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A New Protocol for the Consecutive α- and β-Activation of Propiolates towards Electrophiles, Involving Conjugate Addition of Tertiary Amines and Intramolecular Silyl Migration

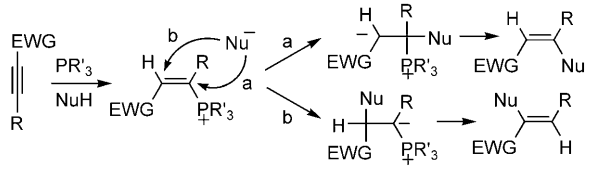
Yuji Matsuya, Kousuke Hayashi, and Hideo Nemoto*[a]

Abstract: Herein, we present a novel approach for the consecutive α- and β-activation of conjugated alkynes and demonstrate the application of this methodology towards the C–C bond-forming reactions of propiolates. This new concept is based on the 1,4-addition of a tertiary amine to a conjugated alkyne, followed by an aldol-type addition to an aldehyde and subsequent intramolecular silyl migration. This sequential process is generally applicable for 3-trimethylsilylpropiolates. The combination of methyl 3-trimethylsilylpropiolate, 1,4-diazobicyclo[2.2.2]octane (DABCO), and aromatic aldehydes brought about domino-type C–C bond formations to afford highly functionalized olefins as the major products. On the other hand, aliphatic aldehydes, including the sterically demanding aromatic aldehyde, 2,6-dimethylbenzaldehyde, produced alkyne derivatives as the sole products from the reaction, presumably, by the reaction pathway common to the first cases. The intramolecular version of the reaction was successfully applied to the cyclization of trimethylsilylpropiolic esters derived from salicylaldehydes, leading to a new formylcoumarin synthesis. Studies of the reaction mechanisms are also described.

Keywords: alkynes · domino reactions · formylcoumarins · silyl-migration · tertiary amines

Introduction

Alkynes conjugated with an electron-withdrawing group or groups (EWG) have been recognized as very versatile tools in organic synthesis, because of their ability to undergo a variety of carbon–carbon or carbon–heteroatom bond-forming reactions.[1] The ability of these compounds to act as Michael acceptors towards nucleophiles has been well-documented,[2] and this type of conjugate addition reaction has often been catalyzed by trialkylphosphines or tertiary amines.[3] In particular cases, the phosphine-catalyzed system has been reported to bring about "umpolung", which facilitates an abnormal nucleophilic attack at the α-position to form a phosphonium ylide. This unique reaction pattern has been applied to the synthesis of dehydroamino acids[4] and several substituted furan derivatives.[5] Consequently, the catalytic activation of conjugated alkynes toward nucleophiles can be achieved at both the α- and β-positions depending upon the reaction conditions (Scheme 1).



Scheme 1. Phosphine-catalyzed α- or β-activation of alkynes towards nucleophiles.

Anionic β-activation of terminal alkynes has been conventionally achieved by direct deprotonation; this method takes advantage of the relatively low pK_a value of the proton attached to the sp carbon. However, the formation of these acetylides requires the use of a stoichiometric amount of a strong metal base.[1,6] Recently, methods for the mild and metal-free catalytic β-activation of conjugated terminal alkynes by indirect deprotonation using tertiary amines or phosphines have been reported; these methods provide efficient syntheses for propargylic alcohol,[7] 1,3-dioxolane,[7] and tetronic acid derivatives.[8] Anionic α-activation of conjugated alkynes is based upon the formation of an allene–

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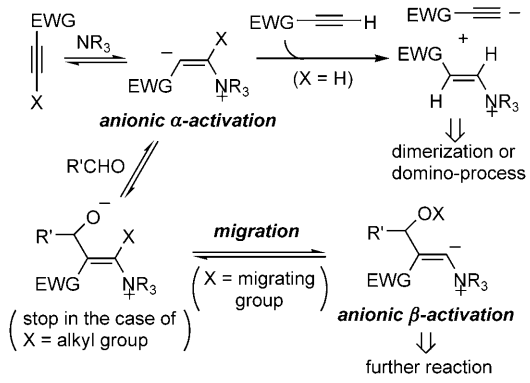
enolate, which is produced either by the Michael-type addition of particular nucleophiles[9] or by hydrometalation[10] followed by reaction with electrophiles. A Lewis acid mediated Chalcogeno–Morita–Baylis–Hillman reaction,[11] an amine-catalyzed reaction of acetylenedicarboxylates with aldehydes or imines,[12] and a phosphine-assisted intramolecular cycloaddition reaction[13] have been also reported. Thus, various activation methods are applicable for conjugated alkynes, increasing their versatility as a synthetic tool.

