: C, 62.93; H, 8.70%.

5-Methoxy-2-[2-(triethoxysilyl)ethyl]acetophenone (16c), 3-Methoxy-2-[2-(triethoxysilyl)ethyl]acetophenone (17c) and 3-Methoxy- 2, 6- bis[2- (triethoxysilyl)ethyl]acetophenone (18c). **16c** and **17c**: A 11 : 89 mixture of isomers, **16c** and **17c**, was obtained by bulb-to-bulb distillation (150 °C/4 mmHg) in 84% total yield (571 mg). Spectral data were obtained from a mixture of **16c** and **17c**. ^1H NMR (mixture of **16c** and **17c**) δ=0.94—1.00 (c, 2 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 9 H, CH_3, **16c**), 1.26 (t, J=7.02 Hz, 9 H, CH_3, **17c**), 2.55 (s, 3 H, $C(O)CH_3$, **17c**), 2.56 (s, 3 H, C(O)-CH_3, **16c**), 2.80—2.86 (c, 2 H, CH_2), 3.83 (s, 3 H, OCH_3), 3.83 (q, J=7.02 Hz, 6 H, OCH_2, **16c**), 3.87 (q, J=7.02 Hz, 6 H, OCH_2, **17c**), 6.94 (d, J=8.10 Hz, 1 H, **17c**), 7.05 (d, J=8.10 Hz, 1 H, **16c**), 7.10 (d, J=8.10 Hz, 1 H, **17c**), 7.11 (s, 1 H, **16c**), 7.20 (d, J=8.10 Hz, 1 H, **17c**), 7.21 (d, J=8.10 Hz, 1 H, **16c**); ^{13}C NMR (major isomer **17c**) δ=11.17 ($SiCH_2$), 18.30 (CH_3), 20.02 (CH_2), 30.49 ($C(O)CH_3$), 55.58 (OCH_3), 58.27 (OCH_2), 112.72, 119.94, 126.28, 132.51, 139.98, 157.74 (Ar), 202.95 (C=O); IR (neat) (mixture of **16c** and **17c**) ν 1690 s cm^{-1}; MS *m/z* (% rel intensity) (minor isomer **16c**) 340 (M^+; 2), 294 (100); (major isomer **17c**) 340 (M^+; 2), 294 (100). HRMS Found: (minor isomer **16c**) *m/z* 340.1725; (major isomer **17c**) *m/z* 340.1682. Calcd for $C_{17}H_{28}O_5Si$: M, 340.1706. Found (mixture of **16c** and **17c**): C, 59.90; H, 8.50%. Calcd for $C_{17}H_{28}O_5Si$: C, 59.97; H, 8.29%.

18c: A product **18c** was prepared by the following procedure. A toluene (3 cm^3) solution of 3-methoxyacetophenone **15c** (300 mg, 2 mmol), **2** (1903 mg, 10 mmol), and **3** (110 mg, 0.12 mmol) was heated at 135 °C (oil bath temperature) for 12 h. The solvent and **2** were removed by rotary evaporation (40 °C/5 mmHg). The residue was purified by bulb-to-bulb distillation (150 °C/2 mmHg). The product **18c** was isolated in 87% yield (934 mg). ^1H NMR δ=0.88—0.94 (c, 4 H, $SiCH_2$), 1.22 (t, J=7.02 Hz, 9 H), 1.24 (t, J=7.02 Hz, 9 H) [(2-CH_3) and (6-CH_3)], 2.49 (s, 3 H, $C(O)CH_3$), 2.49—2.56 (c, 4 H, CH_2), 3.79 (s, 3 H, OCH_3), 3.81 (q, J=7.02 Hz, 6 H), 3.84 (q, J=7.02 Hz, 6 H), [(2′-OCH_2) and (6′-OCH_2)], 6.78 (d, J=8.37 Hz, 1 H), 7.05 (d, J=8.37 Hz, 1 H); ^{13}C NMR δ=11.40, 12.96 [(2-$SiCH_2$) and (6-$SiCH_2$)], 18.28 (CH_3), 21.13 (2-CH_2), 25.48 (6-CH_2), 33.05 ($C(O)CH_3$), 55.38 (OCH_3), 58.29, 58.37 [(2-OCH_2) and (6-OCH_2)], 110.60, 126.92, 127.71, 130.85, 142.17, 155.33 (Ar), 207.67 (C=O); IR (neat) ν 1701 s cm^{-1}; MS *m/z* (% rel intensity) 530 (M^+; 4), 469 (100), 163 (68), 119 (68), 79 (60). Found: C, 56.47; H, 8.76%. Calcd for $C_{25}H_{46}O_8Si_2$: C, 56.57; H, 8.74%.

3-Acetyl-4-[2-(triethoxysilyl)ethyl]-N-ethylacetanilide (16d). A product **16d** was isolated by bulb-to-bulb distillation (180 °C/2 mmHg) in 92% yield (729 mg). ^1H NMR δ=0.95—1.01 (c, 2 H, $SiCH_2$), 1.12 (t, J=7.29 Hz, 3 H, NCH_2CH_3), 1.25 (t, J=7.29 Hz, 9 H, CH_3), 1.84 (s, 3 H, $NC(O)CH_3$), 2.59 (s, 3 H, $C(O)CH_3$), 2.92—2.98 (c, 2 H, CH_2), 3.75 (q, J=7.29 Hz, 2 H, NCH_2), 3.85 (q, J=7.29 Hz, 6 H, OCH_2), 7.20 (dd, J=8.10, 2.16 Hz, 1 H), 7.37 (d, J=8.10 Hz, 1 H), 7.37 (d, J=2.16 Hz, 1 H); ^{13}C NMR δ=12.81 ($SiCH_2$), 13.03 (NCH_2CH_3), 18.24 (CH_3), 22.77 ($NC(O)CH_3$), 26.81 (CH_2), 29.85 ($C(O)CH_3$), 43.87 (NCH_2), 58.37 (OCH_2), 128.12, 130.98, 131.95, 139.10, 140.43, 144.26 (Ar), 169.79 (NC(O)), 201.06 (C=O); IR (neat) ν 1691 s, 1653 s cm^{-1}; MS *m/z* (% rel intensity) 395 (M^+; 2), 349 (72), 70 (100). Found: C, 60.35; H, 8.25; N, 3.70%. Calcd for $C_{20}H_{33}NO_5Si$: C, 60.73; H, 8.41; N, 3.54%.

