Regioselective formation of 2-alkoxyoxetanes in the photoreaction of aromatic carbonyl compounds with β,β-dimethyl ketene silyl acetals: notable solvent and silyl group effects

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Regioselective formation of 2-alkoxyoxetanes **3** was achieved in the photoreactions of aromatic ketones **2** with electron-rich ketene silyl acetals **1**. In the photoreactions, the silyl-migration adduct **5** was also formed together with the oxetane **3**. The product ratios of **3** and **5** were largely dependent on the solvent used and the silyl group of **1**. The exclusive formation of 2-alkoxyoxetanes **3** was controlled by proper choice of the solvent and silyl group.

Introduction

2-Alkoxyoxetanes are versatile synthetic intermediates due to their inherent reactivity, *e.g.* strained structure and acetal moiety.[1] However, in general, the selective formation of 2-alkoxyoxetanes by using the photochemical cycloaddition of ketones with vinyl ethers, the so-called Paternò–Büchi reaction, seems to be difficult. The preferential formation of 3-alkoxyoxetanes would be expected as judged by both the stability of the 1,4-diradical intermediates involved and the effective molecular orbital interaction of HOMO(vinyl ether) with 'HOMO'(carbonyl).[2] Indeed, as shown in eqn. (1), the selective formation of 3-alkoxyoxetanes has been reported, except for conjugated vinyl ethers such as furanes [eqn. (1)].[3]

$$\text{2-alkoxyoxetane} : \text{3-alkoxyoxetane} \tag{1}$$
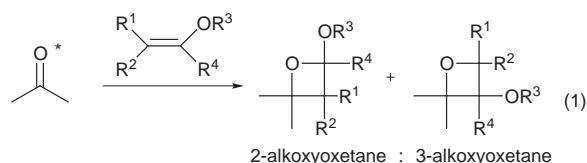
$R^1 = R^2 = R^3 = H$, $R^4 = Et$	25	75	ref. 3a
$R^1 = R^2 = H$, $R^3 = Et$, $R^4 = OEt$	30	70	ref. 3a
$R^1 = Me$, $R^2 = R^4 = H$, $R^3 = Et$	40	60	ref. 3b
$R^1 = R^2 = Me$, $R^3 = Pr^n$, $R^4 = H$	70	30	ref. 3c
$R^1 = R^2 = H$, $R^3 = TMS$, $R^4 = alkyl$	5	95	ref. 3d
$R^1 = R^3 = -(CH_2)_2-$, $R^2 = R^4 = H$	5	95	ref. 3e,f
$R^1 = R^3 = -(CH=CH)-$, $R^2 = R^4 = H$	95	5	ref. 1

To prepare 2-alkoxyoxetanes regioselectively, we have designed Paternò–Büchi type reactions *via* electron transfer oxidation of ketene silyl acetals (KSA), since the spin of the KSA radical cation is mainly localized at the β-carbon (Scheme 1).[4] In fact, we have found the exclusive formation of 2-alkoxyoxetanes in the photoreaction of 2-naphthaldehyde with KSA, together with the silyl-migration adduct [eqn. (2)].[5] Interest-

$$\tag{2}$$
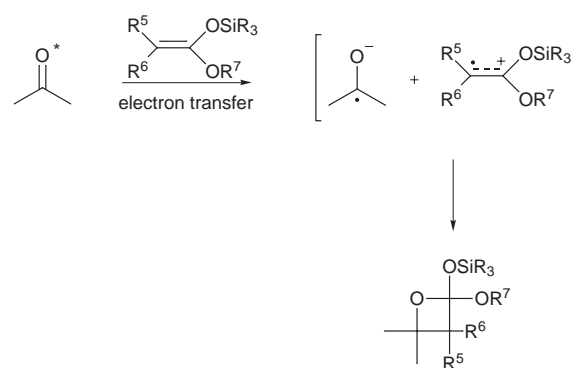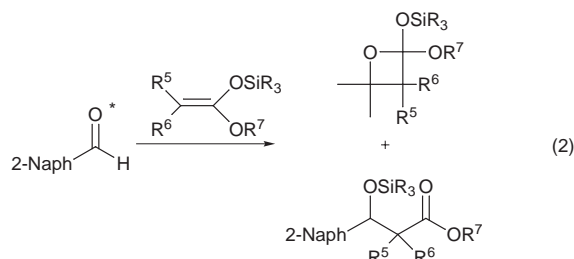
Scheme 1 Regioselective formation of 2-alkoxyoxetanes *via* electron transfer.

ingly, the product ratios, 2-alkoxyoxetane *vs.* silyl-migration adduct, were largely dependent on the solvent used and the silyl group. Consequently, we decided to cover the full range of possible solvents from *n*-hexane to HMPA, silyl groups (SiR₃) from TMS to dimethoxymethylsilyl (DMEOMS) in β,β-dimethyl KSA **1**, and donor- or acceptor-substituted aromatic carbonyl compounds **2**, in order to assess what factor determines the product distribution (**3** *vs.* **4** and **3** *vs.* **5**) [eqn. (3)]. Herein we report the results of our study.

Results

Solvent effects

First of all, in order to know the solvent effects on the formation of 2-alkoxyoxetane **3** and silyl-migration adduct **5**, the photoreaction of 2-naphthaldehyde **2a** (Ar = 2-Naph, R = H, 0.05 M, $E_{red} = -1.68$ V[6] *vs.* SCE, $E_T = 2.57$ eV[7]) with KSA **1a** (SiR₃ = TMS, 0.1 M, $E_{OX} = 0.9$ V[4] *vs.* SCE) was investigated in different solvents (Table 1). In all of the solvents used, no 3-alkoxyoxetane **4aa** (SiR₃ = TMS, Ar = 2-Naph, R = H) was observed in the photoreactions. In non-polar solvents (entries 1–4), the acid-labile 2-siloxy-2-alkoxyoxetane **3aa** (SiR₃ = TMS, Ar = 2-Naph, R = H, 1:1 diastereomeric mixtures), which leads to the ring-opened alcohol **6a** (Ar = 2-Naph, R = H) upon treatment with water, was formed exclusively. The formation of 1:1 diastereomeric mixtures of the oxetane **3aa** was also proved by NMR analysis, especially the peculiar ^{13}C NMR chemical shift of the orthoester carbon (δ 115.99 and 116.49, see Experimental section).[8] In polar solvents (entries 5–8), on the other hand, the silyl migration adduct **5aa** (SiR₃ = TMS, Ar = 2-Naph, R = H) was obtained in isolable amounts. Due to

Table 1 Solvent effects on the product ratios of **3aa** and **5aa** in the photoreaction of silyl ketene acetal **1a** (SiR$_3$ = TMS) with 2-naphthaldehyde **2a**[a]

| Entry | Solvent | Swain's value[b] | | Product ratios (**3aa**:**5aa**)[c] | Yields (%)[d] |
		A	B		
1	n-Hexane	0.00	0.00	>95:5	76
2	Et$_2$O	0.12	0.34	>95:5	79
3	Benzene	0.15	0.59	>95:5	59
4	THF	0.17	0.67	>95:5	84
5	CH$_2$Cl$_2$	0.33	0.80	88:12	87
6[e]	CH$_3$CN	0.37	0.86	79:21	88
7[e]	DMF	0.30	0.93	75:25	68
8[e]	HMPA	0.00	1.07	59:41	67

[a] Photoreactions of **2a** (0.05 M) with **1a** (0.1 M) through a Pyrex filter (>290 nm) were run at 0 °C for 2 h; 2-naphthaldehyde (**2a**) consumption was >95%. [b] A values express an ability to solvate anions and B values express an ability to solvate cations (ref. 8). [c] Relative yields (normalized to 100%) are based on ^{1}H NMR (270 MHz) peak areas; >95:5 means that no **5aa** was observed by ^{1}H NMR. [d] Total isolated yields of **5aa** and **6a**, after converting the oxetane (**3aa**) to the alcohol (**6a**) by treatment with water. [e] A small amount of bis-silyl ether **7a** was obtained in the reactions, 4% (entry 6), 10% (entry 7), 16% (entry 8).
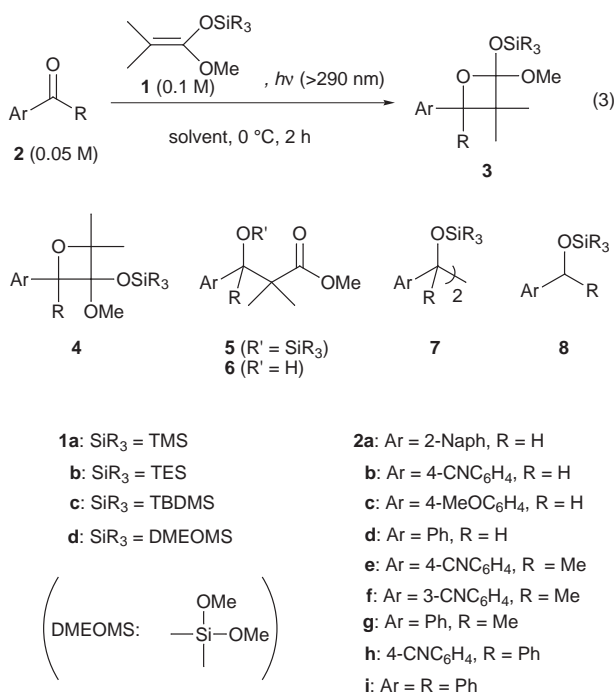
the instability of the 2-alkoxyoxetane **3aa** under the purification conditions on silica gel, the product ratios of **3aa** and **5aa** were determined by direct ^{1}H NMR analyses of the photo-crude mixture (Table 1). The oxetane **3aa** was not converted to the silyl-migration adduct **5aa** even under the photolysis conditions. Since the silyl-migration adduct **5aa** was almost intact under the hydrolysis conditions (rt, H$_2$O–CH$_3$CN 1:1, 12 h), the chemical yields of **3aa** were determined on the basis of the isolated yields of **6a**. Judging from the results obtained in Table 1, the yields of the silyl-migration adduct **5aa** were prone to increase with increasing solvent polarity. Among the solvent parameters, Swain's B value,[9] which expresses an ability to solvate cations, was closely related to the product ratios of **3aa** and **5aa** (*vide infra*). In addition, the bis-silyl ether **7a** (Ar = 2-Naph, R = H) was obtained only in polar solvents (entries 6–8). The formation of **7a** suggests that the radical anion intermediate intervenes in the photoreaction (*vide infra*).