As mentioned previously, treatment of conjugated terminal alkynes with tertiary amines brings about self-dimerization[14] or a domino process in the presence of aldehydes under suitable reaction conditions.[7] Since these reactions are triggered by anionic β-activation through indirect deprotonation of the terminal alkynes, the introduction of an appropriate substituent at the β-position would prevent such reactions and enable simple α-activation to occur, by the conjugate addition of a tertiary amine. Although such amine-catalyzed processes, including subsequent reactions with aldehydes, relate to the Morita–Baylis–Hillman reaction of conjugated alkenes, which involves β-elimination for regeneration of the amine catalysts,[15] conjugated alkynes cannot participate in the β-elimination process owing to the lack of an α-proton. However, we envisaged that β-activation might be possible, provided that the substituent at the β-position was able to migrate onto the alkoxide group in an intramolecular fashion. If this did prove possible, novel consecutive α- and β-activation of conjugated alkynes toward electrophiles could be realized (Scheme 2).



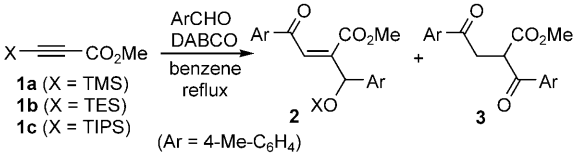
Scheme 2. Our new concept for the consecutive α- and β- activation of alkynes towards electrophiles.

Based on this concept, we have found a new domino-type C–C bond forming reaction between propiolates and aldehydes, which is mediated by tertiary amines (metal-free and traceless activators).[16] Herein we describe, details of our studies into these reactions, and their application towards the synthesis of formylcoumarin.

Results and Discussion

The intermolecular reaction: After taking both the silyl group's migrating ability and its affinity to oxygen into consideration, we chose 3-silylated propiolates as potential substrates for the reaction (Scheme 2) The simplest one, methyl 3-trimethylsilylpropiolate (**1a**) was treated with the tertiary amine 1,4-diazobicyclo[2.2.2]octane (DABCO) in refluxing benzene. After five hours under these conditions the propiolate **1a** was completely recovered (Table 1, entry 1). In the

Table 1. Reaction of silylated propiolates **1** with DABCO in the presence (or absence) of an aromatic aldehyde.[a]

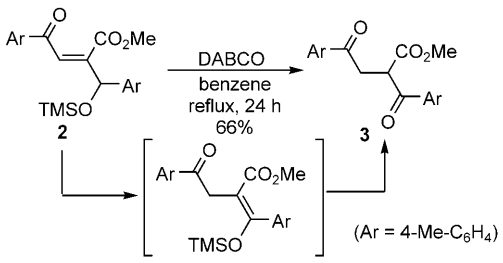


Entry	Substrate	t [h]	Yield [%][b]	Ratio (**2**:**3**)
1[c]	**1a**	5	complete recovery of **1a**	–
2	**1a**	0.666	78	78:22
3	**1b**	18	41	37:63
4	**1c**	24	no reaction	–

[a] The reaction was carried out using the selected aldehyde (0.5 mmol), propiolate (1 mmol), and DABCO (1 mmol) under an Ar atmosphere. [b] Isolated yields (**2** + **3**) based on the aldehyde. [c] In the absence of aldehyde (control experiment).

presence of an aromatic aldehyde, however, rapid consumption of the aldehyde was observed and two products were produced (entry 2); these were separated and purified by column chromatography. The NMR spectra of these products clearly showed the presence of one methyl ester and two aromatic constituents, suggesting that the products were composed of the propiolate and the aldehyde in a 1:2 manner. The structure of the major product **2** was confirmed by the spectral data, which included a 2D NMR spectrum,[17] and the geometry of the olefin was determined by an NOE experiment between the olefinic proton and the methyne proton. More sterically demanding substrates (**1b** and **1c**) were also utilized, but a considerable decrease in the reaction rate was observed in these cases as shown by entries 3 and 4. Although **1b** produced the corresponding products **2** and **3**, the product ratio was reversed as a result of the prolonged reaction time.

The experiment shown in Scheme 3 verified that product **3** arose from product **2**. Exposure of the isolated sample of

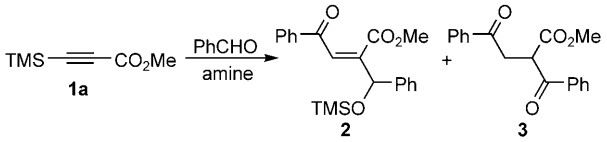


Scheme 3. Conversion of product **2** into product **3**.

compound **2** to DABCO in refluxing benzene resulted in its gradual conversion to compound **3**. This transformation can be explained by base-induced isomerization of the double bond followed by hydrolysis of the resulting silyl enol ether. Thus, this new reaction, involving the simultaneous formation of two C–C bonds, potentially provides a new general method for preparing multifunctionalized olefins **2** by controlling the reaction time.