5- Fluoro- 2- [2- (triethoxysilyl)ethyl]acetophenone (16e), 3-Fluoro- 2- [2- (triethoxysilyl)ethyl]acetophenone (17e) and 3-Fluoro-2,6-bis[2-(triethoxysilyl)ethyl]acetophenone (18e). **16e** and **17e**: A 4 : 96 mixture of isomers, **16e** and **17e**, was obtained by bulb-to-bulb distillation (160 °C/4 mmHg). Spectral data were obtained from a mixture of **16e** and **17e**. The minor product **16e** was detected by GC and GCMS. In the ^1H NMR spectrum of the mixture of **16e** and **17e**, the signals. arising from the minor isomer **16e** could not be observed. The presence of the isomer **16e** was confirmed by using the GCMS and the HRMS. ^1H NMR (major isomer **17e**) ^1H NMR δ=0.94—1.01 (c, 2 H, $SiCH_2$), 1.22 (t, J=7.02 Hz, 9 H, CH_3), 2.57 (s, 3 H, $C(O)CH_3$), 2.87—2.94 (c, 2 H, CH_2), 3.86 (q, J=7.02 Hz, 6 H, OCH_2), 7.13 (ddd, $J_{H-H'}$ $_{H-H'}$ $_{H-F}$=1.35, 8.10, 8.10 Hz, 1 H), 7.22 (dt, $J_{H-F'}$ $_{H-H}$=5.40, 8.10 Hz, 1 H), 7.38 (dd, $J_{H-H'}$ $_{H-H}$=8.10, 1.35 Hz, 1 H); ^{13}C NMR (major isomer **17e**) δ=11.77 ($SiCH_2$), 18.26 (CH_3), 19.19 (d, J_{C-F}=4.9 Hz, CH_2), 30.07 ($C(O)CH_3$), 58.35 (OCH_2), 118.15 (d, J_{C-F}=24.2 Hz), 124.23 (d, J_{C-F}=3.7 Hz), 126.69 (d, J_{C-F}=8.4 Hz), 131.82 (d, J_{C-F}=17.0 Hz), 139.92 (d, J_{C-F}=3.7 Hz), 161.39 (d, J_{C-F}=243.8 Hz) (Ar), 201.13 (C=O); IR (neat) (mixture of **16e** and **17e**) ν 1692 s cm^{-1}; MS *m/z* (% rel intensity) (minor isomer **16e**) 328 (M^+; 1), 282 (100), 128 (59); (major isomer **17e**) 328 (M^+; 1), 282 (100), 128 (50). HRMS Found: (minor isomer **16e**) *m/z* 328.1514; (major isomer **17e**) *m/z* 328.1505. Calcd for $C_{17}H_{28}O_5Si$: M, 328.1506. Found (mixture of **16e** and **17e**): C, 58.51; H, 7.83%. Calcd for $C_{16}H_{25}FO_4Si$: C, 58.51; H, 7.67%.

18e: A product **18e** was prepared by the following procedure. A toluene (3 cm^3) solution of 3-fluoroacetophenone **15e** (276 mg, 2 mmol), **2** (1903 mg, 10 mmol), and **3** (110 mg, 0.12 mmol) was heated at 135 °C (oil bath temperature) for 12 h. The solvent and **2** were removed by rotary evaporation (40 °C/5 mmHg). The residue was purified by bulb-to-bulb distillation (230 °C/4 mmHg). ^1H NMR δ=0.87—0.95 (c, 4 H, $SiCH_2$), 1.21 (t, J=7.02 Hz, 18 H, CH_3), 2.50 (s, 3 H, $C(O)CH_3$), 2.53—2.60 (c, 4 H, CH_2), 3.82 (q, J=7.02 Hz, 12 H, OCH_2), 6.94 (dd, $J_{H-H'}$ $_{H-F}$=8.10, 9.99 Hz, 1 H), 7.06 (dd, $J_{H-H'}$ $_{H-F}$=8.10, 5.40 Hz, 1 H); ^{13}C NMR δ=12.13, 12.98 [(2-$SiCH_2$) and (6-$SiCH_2$)], 18.26 (CH_3), 20.34 (d, J_{C-F}=2.4 Hz, 2′-CH_2), 25.73 (6-CH_2), 32.94 ($C(O)CH_3$), 58.38 (OCH_2), 115.46 (d, J_{C-F}=23.1 Hz), 126.67 (d, J_{C-F}=16.9 Hz), 127.65 (d, J_{C-F}=8.5 Hz), 134.85 (d, J_{C-F}=3.7 Hz), 142.56 (d, J_{C-F}=3.7 Hz), 159.17 (d, J_{C-F}=242.6 Hz) (Ar), 206.45 (C=O); IR (neat) ν 1703 s cm^{-1}; MS

m/z (% rel intensity) 472 ($M^+ - EtOH$; 21), 457 (100), 163 (64). Found: C, 55.48; H, 8.33%. Calcd for $C_{24}H_{43}FO_7Si_2$: C, 55.57; H, 8.36%.