Next, similar solvent effects were also investigated in the photoreaction of **1a** with 4-cyanobenzaldehyde **2b** and 4-methoxybenzaldehyde **2c** (Table 2). In the case of the reaction with 4-cyanobenzaldehyde **2b** (E_{red} = −1.38 V *vs.* SCE,[10]

E_T = 2.89 eV,[7] 1.51 V *vs.* SCE) (entries 1–3), in analogy with the photoreaction of **2a**, the formation of the silyl-migration adduct **5ab** (SiR$_3$ = TMS, Ar = 4-CNC$_6$H$_4$, R = H) was increased with increasing solvent polarity. With **2c** (Ar = 4-MeOC$_6$H$_4$, E_{red} = −2.19 V *vs.* SCE,[11] E_T = 3.05 eV[7]) (entries 4–6), to our surprise, the solvent did play a crucial role not only on the product ratios of 2-alkoxyoxetane **3ac** and silyl-migration adduct **5ac**, but also on the regioselectivity in the oxetane formation. Namely, 3-alkoxyoxetane **4ac** (SiR$_3$ = TMS, Ar = 4-MeOC$_6$H$_4$, R = H) was obtained as an isolable product in non-polar solvents (entries 4,5). The 3-alkoxyoxetane **4ac** was relatively stable under the purification conditions and fully characterized (see Experimental section). The formation of the 3-alkoxyoxetane **4ac** was decreased with increasing solvent polarity.

Let us turn our attention to silyl group effects on the product ratios of 2-alkoxyoxetane **3** and the silyl-migration adduct **5**.

Silyl group effects

In order to obtain more information about the product selectivity (**3** *vs.* **5**), the effects of the silyl group (steric and electronic) on the formation of the oxetane were examined in the photoreactions of **1a–d**, SiR$_3$ = TMS, TES, TBDMS, dimethoxymethylsilyl (DMEOMS), with 2-naphthaldehyde **2a** and 4-cyanobenzaldehyde **2b** in different solvents, n-hexane, Et$_2$O, CH$_2$Cl$_2$ and CH$_3$CN (Table 3). Unfortunately, since 4-cyanobenzaldehyde **2b** was not soluble in n-hexane, the product ratios for the solvent could not be determined. And, unexpectedly, the photoreactions of **1b,c** with **2b** in Et$_2$O gave an inseparable mixture, although the reason is not clear.

In the photoreaction of **1c** (SiR$_3$ = TBDMS), only the oxetanes **3ca** (SiR$_3$ = TBDMS, Ar = 2-Naph, R = H) and **3cb** (SiR$_3$ = TBDMS, Ar = 4-CNC$_6$H$_4$, R = H) were obtained independent of the solvent polarity. In the photoreactions of **1a,b,d** (SiR$_3$ = TMS, TES, DMEOMS), the yields of the silyl-migration adducts **5aa**,**ba**,**da** and **5ab**,**bb**,**db** were increased with increasing solvent polarity (entries 1–7). In contrast to the results for **1c** (SiR$_3$ = TBDMS), the reaction of **1d** (SiR$_3$ = DMEOMS), which has two electron-withdrawing substituents (OMe) on the silicon atom, gave a significant amount of **5da** (SiR$_3$ = DMEOMS, Ar = 2-Naph, R = H) and **5db** (SiR$_3$ = DMEOMS, Ar = 4-CNC$_6$H$_4$, R = H) even in non-polar solvents (entries 1–3, 5–6). From these results, the product ratios, the formation of 2-alkoxyoxetane **3** *vs.* silyl migration adduct **5**, were also sensitively dependent on the silyl group.

Electronic effects of carbonyl compounds

The electronic effects (reduction potential), which are important for the electron transfer step, on the product distributions (2-alkoxyoxetane **3** *vs.* silyl-migration adduct **5**) were examined by using a number of carbonyl compounds, benzaldehyde derivatives **2b–d**, acetophenone derivatives **2e–g**, benzophenone derivatives **2h–i**, in the photoreaction with **1a** (SiR$_3$ = TMS, E_{ox} = 0.9 V *vs.* SCE) (Table 4). First of all, benzaldehyde derivatives **2b–d** were used for the photoreactions in CH$_3$CN. As shown in entries 1–3, the free enthalpy changes (ΔG_{et}) for the direct electron transfer are all negative.† However, the product ratios, the formation of 2-alkoxyoxetane *vs.* silyl-migration adduct, are different, depending upon the used carbonyl compounds. Namely, significant amounts of the silyl-migration adduct **5** were only observed in the photoreaction with p-cyanobenzaldehyde **2b** (ΔG_{et} = −0.67 eV), whereas, in the photoreaction of **2c** (Ar = 4-MeOC$_6$H$_4$, R = H, ΔG_{et} = −0.02 eV), **d** (Ar = Ph, R = H, ΔG_{et} = −0.32 eV), the exclusive formation of the oxetanes **3ac**,**3ad** was observed (entries 2 and 3).

† The free enthalpy changes (ΔG_{et}) in CH$_3$CN were calculated according to Rehm–Weller equation,[12] ΔG_{et} (eV) = E_{ox} − E_{red} − E_T* − E_{coul} (−0.06).

Table 2 Solvent effects on the regioselectivity, 2-alkoxy- **3** *vs.* 3-alkoxy-oxetane **4**, in the photoreactions of *p*-cyanobenzaldehyde **2b** and *p*-methoxybenzaldehyde **2c** with ketene silyl acetal **1a**[a]

Entry	2	E^*_{red}/V[b]	Solvent	Product ratios[c] 3:4	Product ratios[c] 3:5	Yields (%)[d]
1	**2b**	1.51	*n*-Hexane	—[e]	—[e]	—[e]
2	**2b**		Et$_2$O	>95:5	85:15	59
3	**2b**		CH$_3$CN	>95:5	70:30	63
4	**2c**	0.86	*n*-Hexane	79:21	>95:5	75
5	**2c**		Et$_2$O	77:23	>95:5	69
6	**2c**		CH$_3$CN	95:5	94:6	59

[a] Photoreactions of **2b,c** (0.05 M) with **1a** (0.1 M) through a Pyrex filter (>290 nm) were run at 0 °C for 2 h; aldehyde consumptions were >95%. [b] Reduction potentials (*vs.* SCE) at excited triplet states of aldehydes **2b,c**, which were determined by adding the reduction potentials [E_{red}/V *vs.* SCE, for **2b**, E_{red} = −1.38 (ref. 9) and for **2c**, E_{red} = −2.19 (this work)] to the triplet-excited energy [E_T/eV, for **2b**, E_T = 1.51 (ref. 7) and for **2c**, E_T = 3.05 (ref. 7)]. [c] Relative yields (normalized to 100%) are based on ^{1}H NMR (270 MHz) peak areas; >95:5 means that no minor products were observed by ^{1}H NMR. [d] Total isolated yields, after converting the 2-alkoxyoxetanes **3ab** and **3ac** to the alcohols **6b,c** by treatment with water. [e] *p*-Cyanobenzaldehyde **2b** was not dissolved in *n*-hexane.

Table 3 Silyl group effects on the product ratios of 2-alkoxyoxetanes **3** and silyl-migration adducts **5** in the photoreactions of 2-naphthaldehyde **2a** and *p*-cyanobenzaldehyde **2b** with ketene silyl acetal **1a–d**[a]

Entry	Solvent	2	1a (TMS)	1b (TES)	1c (TBDMS)	1d (DMEOMS)
			Yields (%) and product ratios (3:5)[b]			
1	*n*-Hexane	**2a**	76 (>95:5)	73 (>95:5)	72 (>95:5)	83 (71:29)
2	Et$_2$O	**2a**	79 (>95:5)	60 (>95:5)	76 (>95:5)	34 (86:14)
3	CH$_2$Cl$_2$	**2a**	87 (88:12)	63 (>95:5)	89 (>95:5)	89 (56:44)
4	CH$_3$CN	**2a**	88 (79:21)	64 (88:12)	79 (>95:5)	96 (48:52)
5	Et$_2$O	**2b**	59 (85:15)	—[c]	—[c]	94 (58:42)
6	CH$_2$Cl$_2$	**2b**	88 (>95:5)	92 (>95:5)	94 (>95:5)	94 (54:46)
7	CH$_3$CN	**2b**	63 (70:30)	92 (89:11)	75 (>95:5)	75 (32:68)

[a] Photoreactions of **2a,b** (0.05 M) with ketene silyl acetals **1a–d** (0.1 M) were run at 0 °C for 2 h; consumption of **2a,b** was >95%. [b] Total isolated yields (**6** and **5**, %), after converting the oxetane **3** to the alcohol **6** by treatment with water; under these conditions, silyl-migration adducts **5** persisted, except for SiR$_3$ = DMEOMS case. In the case of SiR$_3$ = DMEOMS, some decomposition of **5da,db** was observed, leading to the alcohol **6a,b**. Values in parentheses represent the product ratios of the 2-alkoxyoxetane **3** and the silyl-migration adduct **5**, which were determined on the basis of ^{1}H NMR (270 MHz) peak areas; >95:5 means that no minor product was observed by ^{1}H NMR. [c] Not determined.