With these findings in our hands, we focused on optimizing the reaction conditions. Various trigger nucleophiles and solvents were tested with the propiolate **1a** and benzaldehyde (Table 2). As a nucleophile, triethylamine was inert under the reaction conditions and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) produced a poor result (entries 1 and 2). Although quinuclidine and 3-quinuclidinol afforded moderate to good yields, the saturated product **3** was also formed as a result of the relatively slow reaction rate (entries 3 and 4). DABCO, with its bicyclo[2.2.2]octane skeleton, was the most promising nucleophile among the tertiary amines (entry 5). Heating was found to be required for sufficient progress of the reaction (entry 6). By using 10 mol% of DABCO (entry 7), a comparable yield to entry 5 was obtained, implying that DABCO participated in the reaction in a catalytic fashion; although a prolonged reaction time caused a decrease in the amount of the olefin product **2** isolated. Several other solvents such as THF, 1,2-dichloroethane, and DMF were also utilized, but were found to be ineffective for the reaction (entries 8–10).

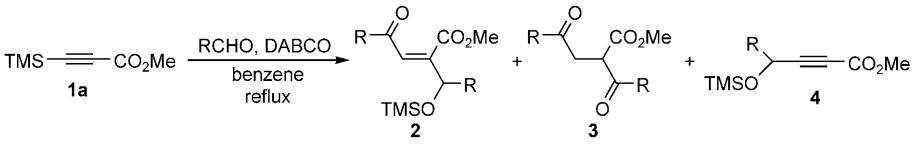
Table 2. Investigation into the optimum reaction conditions required for the synthesis of **2**.



Entry	Amine	Solvent	Conditions	Yield [%]	Ratio (**2**:**3**)
1	Et_3N	benzene	reflux, 2 h	0	–
2	DBU	benzene	reflux, 2 h	11	100:0
3	quinuclidine	benzene	reflux, 3 h	68	21:79
4	3-quinuclidinol	benzene	reflux, 2 h	43	37:63
5	DABCO	benzene	reflux, 40 min	73	74:26
6	DABCO	benzene	RT, 24 h	0	–
7	DABCO[a]	benzene	reflux, 4 h	62	63:37
8	DABCO	THF	reflux, 40 min	24	100:0
9	DABCO	DCE[b]	reflux, 40 min	4	100:0
10	DABCO	DMF	RT, 2 h	10	100:0

[a] A catalytic amount (10 mol% to aldehyde) of DABCO was used. All other experiments were carried out using 2 equiv of amine. [b] 1,2-dichloroethane.

Table 3. Reaction of propiolate **1a** with various aldehydes under the optimum conditions.[a]



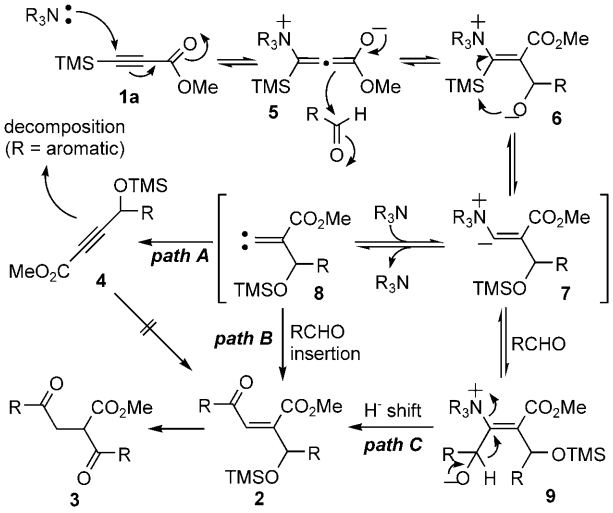
Entry		R	*t* [min]	Yield [%] of (**2**+**3**)	Ratio (**2**:**3**)[b]	Yield [%] of **4**
1	**a**	Ph	40	73	74:26	0
2	**b**	2-Me-C_6H_4	40	56	100:0	0
3	**c**	3-Me-C_6H_4	50	64	78:22	0
4	**d**	4-Me-C_6H_4	40	78	78:22	0
5	**e**	2-MeO-C_6H_4	40	quant.[c]	100:0	0
6	**f**	3-MeO-C_6H_4	45	50	76:24	0
7	**g**	4-MeO-C_6H_4	50	83	83:17	0
8	**h**	2-Br-4,5-$(MeO)_2$-C_6H_2	30	51	100:0	0
9	**i**	1-naphthyl	120	44	100:0	0
10	**j**	2-naphthyl	30	72	63:37	0
11	**k**	4-Cl-C_6H_4	40	43	37:63	0
12	**l**	4-NO_2-C_6H_4	120	0[d]	–	0[d]
13	**m**	pentafluorophenyl	120	0[d]	–	0[d]
14	**n**	2,6-$(Me)_2$-C_6H_3	60	0	–	73
15	**o**	*n*Pr	50	0	–	63
16	**p**	*i*Pr	40	0	–	78
17	**q**	*t*Bu	30	0	–	94