Ethyl 3-Acetyl-4-[2-(triethoxysilyl)ethyl]benzoate (16f). A product **16f** was isolated by bulb-to-bulb distillation (160 °C/3 mmHg) in 91% yield (693 mg). ^{1}H NMR δ=0.93—0.99 (c, 2 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 9 H, CH_3), 1.41 (t, J=7.02 Hz, 3 H, $CO_2CH_2CH_3$), 2.63 (s, 3 H, $C(O)CH_3$), 2.96—3.02 (c, 2 H, CH_2), 3.85 (q, J=7.02 Hz, 6 H, OCH_2), 4.40 (q, J=7.02 Hz, 2 H, CO_2CH_2), 7.38 (d, J=8.10 Hz, 1 H), 8.04 (dd, J=8.10, 1.62 Hz, 1 H), 8.30 (d, J=1.62 Hz, 1 H); ^{13}C NMR δ=12.76 ($SiCH_2$), 14.31 ($CO_2CH_2CH_3$), 18.26 (CH_3), 27.46 (CH_2), 29.80 ($C(O)CH_3$), 58.40 (OCH_2), 61.13 (CO_2CH_2), 128.09, 130.17, 130.82, 132.15, 137.56, 150.06 (Ar), 165.86 (CO_2), 201.22 (C=O); IR (neat) ν 1725 s, 1689 s cm^{-1}; MS *m/z* (% rel intensity) 382 (M^+; 0.3), 336 (100). Found: C, 59.26; H, 8.14%. Calcd for $C_{19}H_{30}O_6Si$: C, 59.66; H, 7.91%.

5- Trifluoromethyl- 2- [2- (triethoxysilyl)ethyl]acetophenone (16g). A product **16g** was isolated by bulb-to-bulb distillation (150 °C/2 mmHg) in 81% yield (592 mg). ^{1}H NMR δ=0.93—0.99 (c, 2 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 9 H, CH_3), 2.62 (s, 3 H, $C(O)CH_3$), 2.95—3.01 (c, 2 H, CH_2), 3.84 (q, J=7.02 Hz, 6 H, OCH_2), 7.43 (d, J=7.83 Hz, 1 H), 7.62 (d, J=7.83 Hz, 1 H), 7.83 (s, 1 H); ^{13}C NMR δ=12.78 ($SiCH_2$), 18.26 (CH_3), 27.28 (CH_2), 29.61 ($C(O)CH_3$), 58.42 (OCH_2), 123.80 (q, J_{C-F}=270.5 Hz, CF_3), 125.53 (q, J_{C-F}=3.6 Hz), 127.79 (q, J_{C-F}=3.6 Hz), 128.15 (q, J_{C-F}=32.7 Hz), 131.25, 138.04, 148.72 (Ar), 200.77 (C=O); IR (neat) ν 1694 s cm^{-1}; MS *m/z* (% rel intensity) 332 ($M^+ - EtOH$; 100), 178 (88), 135 (58), 79 (64). Found: C, 53.71; H, 6.82%. Calcd for $C_{17}H_{25}F_3O_4Si$: C, 53.95; H, 6.66%.

3-Acetyl-4-[2-(triethoxysilyl)ethyl]benzonitrile (16h), 3-Acetyl-2-[2-(triethoxysilyl)ethyl]benzonitrile (17h) and 3-Acetyl-2,4-bis[2-(triethoxysilyl)ethyl]benzonitrile (18h). A 73 : 27 mixture of isomers, **16h** and **17h**, was obtained by bulb-to-bulb distillation (160 °C/4 mmHg) in 78% total yield (538 mg). Spectral data were obtained from a mixture of **16h** and **17h**. ^{1}H NMR (mixture of **16h** and **17h**) δ=0.90—0.96 (c, 2 H, $SiCH_2$, **16h**), 0.98—1.05 (c, 2 H, $SiCH_2$, **17h**), 1.23 (t, J=7.02 Hz, 9 H, CH_3, **16h**), 1.25 (t, J=7.02 Hz, 9 H, CH_3, **17h**), 2.59 (s, 3 H, $C(O)CH_3$), 2.93—3.00 (c, 2 H, CH_2, **16h**), 3.06—3.13 (c, 2 H, CH_2, **17h**), 3.83 (q, J=7.02 Hz, 6 H, OCH_2, **16h**), 3.88 (q, J=7.02 Hz, 6 H, OCH_2, **17h**), 7.35 (t, J=7.83 Hz, 1 H, **17h**), 7.42 (d, J=7.83 Hz, 1 H, **16h**), 7.65 (dd, J=7.83, 1.62 Hz, 1 H, **16h**), 7.71 (dd, J=7.83, 1.35 Hz, 1 H, **17h**), 7.75 (dd, J=7.83, 1.35 Hz, 1 H, **17h**), 7.87 (d, J=1.62 Hz, 1 H, **16h**); ^{13}C NMR (mixture of **16h** and **17h**) δ=12.69 ($SiCH_2$, **16h**), 12.78 ($SiCH_2$, **17h**), 18.26 (CH_3), 27.57 (CH_2, **16h**), 25.79 (CH_2, **17h**), 29.80 ($C(O)CH_3$, **16h**), 30.07 ($C(O)CH_3$, **17h**), 58.46 (OCH_2), 109.85, 114.45 (Ar), 117.40 (CN, **17h**), 118.17 (CN, **16h**), 126.27, 131.68, 132.27, 132.36, 134.23, 135.45, 138.54, 148.27, 150.13 (Ar), 199.96 (C=O, **16h**), 200.70 (C=O, **17h**); IR (neat) (mixture of **16h** and **17h**) ν 2230 m, 1693 s cm^{-1}; MS *m/z* (% rel intensity) (major isomer **16h**) 289 ($M^+ - EtOH$; 100), 135 (69), 79 (60); (minor isomer **17h**) 289 ($M^+ - EtOH$; 100), 135 (74), 79 (52). Found (mixture of **16h** and **17h**): C, 60.47; H, 7.26; N, 4.39%. Calcd for $C_{17}H_{25}NO_4Si$: C, 60.87; H, 7.51; N, 4.18%.