Table 4 Electronic (reduction potential) effects of the carbonyl compounds **2b–i** in the photoreactions with ketene silyl acetal **1a** (SiR$_3$ = TMS) in CH$_3$CN[a]

Entry	2	E_{red}/V[b]	E_T/eV[c]	E^*_{red}[d]	ΔG_{et}/eV[e]	Yields (%)[f]	Product ratios 3:5[g]
Benzaldehyde derivatives							
1	**2b**	−1.38	2.89	1.51	−0.67	63	70:30
2	**2d**	−1.98	3.09	1.16	−0.32	72	95:5
3	**2c**	−2.19	3.05	0.86	−0.02	59	94:6
Acetophenone derivatives							
4[h]	**2e**	−1.58	3.00	1.42	−0.58	43	62:38
5	**2f**	−1.75	3.17	1.42	−0.58	55	>95:5
6	**2g**	−2.14	3.22	1.08	−0.24	64	>95:5
Benzophenone derivatives							
7[i]	**2h**	−1.42	2.90	1.48	−0.64	35	77:23
8	**2i**	−1.83	3.00	1.17	−0.33	69	>95:5

[a] Photoreactions of **2b–i** (0.05 M) with **1a** (0.1 M) through a Pyrex filter (>290 nm) were run at 0 °C for 2 h; ketone consumptions >95%. [b] Reduction potentials *vs.* SCE. The data are selected from ref. 12. [c] Excited triplet energy; from ref. 7. [d] Values describe the reduction potentials (*vs.* SCE) of the excited triplet state of the carbonyls. [e] ΔG_{et} were calculated by Weller equation, $\Delta G_{et} = 0.9 - E_{red} - E_T - 0.06$, see ref. 12. [f] Isolated yields of **5** + **6**, after hydrolysis of 2-alkoxyoxetanes **3** to alcohol **6**. [g] Product ratios were determined on the basis of ^{1}H NMR (270 MHz) peak areas; >95:5 means that no minor product was observed by ^{1}H NMR. [h] Silyl ether **8e** (12%) and bis-silyl ether **7e** (2%) were obtained together with **3ae** and **5ae**. [i] Silyl ether **8h** (26%) was obtained together with **3ah** and **5ah**.

Next, the photoreactions of **1a** with acetophenone derivatives **2e–g** were performed (entries 4–6). In the cases of **2f,g**, the oxetanes **3af,ag** were exclusively formed (entries 5–6). On the other hand, in the photoreaction of 4-cyanoacetophenone **2e** (E^*_{red} = 1.42 V *vs.* SCE, E_{red} = −1.58 V *vs.* SCE,[13] ΔG_{et} = −0.58 eV), the silyl-migrated adduct **5ae** was also obtained together with oxetane **3ae**. It should be noted that the silylated reduction products **8e** (12%), and bis-silylated pinacol **7e** (trace) were also produced in the photoreaction (entry 4). Interestingly,

the photoreaction of 3-cyanoacetophenone **2f** (E^*_{red} = 1.42 V *vs.* SCE, E_{red} = −1.75 V *vs.* SCE[13]) with **1a** gave exclusive formation of the oxetanes **3af** (SiR$_3$ = TMS, Ar = 3-CNC$_6$H$_4$, R = CH$_3$), in spite of the same reduction potential (E^*_{red}) at the excited state of **2e** (Ar = 4-CNC$_6$H$_4$). These results suggest that the reduction potentials (E_{red}) of the ground states, which may express the stability of the radical anion, are also an important factor for controlling the product selectivity. These results are informative for the reaction mechanism (*vide infra*).

Finally, the photoreaction of **1a** with benzophenone derivatives **2h,i** was investigated in CH$_3$CN (entries 7,8). In the case of 4-cyanobenzophenone **2h** (E^*_{red} = 1.48 V *vs.* SCE), the silyl-migration adduct **5ah** (SiR$_3$ = TMS, Ar = 4-CNC$_6$H$_4$, R = Ph) was formed together with the oxetane **3ah** and the silylated reduction product **8h**. Surprisingly, the 2-alkoxyoxetane **3ai** (SiR$_3$ = TMS, Ar = R = Ph) was isolable on silica gel and fully characterized (see Experimental section).

Discussion

Ground state interaction of ketene silyl acetals with carbonyl compounds

In general, silicon compounds act as Lewis acids. For example, silyl-directed aldol-type reactions of ketene N,O-silyl acetals and silacyclobutyl acetals with carbonyl compounds have been recently investigated.[14] The higher-order silicon intermediates, silicates, are proposed in the non-catalyzed aldol-type reactions. Therefore, to test the possibility of such intermediates for the formation of the silyl-migration adducts **5**, the reaction of **1a,d** with **2a,b,e**, which gave significant amounts of **5** as shown in Tables 2–4, was performed under dark conditions at 0 °C. Consequently, no adducts were observed in such conditions (0 °C, 2 h). These results are reasonable, because in general the non-catalyzed (silyl-directed) aldol-type reactions smoothly occurred to give the corresponding silyl-migrating adducts only in poor σ-donor solvents (CH$_2$Cl$_2$, *n*-hexane) but not at all in THF or DMF.[14a] In contrast to the solvent effects of the silyl-directed reactions (non-catalyzed aldol reactions), the yields of the silyl-migration adducts **5** in our photoreactions are prone to increase with increasing solvent polarity (*vide supra*). Therefore, the non-photochemical formation of **5** was excluded. Next we turned our attention to the possibility of ground-state complexation [electron donor acceptor (EDA) complex][15] between the ketene silyl acetals and ketones, in order to examine the possibility of the complex-excitation mechanism. The UV–visible spectra in *n*-hexane and CH$_3$CN were measured for the mixture of **1a,d** (10, 25 mM) with 2-naphthaldehyde (5, 10, 25 mM) at 0 °C. There were no additional absorptions in the range from 300 nm to 600 nm. Therefore, the possibility of such a complex-excitation mechanism may be low.

As mentioned above, we examined several factors for determining the product selectivities (Tables 1–4), both 2-alkoxyoxetanes **3** *vs.* 3-alkoxyoxetanes **4** and oxetane **3** *vs.* silyl-migration adduct **5**. The following results were notable. (1) 3-Alkoxyoxetane **3** was obtained as a minor product only in the photoreaction of 4-anisaldehyde **2c** which has a relatively low electron affinity (entries 5,6 in Table 2). (2) The yield of 3-alkoxyoxetane **4** was decreased with increasing solvent polarity (entries 4–6 in Table 2). (3) The product ratios of **3** and **5** were dependent on the polarity of the solvent used; namely in polar solvents (high Swain's *B* value, CH$_3$CN, HMPA) significant amounts of **5** were produced together with the formation of the silylated pinacol **7** (Tables 1 and 2). (4) The ratios **3**:**5** were also influenced by the silyl group used (Table 3), thus, the silyl-migration order was DMEOMS > TMS > TES > TBDMS. (5) The reduction potentials of both the ground states (entries 4,5 in Table 4) and the excited states (Table 4) also affected the ratios **3**:**5**.

Mechanism

On the basis of the results obtained, the following mechanism was proposed for our photoreactions (Scheme 2). First of all, we would like to concentrate on the solvent and silyl group effects on the product ratios of 2-alkoxyoxetane **3** and the silyl-migration adduct **5**.

Judging from the negative ΔG_{et} (<0 eV) values for the electron transfer reaction from KSA **1** to the carbonyl compounds

2, it is reasonable to postulate that the electron transfer reaction occurs to give the contact radical ion-pair (CIP). In non-polar solvents (low Swain's *B* value), regioselective formation occurs to give the 2-alkoxyoxetanes **3** *via* 1,4 diradical **1,4-DR**, since the spin density of the KSA radical cation is mainly on the β-carbon.[4] In polar solvents (high Swain's *B* value), the rate (k_1) from CIP to the solvent separated ion pairs (SSIP) and/or free radicals (FR) can compete with the 2-alkoxyoxetane formation (k_2) giving the silyl-migration adduct **5**. The mechanism is quite reasonable, because the dimer of the ketyl radical anion, bis-silyl ethers **7** and silyl ether **8**, was obtained only in polar solvents. When the silyl group is considerably bulky (such as TES and TBDMS), the solvation of the cationic silicon atom is suppressed to give the 2-alkoxyoxetane **3** from CIP.[16] In the case of **1d** (SiR$_3$ = DMEOMS), significant amounts of the silyl-migration adduct **5** was observed even in non-polar solvents (low Swain's *B* value) (Table 3). The results can be explained by the enhanced electrophilicity of the silicon atom caused by the introduction of the electronegative oxygen atoms. Let us turn our attention to the formation of 3-alkoxyoxetane **4**.

3-Alkoxyoxetane **4** was obtained only in the photoreaction of electron donor-substituted 4-methoxybenzaldehyde **2c** (Table 2) in non-polar solvents. Judging from the low reduction potential (E^*_{red} = 0.86 *vs.* SCE) of **2c**, the formation of 3-alkoxyoxetane **4ac** may be derived from an exciplex intermediate, which is a common intermediate for Paternò–Büchi reactions depicted in Scheme 2.[2] However, in a polar solvent such as acetonitrile (high relative permittivity ε = 37.5), electron transfer can compete to give regioselective formation of 2-alkoxyoxetane **3**.[17]

Finally, we would like to discuss the observed electronic effects (reduction potential) at the ground state of the carbonyl compounds on the product ratio of **3**:**5** (Table 4). We observed a significant amount of the silyl-migration adduct **5** in the case of 4-cyanoacetophenone **2e**, compared with the case of 3-cyanoacetophenone **2f** (Table 4, entries 4–5). These two carbonyls have the same reduction potential at the excited states and almost the same steric circumstances. However, the observed product ratios of **3**:**5** were totally different (for **2e**; **3ae**:**5ae** = 62:38, for **2f**; **3af**:**5af** = >95:5). The reason is probably derived from the stability of radical anions of **2e,f**, which may be expressed by the reduction potentials of ground state molecules. Thus, the relatively unstable radical anion of 3-cyanoacetophenone **2f** (E_{red} = −1.75 V) reacts with KSA radical cation faster than the separation of the CIP to the SSIP. This consideration may be applied to explain the other cases in Table 4.

Conclusion

We have accumulated the fundamental data to prepare regioselectively the 2-alkoxyoxetanes **3**. Consequently, we found that regioselective formation of 2-alkoxyoxetanes **3** can be achieved by proper choice of both the solvent and the silyl group in KSA **1**. By choosing the TBDMS group, the exclusive formation of 2-alkoxyoxetanes **3** can be obtained in high yields, independent of the solvent used.