[a] The reactions were carried out using the selected aldehyde (0.5 mmol), propiolate (1 mmol), and DABCO (1 mmol) in benzene (1 mL) under an Ar atmosphere. [b] These products could be separated by column chromatography. [c] Isolated in a desilylated form. [d] Afforded a complex mixture.

For the next step in our study, these reactions were performed under optimum conditions with a variety of different aldehydes in order to evaluate the generality of the synthetic process. Various aromatic aldehydes were observed to proceed in a similar manner through the successive C–C bond-forming processes, yielding highly functionalized olefins **2** as a major products with exclusive stereoselectivity (Table 3, entries 1–10). One notable feature was that *ortho*-substituted benzaldehydes did not produce compound **3**, presumably because of the inefficiency of the isomerization due to steric repulsion between the *ortho* and allylic substituents. 4-Chlorobenzaldehyde, a slightly electron-deficient substrate, afforded predominantly product **3k** on a comparable timescale (entry 11), probably due to the higher acidity of the benzylic methyne proton in the initial product **2k**. Highly electron-deficient aromatic aldehydes such as 4-nitro and perfluoro derivatives did not produce any of the products already identified, despite the fact that the aldehydes were completely consumed in the reaction (entries 12 and 13). A notable change in the course of the reaction was observed upon the use of 2,6-dimethylbenzaldehyde (entry 14). The products **2n** and **3n** were not detected in the reaction, and instead the alkyne **4n** was produced as the sole product from the reaction in high yield. Similarly, aliphatic aldehydes were found to afford only the alkyne products **4o–q** (entries 15–17). This dramatic change, which

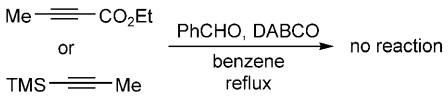
depends upon the structure of aldehydes, has provided us with a greater insight into the reaction mechanism (vide infra).

We propose the following reaction mechanism (Scheme 4) for this new domino-type process on the basis of several of our experimental results. The reaction of ethyl 2-butynoate



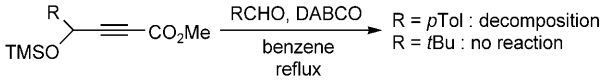
Scheme 4. Proposed reaction mechanism.

or 1-trimethylsilyl-1-propyne with benzaldehyde and DABCO under identical conditions resulted in the complete recovery of all of the substrates (Scheme 5). This fact indi-



Scheme 5. Other alkyne reactions.

cates that both the TMS and electron-withdrawing carbonyl groups are essential for the progress of the reaction. Thus, the sequence starting with the 1,4-addition of the trigger nucleophile, followed by an aldol-type addition to the aldehyde and subsequent silyl migration is a plausible proposal for the initial process. This process also includes the consecutive α- and β-activation of the propiolate as expected. The ammonium ylide intermediate **7**, thus formed, possibly equilibrates with the α-silyloxy alkylidenecarbene **8**,[18] which arises from a net α-elimination of the tertiary amine. With regard to the ammonium ylide/alkylidenecarbene equilibrium, it has been reported that the large polarization value and the high dissociation energy barrier of the ammonium ylide, estimated by the MOPAC program with 2-propylidenecarbene and trimethylamine as simplified model molecules, make the ylide form much more stable than the corresponding carbene.[19] Accordingly, we presumed that the equilibrium between **7** and **8** lay mostly to the ylide form **7**, although the possibility that the functional groups attached to the olefin carbon may have affected the equilibrium could not be ruled out. However, the alkylidenecarbene **8** seems to be an important potential precursor for the alkyne products **4**, as such 1,2-rearrangement reactions (path A) are well-established processes and have significant precedents.[20,21] When the alkyne **4d** (R = *p*Tol)[22] was reacted with *p*-tolualdehyde and DABCO, immediate decomposition occurred to form a complicated mixture, the NMR spectrum of which showed no existence of the olefin product **2d**; whereas the alkyne **4q** (R = *t*Bu) was recovered unchanged under the same conditions (Scheme 6). These results clearly