18h: A product **18h** was prepared by the following procedure. A toluene (3 cm^3) solution of 3-acetylbenzonitrile **15h** (290 mg, 2 mmol), **2** (1903 mg, 10 mmol), and **3** (110 mg, 0.12 mmol) was heated at 135 °C (oil bath temperature) for 48 h. The solvent and **2** were removed by rotary evaporation (40 °C/5 mmHg). The residue was purified by bulb-to-bulb distillation (160 °C/2 mmHg). ^{1}H NMR δ=0.87—1.01 (c, 4 H, $SiCH_2$), 1.22 (t, J=7.02 Hz, 9 H), 1.25 (t, J=7.02 Hz, 9 H) (CH_3), 2.53 (s, 3 H, $C(O)CH_3$), 2.58—2.64 (c, 2H), 2.73—2.79 (c, 2H) (CH_2), 3.81 (q, J=7.02 Hz, 6 H), 3.86 (q, J=7.02 Hz, 6 H) (OCH_2), 7.20 (d, J=7.83 Hz, 1 H), 7.55 (dd, J=7.83, 1.62 Hz, 1 H); ^{13}C NMR δ=12.55, 12.99 ($SiCH_2$), 18.30 (CH_3), 25.88, 26.72 (CH_2), 32.85 ($C(O)CH_3$), 58.51 (OCH_2), 110.14 (Ar), 117.70 (CN), 127.03, 133.26, 142.08, 143.79, 145.01 (Ar), 205.70 (C=O); IR (neat) ν 2222 m, 1704 s cm^{-1}; MS *m/z* (% rel intensity) 525 (M^+; 5), 163 (56), 119 (77), 79 (100). Found: C, 56.97; H, 8.18; N, 2.74%. Calcd for $C_{25}H_{43}NO_7Si_2$: C, 57.11; H, 8.24; N, 2.66%.

3-Acetyl-4-[2-(triethoxysilyl)ethyl]phenyl Acetate (16i) and 3-Acetyl-2-[2-(triethoxysilyl)ethyl]phenyl Acetate (17i). A 28 : 72 mixture of isomers, **16i** and **17i**, was obtained by bulb-to-bulb distillation (150 °C/2 mmHg) in 38% total yield (279 mg). Spectral data were obtained from a mixture of **16i** and **17i**. ^{1}H NMR (minor isomer **16i**) δ=0.92—0.99 (c, 2 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 9 H, CH_3), 2.31 (s, 3 H, $OC(O)CH_3$), 2.56 (s, 3 H, $C(O)CH_3$), 2.90—2.96 (c, 2 H, CH_2), 3.85 (q, J=7.02 Hz, 6 H, OCH_2), 7.13 (dd, J=8.37, 2.70 Hz, 1 H), 7.31 (d, J=8.37 Hz, 1 H), 7.34 (d, J=2.70 Hz, 1 H); (major isomer **17i**) δ=0.87—0.94 (c, 2 H, $SiCH_2$), 1.25 (t, J=7.02 Hz, 9 H, CH_3), 2.36 (s, 3 H, $OC(O)CH_3$), 2.58 (s, 3 H, $C(O)CH_3$), 2.75—2.82 (c, 2 H, CH_2), 3.86 (q, J=7.02 Hz, 6 H, OCH_2), 7.15 (dd, J=7.83, 1.35 Hz, 1 H), 7.28 (t, J=7.83 Hz, 1 H), 7.50 (dd, J=7.83, 1.35 Hz, 1 H); ^{13}C NMR (mixture of **16i** and **17i**) δ=11.70 ($SiCH_2$, **17i**), 12.89 ($SiCH_2$, **16i**), 18.28 (CH_3), 20.58, 20.76 [(CH_2, **17i**) and ($OC(O)CH_3$, **17i**)], 21.03 ($OC(O)CH_3$, **16i**), 26.78 (CH_2, **16i**), 29.67 ($C(O)CH_3$, **16i**), 30.03 ($C(O)CH_3$, **17i**), 58.33 (OCH_2), 122.00, 124.58, 125.64, 126.22, 126.51, 131.64, 136.75, 138.22, 139.55, 142.34, 148.19, 149.54 (Ar), 169.33 ($OC(O)CH_3$, **16i**), 169.58 ($OC(O)CH_3$, **17i**), 200.75 (C=O, **16i**), 201.36 (C=O, **17i**); δ=IR (neat) (mixture of **16i** and **17i**) ν 1766 s, 1691 s cm^{-1}; MS *m/z* (% rel intensity) (minor isomer **16i**) 368 (M^+; 2), 322 (100), 280 (88); (major isomer **17i**) 353 ($M^+ - CH_3$; 5), 322 (95), 280 (100). HRMS Found: (minor isomer **16i**) *m/z* 353.1411; (major isomer **17i**) *m/z* 353.1401. Calcd for $C_{17}H_{28}O_4Si$: $M^+ - CH_3$, 353.1421. Found (mixture of **16i** and **17i**): C, 58.46; H, 7.77%. Calcd for $C_{17}H_{28}O_4Si$: C, 58.67; H, 7.66%.

5-Trifluoromethoxy-2-[2-(triethoxysilyl)ethyl]acetophenone (16j), 3- Trifluoromethoxy- 2- [2- (triethoxysilyl)ethyl]acetophenone (17j) and 3-Trifluoromethoxy-2,6-bis[2-(triethoxysilyl)ethyl]acetophenone (18j). A 68 : 32 mixture of isomers, **16j** and **17j**, was obtained by bulb-to-bulb distillation (100 °C/2 mmHg) in 70% total yield (540 mg). Spectral data were obtained from a mixture of **16j** and **17j**. ^{1}H NMR (mixture of **16j** and **17j**) δ=0.89—0.98 (c, 2 H, $SiCH_2$), 1.23 (t, J=7.02 Hz, 9 H, CH_3, **16j**), 1.25 (t, J=7.02 Hz, 9 H, CH_3, **17j**), 2.57 (s, 3 H, $C(O)CH_3$, **16j**), 2.58 (s, 3 H, $C(O)CH_3$, **17j**), 2.88—2.96 (c, 2 H, CH_2), 3.83 (q, J=7.02 Hz, 6 H, OCH_2, **16j**), 3.86 (q, J=7.02 Hz, 6 H, OCH_2, **17j**), 7.23—7.49 (m, 3 H); ^{13}C NMR (mixture of **16j** and **17j**) δ=11.68 ($SiCH_2$, **17j**), 12.85 ($SiCH_2$, **16j**), 18.22 (CH_3), 20.20 (CH_2, **17j**), 26.72 (CH_2, **16j**), 29.69 ($C(O)CH_3$, **16j**), 30.23 ($C(O)CH_3$, **17j**), 58.31 (OCH_2, **17j**), 58.37 (OCH_2, **16j**), 120.42 (q, J_{C-F}=255.9 Hz, CF_3), 121.35, 122.70, 123.72, 126.47, 126.58, 132.13, 136.82, 138.87, 140.59, 143.32, 146.74, 148.12 (Ar), 200.50 (C=O, **16j**), 201.36 (C=O, **17j**); IR (neat) (mixture of **16j** and **17j**) ν 1695 s cm^{-1}; MS *m/z* (% rel intensity) (mixture of **16j** and **17j**) 348 ($M^+ - EtOH$; 20), 128 (100). Found (mixture of **16j** and **17j**): C, 51.66; H, 6.38%. Calcd for $C_{17}H_{25}F_3O_5Si$: C, 51.76; H, 6.39%.