Experimental

General aspects

All the solvents were dried before use. *n*-Hexane, dichloromethane, acetonitrile, DMF and HMPA were dried and distilled from calcium hydride. Ether, THF and benzene were dried and distilled from sodium benzophenone ketyl prior to use. Ketene silyl acetals **1a**–**d** were prepared by reported methods.[18] The aromatic carbonyl compounds **2** were used after suitable purification by distillation or recrystallization. Flash column chromatography was performed using silica gel (Wakogel C-300) as absorbent.
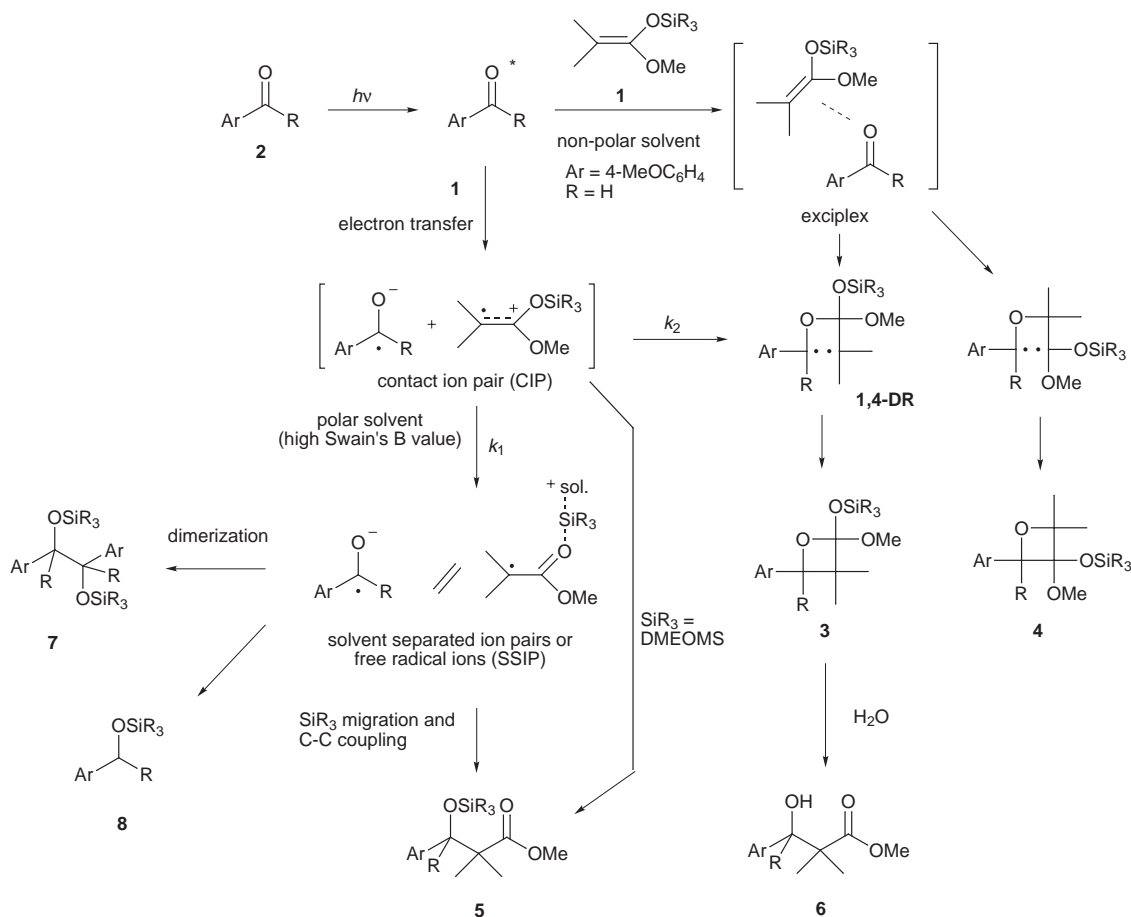
Scheme 2 Proposed mechanism for the photoreactions of ketones **2** with ketene silyl acetals **1**.

Cyclic voltammetry

The cyclic voltammetry measurements were performed on a BAS CV-50W in deaerated acetonitrile containing 0.10 M Et_4NClO_4 as a supporting electrolyte at 293 K. With a scan rate of 400 mV s^{-1}, **2c** showed partially reversible reduction. The measured reduction potentials of **2c** were recorded with respect to Ag/Ag$^+$. The obtained reduction potentials E_p (*vs.* Ag/Ag$^+$) were corrected to the value *vs.* SCE by adding 0.30 V.[19]

Spectroscopic measurements

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-EX-270 spectrometer at 270 MHz and 67.8 MHz, respectively. ^{1}H NMR chemical shifts were reported in ppm (δ_H) using residual CHCl$_3$ (δ 7.26) in the perdeuterated solvent as the internal standard. Mutiplicities were reported as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^{13}C NMR chemical shifts were reported in ppm (δ_C) relative to the internal standard CDCl$_3$ (δ 77.00). Coupling constants J are given in Hz. IR spectra were recorded on an Hitachi 260-30 spectrophotometer. UV–visible spectra were measured on an Hitachi 220A spectrophotometer. Mass spectrometric data were obtained by using a JEOL JNS-BX 303-HF mass spectrometer.

Photolyses

Photolyses were conducted with an Eikohsha 500 W high-pressure mercury lamp.

Preparation of ketene silyl acetals 1a–d

Ketene silyl acetals **1a–d** were prepared by the method reported by Ireland *et al.*[18] Spectroscopic data for a new compound **1d** (SiR$_3$ = DMEOMS) are as follows.

1-Methoxy-1-(dimethoxymethylsiloxy)-2,2-dimethylethylene 1d. Colorless oil, bp 38 °C (5 mmHg) (Found: C, 46.55; H, 8.73. C$_8$H$_{18}$O$_4$Si requires C, 46.57; H, 8.79%); ν_{max}(film)/cm^{-1} 2850–3000, 1710, 1640, 1100; δ_H(270 MHz; CDCl$_3$) 0.16 (s, 3 H), 1.53 (s, 3 H), 1.54 (s, 3 H), 3.54 (s, 3 H), 3.56 (s, 6 H); δ_C(67.8 MHz; CDCl$_3$) −7.90, 16.05, 16.53, 50.42, 57.18, 91.59, 148.18; *m/z* (EI) 458.2096 (M$^+$ 0.2, C$_8$H$_{18}$O$_4$Si requires 458.2098), 443 (2%), 229 (100).

Photoreaction of ketene silyl acetals 1 with aromatic carbonyl compounds 2: general procedure

A test tube shaped reaction flask was flushed with dry argon. The reaction mixture of ketene silyl acetals **1** (1.0×10^{-1} M) and **2** (5.0×10^{-2} M) in deoxygenated solvent was irradiated with a high-pressure mercury lamp through a Pyrex filter. After **2** was consumed, the solvent was removed under reduced pressure using a rotary evaporator. After the formation of oxetanes **3** was identified by NMR, the crude mixture was reacted with water in CH$_3$CN. The organic layer was extracted with Et$_2$O and the solvent was removed by using a rotary evaporator. The products were isolated by flash column chromatography on silica gel. Products and yields were as reported in the text. Spectroscopic data for the new compounds are as follows.

3,3-Dimethyl-2-methoxy-2-trimethylsiloxy-4-(2-naphthyl)-oxetane (1:1 diastereomeric mixtures of 3aa). δ_H(270 MHz; CDCl$_3$) 0.32 (s, 9 H), 0.36 (s, 9 H), 0.78 (s, 3 H), 0.79 (s, 3 H), 1.40 (s, 3 H), 1.44 (s, 3 H), 3.48 (s, 3 H), 3.50 (s, 3 H), 5.19 (s, 1 H), 5.21 (s, 1 H), 7.30–7.52 (m, 6 H), 7.78–7.95 (m, 8 H); δ_C(67.8 MHz; CDCl$_3$; readable signals) 1.37, 18.44, 19.40, 21.49, 23.77, 49.43, 49.92, 51.10, 82.14, 82.89, *115.99, 116.49.*

3,3-Dimethyl-2-methoxy-2-(trimethylsiloxy)-4-(4-cyano-phenyl)oxetane (10:7 diastereomeric mixtures of 3ab). δ_H(270 MHz; CDCl$_3$) 0.23 (s, 9 H), 0.28 (s, 9 H), 0.67 (s, 3 H), 0.69 (s, 3 H), 1.31 (s, 3 H), 1.36 (s, 3 H), 3.37 (s, 3 H), 3.41 (s, 3 H), 4.98

(s, 1 H), 5.01 (s, 1 H), 7.33–7.43 (m, 2 H), 7.59–7.65 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$; readable signals) 1.24, 19.10, 19.27, 21.35, 23.70, 49.26, 49.51, 50.24, 51.48, 81.17, 81.91, 110.98, 111.01, *115.85*, *116.37*, 118.78, 118.85, 125.98, 126.43, 131.88, 144.31, 144.89.

3,3-Dimethyl-2-methoxy-2-(trimethylsiloxy)-4-(4-methoxy-phenyl)oxetane (1:1 diastereomeric mixtures of 3ac). δ_H(270 MHz; CDCl$_3$) 0.37 (s, 9 H), 0.41 (s, 9 H), 0.84 (s, 3 H), 0.86 (s, 3 H), 1.39 (s, 3 H), 1.44 (s, 3 H), 3.51 (s, 3 H), 3.53 (s, 3 H), 3.91 (s, 6 H), 5.05 (s, 1 H), 5.07 (s, 1 H), 6.94–7.01 (m, 2 H), 7.28–7.38 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$; readable signals) 1.28, 18.28, 19.18, 21.30, 23.67, 49.09, 49.33, 49.47, 50.84, 81.91, 82.71, *115.75*, *116.38*.