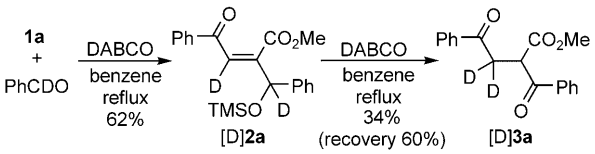


Scheme 6. Reactivity of alkynes **4d** and **4q**.

suggest that the alkyne **4** is not a precursor of the olefin **2**, but is a dead end product of the reaction, although the stability of this compound depends upon the nature of the substituent R. One possible explanation to account for the formation of the olefin **2** is that a direct C–H insertion of the aldehyde onto the alkylidenecarbene **8** (path B) occurs. In general, the reaction of carbenes and aldehydes has been reported to result in the formation of oxirane or dioxorane derivatives via carbonium ylides;[23] this is also the case for alkylidenecarbenes,[20] and such direct insertion processes of aldehydes have not yet been observed. In addition, we can provide no explanation for the complete change of the reaction course (path A or B), via the common carbene intermediate **8**, with the structure of the aldehydes. It is not clear from the available data whether path B is a good model for the present reaction or not. Thus, we propose the more plausible reaction pathway, path C, which includes nucleophilic addition of the anion center of the ylide **7** to the aldehyde, followed by an intramolecular 1,2-hydride shift to produce the olefin **2**. Path C would have an advantage over path A, provided that the equilibrium between **7** and **8** is fully biased towards the ylide form **7**, and the hydride shift would result in the extrusion of the tertiary amine through an addition–elimination process in a 1,4-fashion. It is important to note that we regard all of the transformations mentioned above (from **1a** to **8** or **9**) as a sequence of reversible processes, as this assumption allows us to rationalize that the susceptibility of the intermediate **9** to the irreversible 1,2-hydride shift may control the direction of the reaction towards either product **2** or **4**, respectively. As shown in Table 3, relatively electron-rich aromatic aldehydes afforded product **2** (and in some cases product **3**) in good overall yields, whereas highly electron-poor aldehydes produced neither products **2** or **4** and instead afforded complicated mixtures. These results imply that the former substrates have considerably faster reaction rates for the hydride shift compared to the latter, presumably, because the transition states are effectively stabilized by donation from the π-elec-

tron system of the p orbital on the aromatic ring into the σ^*_{C-H} orbital at the benzylic position. Otherwise, especially in the case of the latter substrates, the reaction would favor path A producing the alkyne **4**, which may decompose due to its inherent instability under the reaction conditions to afford the complex mixtures observed. The fact that the aliphatic aldehydes produced alkynes **4** exclusively might also have been explained in the same manner, except that the alkynes **4**, thus formed, are stable under the reaction conditions. In the case of 2,6-dimethylbenzaldehyde, exclusive formation of **4** was also observed;[24] this can be rationalized by postulating that the effective π–σ^* interaction in the hydride-shift transition state may have been impeded by diminished coplanarity of the aromatic plane with the plane of the conjugated olefin (hydride acceptor); this would be enforced by the steric repulsion of the two *ortho*-substituents. Alternatively, there is a possibility that the intermediate **7** could not react with the sterically congested 2,6-dimethylbenzaldehyde to afford the alkyne product **4** through path A.

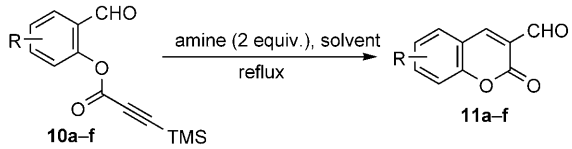
Recently, an acylation reaction of a vinylselenonium ylide with an aromatic aldehyde has been reported.[25] The overall process involved in this reaction is similar to the last step of our reaction (from **7** to **2**). The mechanism proposed in this report involves the intermediacy of an allenoate anion originating from a betaine (corresponding to **9**) produced by β-elimination of selenide through base-induced deprotonation. This mechanism was deduced from the observation that no deuterium was incorporated in the product of the reaction when using benz[D]aldehyde as a substrate. However, when our reaction was performed using benz[D]aldehyde, complete incorporation of deuterium into the products **2** and **3** was observed (Scheme 7). This deuterium was entirely retained in product **2** even in the presence of an excess amount of a proton source, such as MeOH, in the reaction medium. In addition, the use of electron-rich aromatic aldehydes has been reported to decrease the acylation efficiency of the vinylselenonium ylide, which is opposite to the tendency found in our reaction. These contrasts strongly indicate that our reaction involves the *hydride shift* mechanism, instead of *deprotonation*.