18j: Product **18j** was prepared by the following procedure. A toluene (3 cm^3) solution of 3-(trifluoromethoxy)acetophenone **15j** (408 mg, 2 mmol), **2** (1903 mg, 10 mmol), and **3** (110 mg, 0.12 mmol) was heated at 135 °C (oil bath temperature) for 12 h. The solvent and **2** were removed by rotary evaporation (40 °C/5 mmHg). The

residue was purified by bulb-to-bulb distillation (130 °C/2 mmHg). ^{1}H NMR δ=0.85—0.96 (c, 4 H, $SiCH_2$), 1.22 (t, J=7.02 Hz, 9 H), 1.24 (t, J=7.02 Hz, 9 H) [(2-CH_3) and (6-CH_3)], 2.52 (s, 3 H, C(O)-CH_3), 2.53—2.63 (c, 4 H, CH_2), 3.81 (q, J=7.02 Hz, 6 H), 3.84 (q, J=7.02 Hz, 6 H) [(2-OCH_2) and (6-OCH_3)], 7.11—7.15 (m, 2H); ^{13}C NMR δ=11.93, 12.72 [(2-$SiCH_3$) and (6-$SiCH_2$)], 18.21 (CH_3), 21.31 (2-CH_2), 25.86 (6-CH_2), 32.85 (C(O)*C*H_3), 58.33, 58.40 [(2-OCH_3) and (6-OCH_2)], 120.27 (Ar), 120.60 (q, J_{C-F}=254.5 Hz, CF_3), 127.51, 131.91, 137.81, 142.91, 145.53 (Ar), 206.20 (C=O); IR (neat) ν 1705 s cm^{-1}; MS *m/z* (% rel intensity) 584 (M^+; 22), 523 (50), 163 (75), 119 (84), 79 (100). Found: C, 51.64; H, 7.37%. Calcd for $C_{25}H_{43}F_3O_8Si_2$: C, 51.35; H, 7.41%.

2,4-Diacetyl-1-[2-(triethoxysilyl)ethyl]benzene (16k) and 1, 5-Diacetyl-2,4-bis[2-(triethoxysilyl)ethyl]benzene (19). 16k: Bp=140 °C/2 mmHg. ^{1}H NMR δ=0.92—0.99 (c, 2 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 9 H, CH_3), 2.61 (s, 3 H), 2.63 (s, 3 H) [(2-C(O)CH_3) and (4-C(O)CH_3)], 2.95—3.01 (c, 2 H, CH_2), 3.84 (q, J=7.02 Hz, 6 H, OCH_2), 7.40 (d, J=7.83 Hz, 1 H), 7.95 (dd, J=7.83, 1.62 Hz, 1 H), 8.22 (d, J=1.62 Hz, 1 H); ^{13}C NMR δ=12.72 ($SiCH_2$), 18.28 (CH_3), 26.53 (4′-C(O)*C*H_3), 27.46 (CH_2), 29.80 (2′-C(O)*C*H_3), 58.44 (OCH_2), 128.64, 130.98, 131.16, 134.70, 137.86, 150.30 (Ar), 196.96, 201.40 (C=O); IR (neat) ν 1689 s cm^{-1}; MS *m/z* (% rel intensity) 306 (M^+ − EtOH; 78), 79 (100). Found: C, 61.37; H, 8.01%. Calcd for $C_{18}H_{28}O_5Si$: C, 61.33; H, 8.01%.

19: Bp=170 °C/2 mmHg. ^{1}H NMR δ=0.91—0.97 (c, 4 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 18 H, CH_3), 2.60 (s, 6 H, C(O)CH_3), 2.92—2.98 (c, 4 H, CH_2), 3.86 (q, J=7.02 Hz, 12 H, OCH_2), 7.20 (s, 1 H), 7.92 (s, 1 H); ^{13}C NMR δ=12.76 ($SiCH_2$), 18.30 (CH_3), 27.48 (CH_2), 29.63 (C(O)*C*H_3), 58.42 (OCH_2), 130.67, 133.19, 134.77, 148.91 (Ar), 200.54 (C=O); IR (neat) ν 1684 s cm^{-1}; MS *m/z* (% rel intensity) 496 (M^+ − EtOH; 21), 119 (53), 79 (100). Found: C, 57.55; H, 8.58%. Calcd for $C_{26}H_{46}O_8Si_2$: C, 57.53; H, 8.54%.

4,5-Dimethoxy-2-[2-(triethoxysilyl)ethyl]acetophenone (21) and 3,4-Dimethoxy-2,6-bis[2-(triethoxysilyl)ethyl]acetophenone (22). 21: A product **21** was isolated by bulb-to-bulb distillation (170 °C/2 mmHg) in 86% yield. ^{1}H NMR δ=0.95—1.01 (c, 2 H, $SiCH_2$), 1.25 (t, J=7.02 Hz, 9 H, CH_3), 2.56 (s, 3 H, C(O)-CH_3), 2.93—2.99 (c, 2 H, CH_2), 3.86 (q, J=7.02 Hz, 6 H, OCH_2), 3.91 (s, 3 H), 3.93 (s, 3 H) [(4-OCH_3) and (5-OCH_3)], 6.77 (s, 1 H), 7.19 (s, 1 H); ^{13}C NMR δ=12.98 ($SiCH_2$), 18.28 (CH_3), 27.50 (CH_2), 29.54 (C(O)*C*H_3), 55.89, 56.17 [(4-OCH_3) and (5-OCH_3)], 58.37 (OCH_2), 113.21, 113.32, 129.04, 140.22, 146.24, 151.68 (Ar), 199.64 (C=O); IR (neat) ν 1677 s cm^{-1}; MS *m/z* (% rel intensity) 370 (M^+; 5), 324 (100), 190 (82). Found: C, 58.41; H, 8.33%. Calcd for $C_{18}H_{30}O_6Si$: C, 58.35; H, 8.16%.