3,3-Dimethyl-2-methoxy-2-trimethylsiloxy-4-phenyloxetane (1:1 diastereomeric mixtures of 3ad). δ_H(270 MHz; CDCl$_3$) 0.39 (s, 9 H), 0.42 (s, 9 H), 0.84 (s, 3 H), 0.87 (s, 3 H), 1.43 (s, 3 H), 1.48 (s, 3 H), 3.53 (s, 3 H), 3.55 (s, 3 H), 5.11 (s, 1 H), 5.14 (s, 1 H), 7.34–7.55 (m, 5 H); δ_C(67.8 MHz; CDCl$_3$; readable signals) 1.31, 18.33, 18.98, 21.35, 23.70, 49.15, 49.36, 49.60, 50.93, 81.98, 82.79, *115.56*, *116.66*, 125.32, 125.80, 138.58, 139.17.

2-Methoxy-2-trimethylsiloxy-3,3,4-trimethyl-4-(4-cyano-phenyl)oxetane (10:7 diastereomeric mixtures of 3ae). δ_H(270 MHz; CDCl$_3$) 0.19 (s, 9 H), 0.25 (s, 9 H), 0.69 (s, 3 H), 0.70 (s, 3 H), 1.24 (s, 3 H), 1.28 (s, 3 H), 1.57 (s, 3 H), 1.58 (s, 3 H), 3.30 (s, 3 H), 3.37 (s, 3 H), 7.36–7.39 (m, 2 H), 7.58–7.62 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) 1.28, 17.99, 19.93, 21.33, 22.82, 25.29, 25.54, 48.93, 49.81, 51.02, 51.11, 82.32, 82.61, 110.24, *114.74*, *115.29*, 118.83, 118.90, 125.32, 125.70, 131.59, 131.68, 150.35, 150.51.

2-Methoxy-2-trimethylsiloxy-3,3,4-trimethyl-4-(3-cyano-phenyl)oxetane (5:4 diastereomeric mixtures of 3af). δ_H(270 MHz; CDCl$_3$) 0.20 (s, 9 H), 0.26 (s, 9 H), 0.69 (s, 3 H), 0.70 (s, 3 H), 1.24 (s, 3 H), 1.28 (s, 3 H), 1.57 (s, 3 H), 1.59 (s, 3 H), 3.31 (s, 3 H), 3.38 (s, 3 H), 7.41–7.53 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$) 1.29, 17.99, 19.95, 21.42, 22.95, 25.39, 25.61, 49.00, 49.80, 50.93, 50.98, 82.05, 82.28, 111.86, 111.95, *114.81*, *115.36*, 118.89, 119.05, 128.27, 128.52, 128.61, 128.64, 129.04, 129.45, 130.15, 146.54, 146.68.

2-Methoxy-2-trimethylsiloxy-3,3,4-trimethyl-4-phenyloxetane (1:1 diastereomeric mixtures of 3ag). δ_H(270 MHz; CDCl$_3$) 0.30 (s, 9 H), 0.34 (s, 9 H), 0.81 (s, 3 H), 0.83 (s, 3 H), 1.33 (s, 3 H), 1.36 (s, 3 H), 1.69 (s, 6 H), 3.42 (s, 3 H), 3.47 (s, 3 H), 7.28–7.39 (m, 5 H); δ_C(67.8 MHz; CDCl$_3$; readable signals) 1.37, 18.13, 20.06, 21.51, 22.93, 25.82, 26.08, 48.81, 49.83, 50.68, 50.71, 82.77, 83.16, *114.92*, *115.44*, 124.47, 124.78, 126.27, 126.33, 127.67, 144.97, 145.03.

3,3-Dimethyl-2-methoxy-2-trimethylsiloxy-4-phenyl-4-(4-cyanophenyl)oxetane (3:2 diastereomeric mixtures of 3ah). δ_H(270 MHz; CDCl$_3$) 0.22 (s, 9 H), 0.23 (s, 9 H), 1.09 (s, 6 H), 1.13 (s, 3 H), 1.14 (s, 3 H), 3.36 (s, 3 H), 3.38 (s, 3 H), 7.20–7.66 (m, 9 H); δ_C(67.8 MHz; CDCl$_3$) 1.49, 21.21, 23.18, 23.31, 48.66, 48.93, 54.00, 85.59, 85.73, 110.14, 110.28, *114.84*, 118.83, 118.96, 125.32, 125.55, 126.33, 126.52, 126.86, 126.94, 127.89, 127.96, 131.50, 131.63, 142.66, 142.98, 149.67.

3,3-Dimethyl-2-methoxy-2-trimethylsiloxy-4,4-diphenyl-oxetane (3ai). Viscous oil (Found: C, 70.51; H, 7.88. C$_{21}$H$_{28}$O$_3$Si requires C, 70.74; H, 7.92%); v_{max}(film)/cm^{-1} 2850–3100, 1120; δ_H(270 MHz; CDCl$_3$) 0.20 (s, 9 H), 1.09 (s, 3 H), 1.11 (s, 3 H), 3.37 (s, 3 H), 7.14–7.29 (m, 6 H), 7.40–7.51 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$) 1.55, 21.37, 23.40, 48.61, 53.53, 86.09, *114.92*, 125.52, 125.70, 126.58, 126.94, 127.55, 127.62, 144.10, 144.33.

3,3-Dimethyl-2-methoxy-2-triethylsiloxy-4-(2-naphthyl)-oxetane (2:1 diastereomeric mixtures of 3ba). δ_H(270 MHz; CDCl$_3$) 0.68–0.89 (m, 18 H), 0.96–1.12 (m, 18 H), 1.42 (s, 3 H), 1.44 (s, 3 H), 3.42 (s, 3 H), 3.50 (s, 3 H), 5.17 (s, 1 H), 5.21 (s, 1 H), 7.35–7.50 (m, 6 H), 7.81–7.89 (m, 8 H); δ_C(67.8 MHz; CDCl$_3$; readable signals) 5.70, 5.79, 6.54, 6.88, 18.49, 19.48, 21.93, 23.58, 50.17, 50.33, 82.14, 82.41, *116.10*, *116.28*, 123.56, 123.90, 124.15, 124.44, 125.59, 125.97, 127.55, 127.62, 127.89, 127.96.

3,3-Dimethyl-2-methoxy-2-triethylsiloxy-4-(4-cyanophenyl)-oxetane (5:3 diastereomeric mixtures of 3bb). δ_H(270 MHz; CDCl$_3$) 0.63–0.80 (m, 12 H), 0.73 (s, 3 H), 0.77 (s, 3 H), 0.91–1.10 (m, 18 H), 1.32 (s, 3 H), 1.35 (s, 3 H), 3.30 (s, 3 H), 3.41 (s, 3 H), 4.94 (s, 1 H), 4.99 (s, 1 H), 7.32–7.38 (m, 4 H), 7.58–7.62 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$) 5.55, 5.61, 6.42, 6.65, 18.35, 19.34, 21.71, 23.52, 50.12, 50.19, 50.60, 51.75, 81.12, 81.46, 110.89, 110.94, *115.92*, *116.16*, 118.67, 118.71, 125.93, 126.34, 131.32, 131.73, 144.42, 144.69.

3,3-Dimethyl-2-methoxy-2-(tert-butyldimethylsiloxy)-4-(2-naphthyl)oxetane (3:5 diastereomeric mixtures of 3ca). δ_H(270 MHz; CDCl$_3$) 0.33 (s, 6 H), 0.36 (s, 6 H), 0.79 (br s, 6 H), 0.98 (s, 9 H), 1.03 (s, 9 H), 1.42 (br s, 6 H), 3.43 (s, 3 H), 3.50 (s, 3 H), 5.17 (s, 1 H), 5.23 (s, 1 H), 7.42–7.55 (m, 6 H), 7.75–7.92 (m, 8 H); δ_C(67.8 MHz; CDCl$_3$; readable signals) −3.30, −3.07, −3.02, −2.89, 18.22, 18.56, 19.52, 21.96, 22.63, 23.56, 25.61, 25.84, 50.06, 50.34, 51.63, 82.30, 82.57, *116.38*, *116.46*.

3,3-Dimethyl-2-methoxy-2-(tert-butyldimethylsiloxy)-4-(4-cyanophenyl)oxetane (1:1 diastereomeric mixture of 3cb). δ_H(270 MHz; CDCl$_3$) 0.21 (s, 3 H), 0.23 (s, 3 H), 0.24 (s, 3 H), 0.27 (s, 3 H), 0.67 (s, 3 H), 0.69 (s, 3 H), 0.90 (s, 3 H), 0.95 (s, 3 H), 1.33 (s, 3 H), 1.35 (s, 3 H), 3.23 (s, 3 H), 3.41 (s, 3 H), 4.96 (s, 1 H), 5.03 (s, 1 H), 7.31–7.39 (m, 4 H), 7.59–7.63 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$; readable signals) −3.39, −3.20, −3.05, −3.02, 25.59, 49.83, 50.35, 50.66, 52.01, 81.30, 81.64, 110.94, 111.03, *116.08*, *116.33*, 118.71, 118.76, 125.88, 126.43, 131.78, 144.38, 144.76.

3,3-Dimethyl-2-methoxy-2-(dimethoxymethylsiloxy)-4-(2-naphthyl)oxetane 3da. δ_H(270 MHz; CDCl$_3$) 0.32 (s, 3 H), 0.83 (s, 3 H), 1.34 (s, 3 H), 3.54 (s, 3 H), 3.625 (s, 3 H), 3.633 (s, 3 H), 5.20 (s, 1 H), 7.32–7.63 (m, 3 H), 7.76 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$; readable signals) −6.52, 18.94, 21.48, 49.01, 50.26, 51.04, 82.53, *115.18*, 122.61, 123.60, 124.33, 128.00, 129.41, 134.48, 135.00.