Scheme 7. Experiments using benz[D]aldehyde.

The intramolecular reaction: Following studies on this domino-type reaction focused on the intramolecular variation. For this purpose, trimethylsilylpropiolic esters derived from salicylaldehydes were chosen as substrates on the basis of their ready availability and the suitable distance between the two reaction sites for the cyclization, the formyl group and the alkyne part. The substrates (**10a–f**) were prepared from substituted salicylaldehydes and 3-trimethylsilylpropiolic acid in moderate to good yields (52–88%) using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) and 4-dimethylaminopyridine (DMAP).[26] When the parent substrate **10a** was allowed to react with two equivalents of DABCO in refluxing benzene, the cyclization produced the 3-formylcoumarin **11a** in a 63% yield (Table 4, entry 1). Unlike the intermolecular reaction, when other solvents were used for the reaction comparable yields were obtained (entries 2–4), with the combination of THF and quinuclidine bringing about a superior result with regards to reaction rate (entry 5). The results of the coumarin-forming reactions for variously substituted compounds under optimum conditions are summarized in Table 4 (entries 5–10). In all cases the 3-formylcoumarin derivatives were produced in moderate to good yields with the exception of the chloro-substituted compound **10f**, which afforded product **11f** in a low yield as a result of the competitive cleavage of the ester bond.

Table 4. Formylcoumarin-forming reactions.



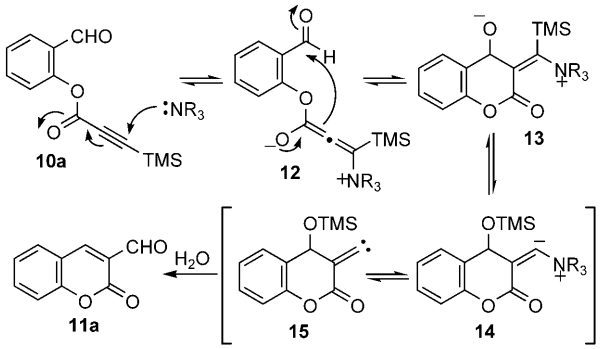
Entry		R[a]	Amine	Solvent	t [h]	Yield [%][b]
1	**a**	H	DABCO	benzene	8	63
2	**a**	H	DABCO	DCE[c]	5	62
3	**a**	H	DABCO	DMF[d]	0.5	39
4	**a**	H	DABCO	THF	3	64
5	**a**	H	quinuclidine	THF	0.666	64
6	**b**	5-Me	DABCO	THF	2.5	81
7	**c**	5-MeO	DABCO	benzene	7	47
8	**d**	4-MeO	DABCO	THF	1	46
9	**e**	5,6-benzo	quinuclidine	THF	0.333	50
10	**f**	5-Cl	DABCO	THF	1	26

[a] The numbering on the aromatic ring starts from the carbon bearing the formyl group and proceeds clockwise. [b] Isolated yields. [c] 1,2-Dichloroethane. [d] The reaction was performed at 80 °C.

The coumarin nucleus is widely found in nature, and biologically significant activities of coumarin derivatives have made the development of new methodologies for the mild and concise construction of the coumarin nucleus important.[27] Although there are well-established methods based on Pechmann condensation or Knoevenagel condensation, the harsh reaction conditions involved limit the scope of these reactions and the functional group compatibility. Recent reports on coumarin formation utilizing the Morita–Baylis–Hillman reactions of salicylaldehydes with acrylates suffer from a lack of regiocontrol in the cyclization step (coumarins or chromenes) and produce low yields of target compounds.[28] In particular, efficient approaches for the syn-

thesis of 3-formylcoumarins are quite limited.[29] The reaction described here may provide a new and general methodology for the synthesis of 3-formylcoumarins.