22: A product **22** was prepared by the following procedure. A toluene (3 cm^3) solution of 3,4-dimethoxyacetophenone **20** (360 mg, 2 mmol), **2** (1903 mg, 10 mmol), and **3** (110 mg, 0.12 mmol) was heated at 135 °C (oil bath temperature) for 24 h. The solvent and **2** were removed by rotary evaporation (40 °C/5 mmHg). The residue was purified by bulb-to-bulb distillation (190 °C/2 mmHg). The product **22** was isolated in 90% yield (1012 mg). ^{1}H NMR δ=0.87—0.96 (c, 4 H, $SiCH_2$), 1.21 (t, J=7.02 Hz, 9 H) 1.23 (t, J=7.02 Hz, 9 H) [(2-CH_3) and (6-CH_3)], 2.47 (s, 3 H, C(O)CH_3), 2.51—2.57 (c, 4 H, CH_2), 3.76—3.86 (m, 12 H, OCH_2), 3.79 (s, 3 H), 3.84 (s, 3 H) [(3-OCH_3) and (4-OCH_3)], 6.64 (s, 1 H); ^{13}C NMR δ=12.56, 13.03 [(2-$SiCH_2$) and (6-$SiCH_2$)], 18.24 (CH_3), 21.26, 26.29 [(2-CH_2) and (6-CH_2)], 33.25 (C(O)*C*H_3), 55.62 [(3-OCH_3) or (4-OCH_3)], 58.29, 58.38 [(2-OCH_2) and (6-OCH_2)], 60.56 [(3-OCH_3) or (4-OCH_3)], 110.41, 133.84, 134.45, 135.27, 144.78, 152.58 (Ar), 207.35 (C=O); IR (neat) ν 1697 s cm^{-1}; MS *m/z* (% rel intensity) 560 (M^+; 5), 517 (60), 499 (100), 163 (76), 119 (61), 79 (64). Found: C, 55.72; H, 8.61%. Calcd for $C_{26}H_{48}O_9Si_2$: C, 55.68; H, 8.63%.

3, 4, 5- Trimethoxy- 2- [2- (triethoxysilyl)ethyl]acetophenone (24). A product **24** was isolated by bulb-to-bulb distillation (180 °C/2 mmHg) in 79% yield (614 mg). ^{1}H NMR δ=0.90—0.97 (c, 2 H, $SiCH_2$), 1.25 (t, J=7.02 Hz, 9 H, CH_3), 2.55 (s, 3 H, C(O)CH_3), 2.80—2.86 (c, 2 H, CH_2), 3.87 (s, 3 H), 3.87 (s, 3 H), 3.91 (s, 3 H) [(3-OCH_3), (4-OCH_3), and (5-OCH_3)], 3.88 (q, J=7.02 Hz, 6 H, OCH_2), 6.89 (s, 1 H); ^{13}C NMR δ=12.51 ($SiCH_2$), 18.30 (CH_3), 20.09 (CH_2), 30.10 (C(O)*C*H_3), 56.17, 60.70, 60.95 [(3-OCH_3), (4-OCH_3), and (5-OCH_3)], 58.28 (OCH_2), 108.09, 131.91, 133.73, 145.01, 150.82, 152.15 (Ar), 201.31 (C=O); IR (neat) ν 1686 s cm^{-1}; MS *m/z* (% rel intensity) 400 (M^+; 1), 354 (94), 339 (100), 220 (76), 79 (70). Found: C, 56.67; H, 8.19%. Calcd for $C_{19}H_{32}O_7Si$: C, 56.97; H, 8.05%.

3,5-Dimethoxy-2-[2-(triethoxysilyl)ethyl]acetophenone (26). A product **26** was isolated by bulb-to-bulb distillation (140 °C/2 mmHg) in 84% yield (677 mg). ^{1}H NMR δ=0.91—0.97 (c, 2 H, $SiCH_2$), 1.25 (t, J=7.02 Hz, 9 H, CH_3), 2.53 (s, 3 H, C(O)-CH_3), 2.70—2.77 (c, 2 H, CH_2), 3.81 (s, 3 H), 3.82 (s, 3 H) [(3-OCH_3) and (5-OCH_3)], 3.86 (q, J=7.02 Hz, 6 H, OCH_2), 6.53 (s, 1 H), 6.56 (s, 1 H); ^{13}C NMR δ=11.47 ($SiCH_2$), 18.28 (CH_3), 19.59 (CH_2), 30.57 (C(O)*C*H_3), 55.42, 55.56 [(3-OCH_3) and (5-OCH_3)], 58.24 (OCH_2), 100.59, 103.29, 124.60, 140.59, 158.18, 158.74 (Ar), 203.16 (C=O); IR (neat) ν 1691 s cm^{-1}; MS *m/z* (% rel intensity) 370 (M^+; 2), 324 (100), 309 (56), 190 (53). Found: C, 58.41; H, 8.28%. Calcd for $C_{18}H_{30}O_6Si$: C, 58.35; H, 8.16%.