3,3-Dimethyl-2-methoxy-2-(dimethoxymethylsiloxy)-4-(4-cyanophenyl)oxetane 3db. δ_H(270 MHz; CDCl$_3$) 0.24 (s, 3 H), 0.75 (s, 3 H), 1.32 (s, 3 H), 3.45 (s, 3 H), 3.56 (s, 3 H), 3.57 (s, 3 H), 5.02 (s, 1 H), 7.39–7.49 (m, 2 H), 7.58–7.64 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$; readable signals) −6.61, 18.85, 21.40, 49.15, 50.26, 50.30, 51.84, 81.64, 110.51, *115.06*, 118.78, 126.20, 131.82, 144.06.

4,4-Dimethyl-3-methoxy-3-trimethylsiloxy-2-(4-methoxy-phenyl)oxetane (2:1 diastereomeric mixture of 4ac). Viscous oil (Found: C, 61.87; H, 8.48. C$_{16}$H$_{26}$O$_4$Si requires C, 61.90; H, 8.44%); v_{max}(film)/cm^{-1} 2800–3050, 1620, 1520, 850; δ_H(270 MHz; CDCl$_3$) −0.04 (s, 9 H), 0.21 (s, 9 H), 1.40 (s, 3 H), 1.46 (s, 3 H), 1.48 (s, 3 H), 1.51 (s, 3 H), 2.90 (s, 3 H), 3.34 (s, 3 H), 3.81 (s, 3 H), 3.82 (s, 3 H), 5.42 (s, 1 H), 5.50 (s, 1 H), 6.84–6.93 (m, 4 H), 7.37–7.40 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$) 1.17, 1.40, 23.20, 23.70, 24.44, 25.00, 50.77, 51.07, 55.08, 55.15, 87.15, 89.15, 90.80, 90.98, 102.07, 120.95, 113.10, 113.26, 128.90, 129.20, 159.17, 159.48; m/z (CI) 311.1672 (M$^+$ + 1, 35%, C$_{16}$H$_{26}$O$_4$Si requires 311.1679), 253 (49), 174 (100).

Methyl 2,2-dimethyl-3-trimethylsiloxy-3-(2-naphthyl)propion-ate 5aa. Colorless powder, mp 79–83 °C (Found: C, 69.07; H, 7.99. C$_{19}$H$_{26}$O$_3$Si requires C, 69.05; H, 7.93%); v_{max}(KBr)/cm^{-1} 2900–3050, 1740, 1095; δ_H(270 MHz; CDCl$_3$) −0.02 (s, 9 H), 1.05 (s, 3 H), 1.18 (s, 3 H), 3.70 (s, 3 H), 5.16 (s, 1 H), 7.14–7.49 (m, 3 H), 7.70–7.86 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$) −0.02, 19.21, 21.80, 49.29, 51.70, 79.26, 125.70, 125.84, 126.02, 126.61, 126.90, 127.57, 127.94, 132.69, 132.90, 138.47, 177.30; m/z (EI) 330.1653 (M$^+$, 1%, C$_{19}$H$_{26}$O$_3$Si requires 330.1651), 315 (4%), 229 (100).

Methyl 2,2-dimethyl-3-trimethylsiloxy-3-(4-cyanophenyl)-propionate 5ab. Colorless powder, mp 79–81 °C (Found: C, 62.88; H, 7.61. C$_{16}$H$_{23}$NO$_3$Si requires C, 62.92; H, 7.59%); v_{max}(KBr)/cm^{-1} 2900–3000, 2250, 1740; δ_H(270 MHz; CDCl$_3$) −0.04 (s, 9 H), 0.97 (s, 3 H), 1.10 (s, 3 H), 3.66 (s, 3 H), 5.00 (s, 1 H), 7.37–7.40 (m, 2 H), 7.57–7.60 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) −0.14, 19.55, 21.12, 48.91, 51.84, 78.40, 111.29, 118.78,

128.34, 131.36, 146.56, 176.57; *m/z* (EI) 305.1432 (M$^+$, 0.2%, C$_{16}$H$_{23}$NO$_3$Si requires 305.1447), 290 (15), 204 (100).

Methyl 2,2-dimethyl-3-trimethylsiloxy-3-(4-methoxyphenyl)-propionate 5ac. Colorless powder, mp 44–46 °C (Found: C, 61.87; H, 8.31. C$_{16}$H$_{26}$O$_4$Si requires C, 61.90; H, 8.44%); ν_{max}(KBr)/cm^{-1} 2900–3050, 1760, 1100; δ_H(270 MHz; CDCl$_3$) −0.05 (s, 9 H), 0.97 (s, 3 H), 1.10 (s, 3 H), 3.66 (s, 3 H), 3.80 (s, 3 H), 4.92 (s, 1 H), 6.80–6.83 (m, 2 H), 7.16–7.19 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) −0.05, 19.00, 21.67, 49.09, 51.65, 55.11, 78.74, 112.71, 128.82, 132.88, 158.80, 177.43; *m/z* (EI) 310.1604 (M$^+$, 1%, C$_{16}$H$_{26}$O$_4$Si requires 310.1601), 295 (5), 209 (100).

Methyl 2,2-dimethyl-3-trimethylsiloxy-3-phenylpropionate 5ad. Colorless powder, mp 79–81 °C (Found: C, 64.45; H, 8.54. C$_{15}$H$_{24}$O$_3$Si requires C, 64.24; H, 8.63%); ν_{max}(KBr)/cm^{-1} 2950–3050, 1760, 1100; δ_H(270 MHz; CDCl$_3$) 0.02 (s, 9 H), 1.05 (s, 3 H), 1.18 (s, 3 H), 3.73 (s, 3 H), 5.03 (s, 1 H), 7.33 (m, 5 H); δ_C(67.8 MHz; CDCl$_3$) −0.07, 19.01, 21.71, 49.02, 51.66, 79.10, 127.33, 127.37, 127.76, 140.74, 177.34; *m/z* (CI) 281.1563 (M$^+$ + 1, 7%, C$_{15}$H$_{25}$O$_3$Si requires 281.1573), 265 (51).

Methyl 2,2-dimethyl-3-trimethylsiloxy-3-(4-cyanophenyl)-butanoate 5ae. Viscous oil (Found: C, 63.75; H, 7.77. C$_{17}$H$_{25}$NO$_3$Si requires C, 63.91; H, 7.89%); ν_{max}(film)/cm^{-1} 2900–3050, 1720, 1050; δ_H(270 MHz; CDCl$_3$) 0.04 (s, 9 H), 1.04 (s, 3 H), 1.11 (s, 3 H), 1.76 (s, 3 H), 3.52 (s, 3 H), 7.39–7.43 (m, 2 H), 7.55–7.58 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) 2.05, 21.06, 21.58, 24.46, 51.45, 52.13, 80.07, 110.64, 118.85, 127.62, 130.85, 151.00, 175.85; *m/z* (CI) 320.1666 (M$^+$ + 1, 100%, C$_{17}$H$_{25}$NO$_3$Si requires 320.1682), 304 (21).

Methyl 2,2-dimethyl-3-trimethylsiloxy-3-(4-cyanophenyl)-3-phenylpropionate 5ah. Viscous oil (Found: C, 69.15; H, 6.98. C$_{22}$H$_{27}$NO$_3$Si requires C, 69.26; H, 7.13%); ν_{max}(film)/cm^{-1} 2900–3000, 2250, 1740, 1120; δ_H(270 MHz; CDCl$_3$) −0.16 (s, 9 H), 1.24 (s, 3 H), 1.28 (s, 3 H), 3.66 (s, 3 H), 7.27 (m, 5 H), 7.44–7.48 (m, 2 H), 7.53–7.56 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) 1.08, 21.85, 24.30, 50.44, 51.88, 85.66, 110.73, 118.87, 127.53, 127.66, 129.54, 130.35, 130.42, 144.19, 151.61, 177.50; *m/z* (CI) 382.1851 (M$^+$ + 1, 100%, C$_{22}$H$_{27}$NO$_3$Si requires 382.1839), 366 (25), 309 (31).

Methyl 2,2-dimethyl-3-triethylsiloxy-3-(2-naphthyl)propionate 5ba. Viscous oil (Found: C, 70.87; H, 8.65. C$_{22}$H$_{32}$O$_3$Si requires C, 70.92; H, 8.66%); ν_{max}(film)/cm^{-1} 2900–3000, 1750, 1080; δ_H(270 MHz; CDCl$_3$) 0.47 (q, *J* 7.5, 6 H), 0.85 (t, *J* 7.5, 9 H), 1.03 (s, 3 H), 1.21 (s, 3 H), 3.69 (s, 3 H), 5.19 (s, 1 H), 7.46–7.49 (m, 3 H), 7.71–7.85 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$) 4.71, 6.72, 19.27, 21.87, 49.38, 51.68, 79.26, 125.70, 125.84, 126.11, 126.69, 126.81, 127.58, 127.96, 132.63, 132.92, 138.58, 177.34; *m/z* (EI) 372.2122 (M$^+$, 1%, C$_{22}$H$_{32}$O$_3$Si requires 372.2121), 271 (100).

Methyl 2,2-dimethyl-3-triethylsiloxy-3-(4-cyanophenyl)-propionate 5bb. Viscous oil; ν_{max}(film)/cm^{-1} 2850–2950, 2200, 1730, 1000; δ_H(270 MHz; CDCl$_3$) 0.44 (q, *J* 8.1, 6 H), 0.82 (t, *J* 8.1, 9 H), 0.95 (s, 3 H), 1.14 (s, 3 H), 3.65 (s, 3 H), 5.03 (s, 1 H), 7.36–7.41 (m, 2 H), 7.56–7.60 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) 4.57, 6.62, 19.57, 21.17, 49.00, 51.83, 78.42, 111.30, 118.78, 128.41, 131.29, 146.61, 176.57; *m/z* (CI) 348.2011 (M$^+$ + 1, 100%, C$_{19}$H$_{30}$NO$_3$Si requires 348.1995), 318 (25).