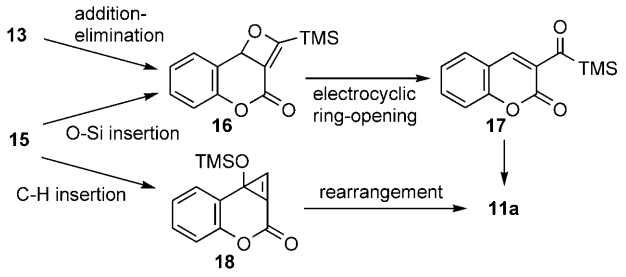
A similar reaction mechanism to that depicted in Scheme 4 is proposed for the coumarin-forming reaction (Scheme 8). After the cyclization, subsequent silyl migration



Scheme 8. A plausible reaction mechanism for the formation of the formylcoumarins.

gives the ammonium ylide **14** (or the carbene **15**), which reacts with water to form the formylcoumarin concomitant with silanol elimination. The ylide **14** did not participate in the reaction with another aldehyde, even when an equimolar amount of benzaldehyde was present in the reaction mixture. The decreased flexibility in the conformation of the ylide **14** compared to ylide **7** is the most likely explanation for this distinct difference between the intra- and the intermolecular reactions.

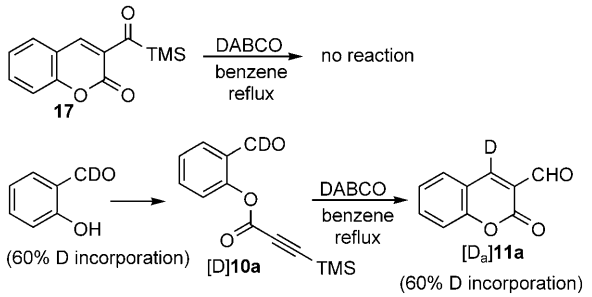
Other possible reaction pathways leading to the formylcoumarins **11** are illustrated in Scheme 9. A bond-insertion process is one of the principal features of alkylidenecarbene



Scheme 9. Alternative reaction pathways for formylcoumarin formation.

reactions, and is a feature that is attributed to their strongly electrophilic nature.[20] For example, the O–Si insertion reactions of several β-silyloxy alkylidenecarbenes to form silylated dihydrofurans has been reported.[18] If a similar insertion reaction occurs in our case, the alkylidenecarbene **15** may be transformed into an oxetene intermediate **16**, which can be also derived from the betaine **13** by an addition–elimination process. Electrocyclic ring-opening of the oxetene **16** and subsequent transformation would afford the formylcoumarin **11** via the acylsilane **17**.[30] Additionally, there is a possibility that the products **11a–f** arise from an intramolecular C–H insertion reaction (formation of **18**) followed by a rearrangement, as the intramolecular C–H insertion of alkylidenecarbenes is a well-known process.[31]

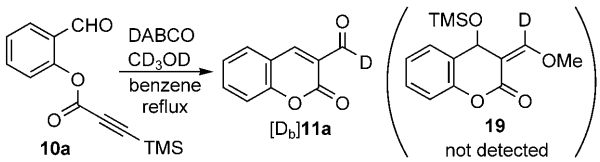
However, these possibilities were excluded by the following experiments. Firstly, the acylsilane **17**[32] was exposed to the coumarin forming conditions (DABCO, benzene, reflux), but was recovered unchanged by the reaction conditions (Scheme 10). Secondly, deuterated salicylaldehyde[33]



Scheme 10. Experiments conducted to clarify the reaction mechanism of formylcoumarin formation.

was transformed into the substrate [D]**10a** (60% D-incorporation), which upon treatment with DABCO in refluxing benzene generated the formylcoumarin [D_a]**11a**, the deuterium in which was retained on the same carbon as the substrate. These results unambiguously verified that the formylcoumarin-forming reaction did not involve the pathways shown in Scheme 9.

The fact that the formyl hydrogen in the products **11a–f** originated from an external proton sources was confirmed by the experiment shown in Scheme 11. When the reaction

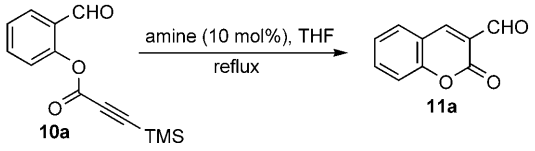


Scheme 11. Coumarin-forming reaction in the presence of [D_4]MeOH.

was performed in the presence of a small amount of [D_4]MeOH, the deuterium was incorporated into the formyl group of the product.[34] Although we initially expected that a deuterated enol ether product **19** would be formed, we could not trap it because of its immediate hydrolysis in the workup process. The mechanism above suggests that water is essential to regenerate the tertiary amine. In fact, the reaction using 10 mol% of the amine was very sluggish in the absence of water, while addition of water into the reaction

medium improved the yield of the 3-formylcoumarin by up to 50% (Table 5).

Table 5. The effect of water on the catalytic activity of amines.