3, 4- Ethylenedioxy- 2- [2- (triethoxysilyl)ethyl]acetophenone (28) and 3,4-Ethylenedioxy-2,6-bis[2-(triethoxysilyl)ethyl]acetophenone (29). 28: Bp=160 °C/2 mmHg. ^{1}H NMR δ=0.94—1.01 (c, 2 H, $SiCH_2$), 1.26 (t, J=7.02 Hz, 9 H, CH_3), 2.52 (s, 3 H, C(O)CH_3), 2.91—2.98 (c, 2 H, CH_2), 3.89 (q, J=7.02 Hz, 6 H, $SiOCH_2$), 4.27 (s, 4 H, OCH_2), 6.74 (d, J=8.64 Hz, 1 H), 7.22 (d, J=8.64 Hz, 1 H); ^{13}C NMR δ=11.04 ($SiCH_2$), 18.30 (CH_3), 19.59 (CH_2), 29.62 (C(O)*C*H_3), 58.28 ($SiOCH_2$), 63.97, 64.35 [(3-OCH_2) and (4-OCH_2)], 114.02, 122.98, 131.02, 135.29, 141.56, 146.15 (Ar), 200.30 (C=O); IR (neat) ν 1677 s cm^{-1}; MS *m/z* (% rel intensity) 368 (M^+; 1), 322 (100), 188 (82). Found: C, 58.41; H, 7.79%. Calcd for $C_{18}H_{28}O_6Si$: C, 58.67; H, 7.66%.

29: Bp=180 °C/2 mmHg. ^{1}H NMR δ=0.87—0.96 (c, 4 H, $SiCH_2$), 1.22 (t, J=7.02 Hz, 9 H), 1.24 (t, J=7.02 Hz, 9 H) [(2-CH_3) and (6-CH_3)], 2.47 (s, 3 H, C(O)CH_3), 2.46—2.55 (c, 4 H, CH_2), 3.81 (q, J=7.02 Hz, 6 H), 3.84 (q, J=7.02 Hz, 6 H) [(2-$SiOCH_2$) and (6-$SiOCH_2$)], 4.23 (s, 4 H, OCH_2), 6.62 (s, 1 H); ^{13}C NMR δ=11.56, 12.87 [(2-$SiCH_2$) and (6-$SiCH_2$)], 18.26 (CH_3), 20.78 (2-CH_2), 25.66 (6-CH_2), 33.30 (C(O)*C*H_3), 58.33, 58.38 [(2-$SiOCH_2$) and (6-$SiOCH_2$)], 64.22, 64.31 [(3-OCH_2) or (4-OCH_2)], 114.83, 128.70, 132.22, 134.68, 139.19, 143.45 (Ar), 207.33 (C=O); IR (neat) ν 1695 s cm^{-1}; MS *m/z* (% rel intensity) 558 (M^+; 4), 497 (62), 163 (100), 119 (62), 79 (71). Found: C, 55.87; H, 8.44%. Calcd for $C_{26}H_{46}O_9Si_2$: C, 55.88; H, 8.30%.

3,4-Methylenedioxy-2-[2-(triethoxysilyl)ethyl]acetophenone (31), 4, 5- Methylenedioxy- 2- [2- (triethoxysilyl)ethyl]acetophenone (32) and 3,4-Methylenedioxy-2,6-bis[2-(triethoxysilyl)ethyl]acetophenone (33). A 82 : 18 mixture of isomers, **31** and **32**, was obtained by bulb-to-bulb distillation (150 °C/4 mmHg). Spectral data were obtained from a mixture of **31** and **32**. ^{1}H NMR (mixture of **31** and **32**) δ=0.92—1.02 (c, 2 H, $SiCH_2$), 1.25 (t, J=7.02 Hz, 9 H, CH_3), 2.53 (s, 3 H, C(O)CH_3), 2.88—3.00 (c, 2 H, CH_2), 3.88 (q, J=7.02 Hz, 6 H, OCH_2), 5.99 (s, 2 H, OCH_2O, **32**), 6.01 (s, 2 H, OCH_2O, **31**), 6.68 (d, J=8.10 Hz, 1 H, **31**), 6.76 (s, 1 H, **32**), 7.14 (s, 1 H, **32**), 7.34 (d, J=8.10 Hz, 1 H, **31**); ^{13}C NMR

(mixture of **31** and **32**) δ=10.87 ($SiCH_2$, **31**), 12.99 ($SiCH_2$, **32**), 18.28 (CH_3), 20.24 (CH_2, **31**), 27.69 (CH_2, **32**), 29.27 (C(O)CH_3, **31**), 29.63 (C(O)CH_3, **32**), 58.33 (OCH_2), 101.44 (OCH_2O, **31**), 101.55 (OCH_2O, **32**), 105.12, 109.40, 110.64, 125.73, 127.80, 131.43, 141.98, 146.72, 149.70, 150.06 (Ar), 199.28 (C=O); IR (neat) ν 1679 s cm^{-1}; MS *m/z* (% rel intensity) (major isomer **31**) 354 (M^+; 1), 308 (100); (minor isomer **32**) 354 (M^+; 4), 308 (99), 174 (100), 79 (52). Found (mixture of **31** and **32**): C, 57.60; H, 7.39%. Calcd for $C_{17}H_{26}O_6Si$: C, 57.53; H, 7.32%.

33: Bp=180 °C/2 mmHg. ^{1}H NMR δ=0.87—0.98 (c, 4 H, $SiCH_2$), 1.23 (t, J=7.02 Hz, 9 H), 1.23 (t, J=7.02 Hz, 9 H) [(2′-CH_3) and (6′-CH_3)], 2.48 (s, 3 H, C(O)CH_3), 2.48—2.57 (c, 4 H, CH_2), 3.82 (q, J=7.02 Hz, 6 H), 3.83 (q, J=7.02 Hz, 6 H) [(2-OCH_2) and (6-OCH_2)], 5.93 (s, 2 H, OCH_2O), 6.59 (s, 1 H); ^{13}C NMR δ=11.31, 13.30 [(2-$SiCH_2$) and (6-$SiCH_2$)], 18.28 (CH_3), 20.90 (2-CH_2), 26.26 (6-CH_2), 33.32 (C(O)CH_3), 58.40 (OCH_2), 100.92 (OCH_2O), 106.69, 121.60, 133.78, 134.75, 143.65, 147.35 (Ar), 207.06 (C=O); IR (neat) ν 1696 s cm^{-1}; MS *m/z* (% rel intensity) 544 (M^+; 6), 483 (100), 411 (52), 163 (92), 119 (61), 79 (75). Found: C, 54.93; H, 8.23%. Calcd for $C_{25}H_{44}O_9Si_2$: C, 55.12; H, 8.14%.