Methyl 2,2-dimethyl-3-(dimethoxymethylsiloxy)-3-(2-naphthyl)propionate 5da. Viscous oil; ν_{max}(film)/cm^{-1} 2950–3000, 1740, 1080; δ_H(270 MHz; CDCl$_3$) −0.01 (s, 3 H), 1.07 (s, 3 H), 1.24 (s, 3 H), 2.17 (s, 3 H), 3.37 (s, 3 H), 3.39 (s, 3 H), 3.71 (s, 3 H), 5.39 (s, 1 H), 7.46–7.52 (m, 3 H), 7.75–7.85 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$) −7.81, 19.19, 21.85, 49.08, 50.35, 51.79, 79.01, 125.79, 125.89, 125.95, 126.69, 127.06, 127.57, 127.80, 132.63, 132.92, 137.48, 176.98; *m/z* (EI) 362.1544 (M$^+$, 2%, C$_{19}$H$_{26}$O$_5$Si requires 362.1550), 347 (1).

Methyl 2,2-dimethyl-3-(dimethoxymethylsiloxy)-3-(4-cyanophenyl)propionate 5db. Viscous oil (Found: C, 56.66; H, 7.32. C$_{16}$H$_{24}$NO$_5$Si requires C, 56.78; H, 7.15%); ν_{max}(film)/cm^{-1} 2900–3050, 2250, 1750, 1080; δ_H(270 MHz; CDCl$_3$) −0.01 (s, 3 H), 0.99 (s, 3 H), 1.16 (s, 3 H), 3.67 (s, 3 H), 5.23 (s, 1 H), 7.41–

7.44 (m, 2 H), 7.59–7.62 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) −7.98, 19.54, 21.15, 48.72, 50.80, 51.88, 78.10, 111.48, 118.67, 128.28, 131.40, 145.53, 176.23; *m/z* (EI) 338.1429 (M$^+$, 63%, 338.1424), 306 (100).

Methyl 2,2-dimethyl-3-hydroxy-3-(2-naphthyl)propionate 6a. Colorless powder, mp 112–115 °C (Found: C, 74.32; H, 7.04. C$_{16}$H$_{18}$O$_3$ requires C, 74.40; H, 7.02%); ν_{max}(KBr)/cm^{-1} 3350–3700, 2800–3100, 1735; δ_H(270 MHz; CDCl$_3$) 1.16 (s , 3 H), 1.20 (s, 3 H), 3.29 (d, *J* 3.8, 1 H, OH), 3.74 (s, 3 H), 5.07 (d, *J* 3.8, 1 H), 7.42–7.50 (m, 3 H), 7.75–7.86 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$) 19.12, 23.15, 47.89, 52.15, 78.78, 125.64, 125.91, 126.04, 126.67, 127.28, 127.57, 128.01, 132.79, 132.97, 137.45, 178.24; *m/z* (EI) 258.1241 (M$^+$, 18%, C$_{16}$H$_{18}$O$_3$ requires 258.1256), 157 (100), 129 (59), 102 (71).

Methyl 2,2-dimethyl-3-hydroxy-3-(4-cyanophenyl)propionate 6b. Colorless powder, mp 56–58 °C (Found: C, 66.76; H, 6.51. C$_{13}$H$_{15}$NO$_3$ requires C, 66.94; H, 6.48%); ν_{max}(KBr)/cm^{-1} 3350–3600, 2850–3000, 2250, 1720; δ_H(270 MHz; CDCl$_3$) 1.08 (s, 3 H), 1.10 (s, 3 H), 3.45 (d, *J* 4.1, 1 H, OH), 3.71 (s, 3 H), 4.93 (d, *J* 4.1, 1 H), 7.39–7.43 (m, 2 H), 7.58–7.61 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) 19.10, 22.61, 47.57, 52.26, 77.76, 114.43, 118.67, 128.37, 131.46, 145.30, 177.68; *m/z* (CI) 234.1151 (M$^+$ + 1, 100%, C$_{13}$H$_{16}$NO$_3$ requires 234.1131), 216 (55).

Methyl 2,2-dimethyl-3-hydroxy-3-(4-methoxyphenyl)propionate 6c. White powder, mp 83–85 °C (Found: C, 65.46; H, 7.58. C$_{13}$H$_{18}$O$_4$ requires C, 65.53; H, 7.61%); ν_{max}(KBr)cm^{-1} 3300–3600, 2900–3000, 1620; δ_H(270 MHz; CDCl$_3$) 1.09 (s, 3 H), 1.13 (s, 3 H), 3.00 (d, *J* 3.8, 1 H, OH), 3.72 (s, 3 H), 3.80 (s, 3 H), 4.85 (d, *J* 3.8, 1 H), 6.84–6.87 (m, 2 H), 7.20–7.26 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) 18.96, 22.95, 47.75, 52.04, 55.19, 78.26, 113.10, 128.68, 132.06, 159.08, 178.24; *m/z* (EI) 238.1228 (M$^+$, 4%, C$_{13}$H$_{18}$O$_4$ requires 238.1206), 221 (1), 207 (2), 137 (100).

Methyl 2,2-dimethyl-3-hydroxy-3-phenylpropionate 6d. White powder, mp 68–70 °C (Found: C, 69.12; H, 7.77. C$_{12}$H$_{16}$O$_3$ requires C, 69.21; H, 7.74%); ν_{max}(KBr)/cm^{-1} 3350–3600, 2950–3050, 1730; δ_H(270 MHz; CDCl$_3$) 1.11 (s, 3 H), 1.14 (s, 3 H), 3.05 (d, *J* 3.2, 1 H, OH), 3.73 (s, 3 H), 4.90 (d, *J* 3.2, 1 H), 7.20–7.35 (m, 5 H); δ_C(67.8 MHz; CDCl$_3$) 18.98, 23.04, 47.66, 52.10, 78.65, 127.62, 127.75 (2C), 139.87, 178.18; *m/z* (EI) 208.1104 (M$^+$, 2%, C$_{12}$H$_{16}$O$_3$ requires), 149 (2), 102 (100).

Methyl 2,2-dimethyl-3-hydroxy-3-(4-cyanophenyl)butanoate 6e. Viscous oil; ν_{max}(film)/cm^{-1} 3400–3650, 2950–3000, 2300, 1760; δ_H(270 MHz; CDCl$_3$) 1.12 (s, 3 H), 1.15 (s, 3 H), 1.60 (s, 3 H), 3.70 (s, 3 H), 4.58 (s, 1 H), 7.55–7.63 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$) 21.53, 21.62, 24.88, 50.18, 51.67, 76.95, 111.50, 118.81, 128.18, 130.98, 148.77, 178.13; *m/z* (CI) 248.1289 (M$^+$ + 1, 100%, C$_{14}$H$_{18}$NO$_3$ requires 248.1287), 230 (18).

Methyl 2,2-dimethyl-3-hydroxy-3-(3-cyanophenyl)butanoate 6f. Viscous oil (Found: C, 67.89; H, 6.88. C$_{14}$H$_{17}$NO$_3$ requires C, 68.00; H, 6.93%); ν_{max}(film)/cm^{-1} 3300–3600, 2850–3100, 2250, 1720; δ_H(270 MHz; CDCl$_3$) 1.11 (s, 3 H), 1.13 (s, 3 H), 1.60 (s, 3 H), 3.71 (s, 3 H), 4.60 (s, 1 H), 7.39–7.78 (m, 4 H); δ_C(67.8 MHz; CDCl$_3$) 21.53, 21.57, 24.89, 49.92, 52.40, 76.75, 111.50, 119.03, 128.10, 130.64, 131.07, 131.72, 144.85, 178.54; *m/z* (CI) 248.1284 (M$^+$ + 1, 88%, C$_{14}$H$_{18}$NO$_3$ requires 248.1287), 230 (76).

Methyl 2,2-dimethyl-3-hydroxy-3-phenylbutanoate 6g. Viscous oil (Found: C, 70.11; H, 8.05. C$_{13}$H$_{18}$O$_3$ requires C, 70.25; H, 8.16%); ν_{max}(film)/cm^{-1} 3400–3600, 2950–3050, 1700; δ_H(270 MHz; CDCl$_3$) 1.02 (s, 3 H), 1.03 (s, 3 H), 1.48 (s, 3 H), 3.54 (s, 3 H), 4.29 (s, 1 H), 7.11–7.20 (m, 3 H), 7.28–7.33 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) 21.57, 21.73, 24.39, 50.19, 52.11, 77.00, 126.86, 127.08, 127.22, 143.23, 178.94; *m/z* (EI) 222.1241 (M$^+$, 4%, C$_{13}$H$_{18}$O$_3$ requires 222.1256), 205 (9), 121 (100).

Methyl 2,2-dimethyl-3-hydroxy-3-(4-cyanophenyl)-3-phenylpropionate 6h. Viscous oil (Found: C, 73.56; H, 6.08; C$_{19}$H$_{19}$NO$_3$ requires C, 73.77; H, 6.19%); ν_{max}(film)cm^{-1} 3400–3550, 2900–3000, 2230, 1720; δ_H(270 MHz; CDCl$_3$) 1.32 (s,

3 H), 1.34 (s, 3 H), 3.75 (s, 3 H), 5.21 (s, 1 H), 7.27 (m, 5 H), 7.44–7.47 (m, 2 H), 7.54–7.57 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) 23.85, 23.96, 48.79, 52.74, 81.94, 110.84, 118.74, 127.42, 127.57, 128.28, 129.40, 130.98, 179.82; m/z (EI) 309.1352 (M$^+$, 1%, C$_{19}$H$_{19}$NO$_3$ requires 309.1365), 208 (61).

Methyl 2,2-dimethyl-3-hydroxy-3,3-diphenylpropionate 6i. Viscous oil (Found: C, 75.98; H, 7.08. C$_{18}$H$_{20}$O$_3$ requires C, 76.03; H, 7.09%); ν_{max}(film)/cm^{-1} 3400–3600, 2900–3100, 1740; δ_H(270 MHz; CDCl$_3$) 1.34 (s, 6 H), 3.73 (s, 3 H), 5.10 (s, 1 H), 7.22–7.34 (m, 10 H); δ_C(67.8 MHz; CDCl$_3$) 23.99 (2C), 48.91, 52.51, 82.05, 126.88, 127.03, 127.17, 128.55, 180.32; m/z (EI) 284.1413 (M$^+$, 0.3%, C$_{18}$H$_{20}$O$_3$ requires 284.1413), 208 (2), 253 (1), 183 (100).