3, 5- Bis(trifluoromethyl)- 2- [2- (triethoxysilyl)ethyl]acetophenone (35). A product **35** was isolated by bulb-to-bulb distillation (100 °C/2 mmHg) in 41% yield (370 mg). ^{1}H NMR δ=0.85—0.92 (c, 2 H, $SiCH_2$), 1.25 (t, J=7.02 Hz, 9 H, CH_3), 2.69 (s, 3 H, C(O)CH_3), 3.03—3.10 (c, 2 H, CH_2), 3.86 (q, J=7.02 Hz, 6 H, OCH_2), 7.83 (s, 1 H), 7.96 (s, 1 H); ^{13}C NMR δ=13.84 ($SiCH_2$), 18.22 (CH_3), 23.09 (CH_2), 30.80 (C(O)CH_3), 58.46 (OCH_2), 123.10 (q, J_{C-F}=274.1 Hz), 123.54 (q, J_{C-F}=274.1 Hz) [(3-CF_3) and (5-CF_3)], 125.10, 127.55, 128.54 (q, J_{C-F}=34.0 Hz), 130.52 (q, J_{C-F}=30.4 Hz), 142.59, 146.95 (Ar), 201.08 (C=O); IR (neat) ν 1709 s cm^{-1}; MS *m/z* (% rel intensity) 431 ($M^+ - CH_3$; 11), 246 (100), 163 (70), 135 (63), 119 (50), 79 (54). Found: C, 48.52; H, 5.51%. Calcd for $C_{18}H_{24}F_6O_4Si$: C, 48.43; H, 5.42%.

3-Fluoro-4-methoxy-2-[2-(triethoxysilyl)ethyl]acetophenone (37), 5- Fluoro- 4- methoxy- 2- [2- (triethoxysilyl)ethyl]acetophenone (38) and 3-Fluoro-4-methoxy-2,6-bis[2-(triethoxysilyl)ethyl]acetophenone (39). A 75 : 25 mixture of isomers, **37** and **38**, was obtained by bulb-to-bulb distillation (130 °C/2 mmHg). Spectral data were obtained from a mixture of **37** and **38**. ^{1}H NMR (mixture of **37** and **38**) δ=0.94—1.01 (c, 2 H, $SiCH_2$), 1.25 (t, J=7.02 Hz, 9 H, CH_3, **38**), 1.26 (t, J=7.02 Hz, 9 H, CH_3, **37**), 2.53 (s, 3 H, C(O)CH_3, **38**), 2.55 (s, 3 H, C(O)CH_3, **37**), 2.95—3.06 (c, 2 H, CH_2), 3.86 (q, J=7.02 Hz, 6 H, OCH_2, **38**), 3.88 (q, J=7.02 Hz, 6 H, OCH_2, **37**), 3.93 (s, 3 H, OCH_3, **37**), 3.94 (s, 3 H, OCH_3, **38**), 6.81 (dd, $J_{H-H'}$ $_{H-F}$=8.37, 8.37 Hz, 1 H, **37**), 6.85 (d, J_{H-F}=8.10 Hz, 1 H, **38**), 7.45 (d, J_{H-F}=12.42 Hz, 1 H, **38**), 7.51 (dd, $J_{H-H'}$ $_{H-F}$=8.37, 1.89 Hz, 1 H, **37**); ^{13}C NMR (mixture of **37** and **38**) δ=11.64 ($SiCH_2$, **38**), 12.83 ($SiCH_2$, **38**), 18.28 (CH_3), 19.18 (d, J_{C-F}=6.1 Hz, CH_2, **37**), 27.68 (CH_2, **38**), 29.31 (C(O)CH_3), 56.15 (OCH_3), 58.35 (OCH_2), 109.04, 115.24, 117.78 (d, J_{C-F}=18.2 Hz), 126.42 (d, J_{C-F}=3.6 Hz), 128.75, 130.35, 134.22 (d, J_{C-F}=13.4 Hz), 143.64 (d, J_{C-F}=3.6 Hz), 149.39 (d, J_{C-F}=243.8 Hz), 150.14 (d, J_{C-F}=20.6 Hz), 150.31 (d, J_{C-F}=24.3 Hz), 150.66 (d, J_{C-F}=242.5 Hz) (Ar), 198.54 (C=O, **38**), 199.14 (C=O, **37**); IR (neat) ν 1680 s cm^{-1}; MS *m/z* (% rel intensity) 358 (M^+; 0.1), 312 (100). Found (mixture of **37** and **38**): C, 56.62; H, 7.63%. Calcd for $C_{17}H_{27}FO_5Si$: C, 56.96; H, 7.59%.

39: Bp=190 °C/4 mmHg. ^{1}H NMR δ=0.89—0.96 (c, 4 H, $SiCH_2$), 1.23 (t, J=7.02 Hz, 18 H, CH_3), 2.49 (s, 3 H, C(O)CH_3), 2.53—2.59 (c, 4 H, CH_2), 3.83 (q, J=7.02 Hz, 12 H, OCH_2), 3.88 (s, 3 H, OCH_3), 6.69 (d, J_{H-F}=7.83 Hz, 1 H); ^{13}C NMR δ=12.08, 13.16 [(2-$SiCH_2$) and (6-$SiCH_2$)], 18.24 (CH_3), 20.33 (d, J_{C-F}=3.6 Hz, 2-CH_2), 26.29 (6-CH_2), 33.21 (C(O)CH_3), 56.17 (OCH_3), 58.38, 58.42 [(2-OCH_2) and (6-OCH_2)], 111.18, 128.14 (d, J_{C-F}=14.6 Hz), 134.09, 135.37 (d, J_{C-F}=3.6 Hz), 147.54 (d, J_{C-F}=10.9 Hz), 148.63 (d, J_{C-F}=241.4 Hz) (Ar), 206.27 (C=O); IR (neat) ν 1693 s cm^{-1}; MS *m/z* (% rel intensity) 502 ($M^+ - EtOH$; 13), 487 (100), 163 (100), 119 (68), 79 (76). Found: C, 54.65; H, 8.30%. Calcd for $C_{25}H_{45}FO_8Si_2$: C, 54.72; H, 8.27%.

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