1,2-Bis(trimethylsiloxy)-1,2-di(2-naphthyl)ethane (1 : 1 diastereomeric mixtures of 7a). White powder, mp 151–153 °C (Found: C, 73.26; H, 7.51. C$_{28}$H$_{34}$O$_2$Si$_2$ requires C, 73.31; H, 7.47%); ν_{max}(KBr)/cm^{-1} 1250, 1100, 840, 750; δ_H(270 MHz; CDCl$_3$) −0.29 (s, 18 H), −0.05 (s, 18 H), 4.76 (s, 2 H), 4.96 (s, 2 H), 7.24–7.28 (m, 4 H), 7.41–7.50 (m, 8 H), 7.59–7.66 (m, 4 H), 7.72–7.88 (m, 12 H); δ_C(67.8 MHz; CDCl$_3$) 0.00, 0.41, 79.89, 80.14, 125.36, 125.39, 125.55, 125.64, 125.71, 125.97, 126.27, 126.86, 127.02, 127.50, 127.60, 127.94, 132.74, 132.94, 133.00, 139.39, 140.47; m/z (EI) 458.2096 (M$^+$, 0.2%, C$_{28}$H$_{34}$O$_2$Si$_2$ requires 458.2098), 443 (2), 229 (100).

2,3-Bis(4-cyanophenyl)-2,3-bis(trimethylsiloxy)butane (diastereomeric mixture of 7e). Viscous oil (Found: C, 66.01; H, 7.32; N, 6.48. C$_{24}$H$_{32}$N$_2$O$_2$Si$_2$ requires C, 66.01; H, 7.39; N, 6.42%); ν_{max}(film)/cm^{-1} 2980, 1050; δ_H(270 MHz; CDCl$_3$) −0.13 (s, 18 H), 0.06 (s, 18 H), 1.36 (s, 6 H), 1.78 (s, 6 H), 6.91–6.94 (m, 2 H), 7.31–7.34 (m, 8 H), 7.58–7.65 (m, 8 H); δ_C(67.8 MHz; CDCl$_3$) 1.91, 2.07, 23.18, 23.70, 81.10, 110.60, 128.21, 128.66, 129.96, 130.71, 150.94; m/z (CI) 437.2079 (M$^+$ + 1, 100%, C$_{24}$H$_{32}$N$_2$O$_2$Si$_2$ requires 437.2080), 421 (6).

1-(4-Cyanophenyl)-1-trimethylsiloxyethane 8e. Viscous oil (Found: C, 65.77; H, 7.88. C$_{12}$H$_{17}$NOSi requires C, 65.71; H, 7.81%); ν_{max}(film)/cm^{-1} 2900–3000, 2250, 1100; δ_H(270 MHz; CDCl$_3$) 0.09 (s, 9 H), 1.41 (d, J 6.4, 3 H), 4.88 (q, J 6.4, 1 H), 7.42–7.45 (m, 2 H), 7.60–7.63 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) −0.02, 26.70, 69.88, 110.57, 119.03, 125.97, 132.13, 151.95; m/z (EI) 219.1089 (M$^+$, 1%, C$_{12}$H$_{17}$NOSi requires 219.1107), 204 (100).

(4-Cyanophenyl)(phenyl)trimethylsiloxymethane 8h. Viscous oil (Found: C, 72.45; H, 6.15. C$_{17}$H$_{19}$NOSi requires C, 72.55; H, 6.09%); ν_{max}(film)/cm^{-1} 3300–3600, 2950–3050, 1720; δ_H(270 MHz; CDCl$_3$) 0.07 (s, 9 H), 5.76 (s, 1 H), 7.30 (s, 5 H), 7.45–7.48 (m, 2 H), 7.52–7.60 (m, 2 H); δ_C(67.8 MHz; CDCl$_3$) 0.00, 75.90, 110.69, 118.92, 126.52, 126.86, 127.67, 128.48, 132.07, 143.45, 150.19; m/z (EI) 281.1237 (M$^+$, 49%, C$_{17}$H$_{19}$NOSi requires 281.1236), 266 (79).

Acknowledgements

References

1 (*a*) S. L. Schreiber, A. H. Hoveyda and H. Wu, *J. Am. Chem. Soc.*, 1983, **105**, 660; (*b*) S. L. Schreiber and K. Satake, *J. Am. Chem. Soc.*, 1983, **105**, 6723; (*c*) J. A. Porco and S. L. Schreiber, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon Press, New York, 1991, vol. 5, pp. 168–188; (*d*) A. Zamojeski and S. Jarosz, *Tetrahedron Lett.*, 1982, **38**, 1447; (*e*) M. Abe, M. Ikeda and M. Nojima, *J. Chem. Soc., Perkin Trans. 1*, following paper in this issue.

2 For review, see; (*a*) A. G. Griesbeck, in *Organic Photochemistry and Photobiology*, eds. W. M. Horspool and P. Song, CRC Press, New York, 1995, pp. 522–535; (*b*) C. Rivas and F. Vargas, in *Organic Photochemistry and Photobiology*, eds. W. M. Horspool and P. Song, CRC Press, New York, 1995, pp. 536–549; (*c*) A. G. Griesbeck, in *Organic Photochemistry and Photobiology*, eds. W. M. Horspool and P. Song, CRC Press, New York, 1995, pp. 550–559; (*d*) H. A. J. Carless, in *Organic Photochemistry and Photobiology*, eds. W. M. Horspool and P. Song, CRC Press, New York, 1995, pp. 560–569; (*e*) H. A. J. Carless, in *Synthetic Organic Photochemistry*, ed. W. M. Horspool, Plenum Press, New York, 1984, pp. 425–488; (*f*) N. J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Co., Inc., Menlo Park, 1978, pp. 432–452.

3 (*a*) S. H. Schroeter and C. M. Orlando, *J. Org. Chem.*, 1969, **34**, 1181; (*b*) N. J. Turro and P. A. Wriede, *J. Am. Chem. Soc.*, 1970, **92**, 320; (*c*) S. H. Schroeter, *J. Chem. Soc., Chem Commun.*, 1969, 12; (*d*) T. Bach, *Tetrahedron Lett.*, 1991, **32**, 7037; (*e*) H. A. Carless and D. J. Haywood, *J. Chem. Soc., Chem. Commun.*, 1980, 1067; (*f*) A. G. Griesbeck, S. Stadtmüller, *J. Am. Chem. Soc.*, 1990, **112**, 1281.

4 S. Fukuzumi, M. Fujita, J. Otera and Y. Fujita, *J. Am. Chem. Soc.*, 1992, **114**, 10 271.

5 M. Abe, M. Ikeda, Y. Shirodai and M. Nojima, *Tetrahedron Lett.*, 1996, **37**, 5901.

6 S. Fukuzumi, T. Okamoto and J. Otera, *J. Am. Chem. Soc.*, 1994, **116**, 5503.

7 S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, Inc., New York, 1993, p. 75.

8 J. Mattay and J. Runsink, *J. Org. Chem.*, 1985, **50**, 2815.

9 C. G. Swain, M. S. Swain, A. L. Powell and S. Alunni, *J. Am. Chem. Soc.*, 1983, **105**, 502.

10 A. Takuwa, J. Shiiji and Y. Nishigaichi, *Tetrahedron Lett.*, 1993, **34**, 3457.

11 This work; see Experimental section.

12 (*a*) A. Weller, *Pure Appl. Chem.*, 1968, **16**, 115; (*b*) D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.

13 P. J. Wagner, R. J. Truman, A. E. Puchalski and R. Wake, *J. Am. Chem. Soc.*, 1986, **108**, 7727.

14 (*a*) A. G. Myers and K. L. Widdowson, *J. Am. Chem. Soc.*, 1990, **112**, 9672; (*b*) A. G. Myers, K. L. Widdowson and P. J. Kukkola, *J. Am. Chem. Soc.*, 1992, **114**, 2765; (*c*) A. G. Myers, S. E. Kephart and H. Chen, *J. Am. Chem. Soc.*, 1992, **114**, 7922; (*d*) P. M. Bodnar, W. S. Palmer, J. T. Shaw, J. H. Smitrovich, J. D. Sonnenburg, A. L. Presley and K. A. Woerpel, *J. Am. Chem. Soc.*, 1995, **117**, 10 575; (*e*) S. E. Denmark, S. B. D. Winter, X. Su and K.-T. Wong, *J. Am. Chem. Soc.*, 1996, **118**, 7404.

15 EDA complex of silyl enol ether, see R. Rathore and J. K. Kochi, *J. Org. Chem.*, 1996, **61**, 627.

16 (*a*) J. P. Dinnocenzo, S. Farid, J. I. Goodman, I. R. Gold, W. P. Todd and S. L. Mattes, *J. Am. Chem. Soc.*, 1989, **111**, 8973; (*b*) K. P. Dockery, J. P. Dinnocenzo, S. Farid, J. L. Goodman and W. P. Todd, *J. Am. Chem. Soc.*, 1997, **119**, 1876.

17 (*a*) J. Mattay, J. Gersdorf and K. Buchkremer, *Chem. Ber.*, 1987, **120**, 307; (*b*) J. Gersdorf, J. Mattay and H. Görner, *J. Am. Chem. Soc.*, 1987, **109**, 1203; (*c*) J. Santamaria, in *Photoinduced Electron Transfer*, eds. M. A. Fox and M. Chanon, Elsevier, New York, 1988, Part C, pp. 483–540.

18 R. E. Ireland, P. Wipf and J. D. Armstrong, *J. Org. Chem.*, 1991, **56**, 650.

19 (*a*) L. Miller, G. D. Nordblom and E. A. Mayeda, *J. Org. Chem.*, 1972, **37**, 916; (*b*) K. Yoshida, in *Electrooxidation in Organic Chemistry*, Krieger Publishing Company, Malabar, FL, 1993, pp. 43–44.

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