Entry	Amine	Additive	t [h]	Yield [%]
1	DABCO	MS4Å	24	8
2	DABCO	none	24	24
3	DABCO	H_2O (1 equiv)	24	43
4	quinuclidine	H_2O (1 equiv)	2	50

Conclusion

In this paper, we described the novel consecutive activation of conjugated alkynes mediated by tertiary amines. The key step in these reactions involves an intramolecular migration of the silyl group. Our intended application of these reactions is in the preparation of multifunctionalized olefins through domino-type C–C bond formations by using aromatic aldehydes. In addition, it was found that the reaction was applicable to an intramolecular version, which has lead to a new 3-formylcoumarin synthesis. However, it is worth noting that the second reaction partner in this synthesis was not an aldehyde but water. As a result of our studies it has been shown that the silylated propiolates have great potential as a versatile tool in organic synthesis. The concept described here could, we believe, open new possibilities for the chemistry of conjugated alkynes. Further synthetic applications of the reaction provided by this work are currently underway in our laboratory, and will be reported in due course.

Experimental Section

General remarks: All nonaqueous reactions were carried out under an Ar atmosphere. Reagents were purchased from commercial sources and used as received. Anhydrous solvents were prepared by distillation over CaH_2 or purchased as high-grade reagents. ^1H and ^{13}C NMR spectra were obtained on a Varian Gemini 300 (300 MHz for ^1H and 75.46 MHz for ^{13}C NMR spectra) instrument or a Varian UNITY plus 500 (500 MHz for ^1H and 125 MHz for ^{13}C) instrument, using tetramethylsilane or chloroform as an internal reference. Mass spectra were recorded on a JEOL D-200 or a JEOL AX 505 mass spectrometer, and the ionization method was electron impact (EI, 70 eV). IR spectra were recorded on a Perkin–Elmer 1600 spectrometer. Melting points were taken using a Yanagimoto micro melting point apparatus and are uncorrected. Column chromatography was carried out by employing Cica Silica Gel 60N (spherical, neutral, 40–50 μm or 63–210 μm).

General procedure for the reaction of propiolate 1a with aldehydes: A solution of methyl 3-trimethylsilylpropiolate (156 mg, 1 mmol),[35] aldehyde (0.5 mmol), and DABCO (112 mg, 1 mmol) in anhydrous benzene (1 mL) was refluxed for 0.5–2 h. After this time, the reaction mixture was cooled to room temperature and diluted with CH_2Cl_2 (20 mL) producing a brown solution. This solution was washed with hydrochloric acid (10%), and a color change noted from brown to pale yellow. The organic layer was then washed with brine and dried over $MgSO_4$. After evaporation of the solvent the residue was purified by silica-gel column chromatography (CH_2Cl_2 then 10% AcOEt/CH_2Cl_2), which afforded the products **2**, **3**, or **4** as a colorless oils. The yields from these reactions are listed in Table 3.

Methyl (*Z*)-4-oxo-4-phenyl-2-[phenyl(trimethylsilyloxy)methyl]but-2-enoate (2a): ^1H NMR ($CDCl_3$): $\delta=-0.03$ (s, 9H), 3.41 (s, 3H), 5.56 (d, $J=1.7$ Hz, 1H), 6.12 (d, $J=1.7$ Hz, 1H), 7.17–7.31 (m, 7H), 7.43 (t, $J=7.3$ Hz, 1H), 7.66 ppm (d, $J=8.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta=-0.31$, 51.55, 75.48, 117.55, 126.86, 128.11, 128.17, 128.38, 128.47, 132.88, 136.31, 139.68, 159.82, 165.55, 197.13 ppm; IR (neat): $\tilde{\nu}=1724$, 1669 cm^{-1}; MS (EI): *m/z*: 368 $[M]^+$; HRMS: calcd for $C_{21}H_{24}O_4Si$: 368.1444 $[M]^+$; found: 368.1443.

Methyl 2-benzoyl-4-oxo-4-phenylbutyrate (3a): ^1H NMR ($CDCl_3$): $\delta=$ 3.10 (d, $J=6.4$ Hz, 2H), 3.70 (s, 3H), 5.80 (t, $J=6.4$ Hz, 1H), 7.46 (t, $J=$ 7.3 Hz, 4H), 7.58 (t, $J=7.3$ Hz, 2H), 7.97 ppm (d, $J=7.3$ Hz, 4H); ^{13}C NMR ($CDCl_3$): $\delta=33.18$, 52.25, 52.28, 128.64, 128.94, 133.77, 135.34, 171.82, 195.11 ppm; IR (neat): $\tilde{\nu}=1729$, 1686 cm^{-1}; MS (EI): *m/z*: 296 $[M]^+$; HRMS: calcd for $C_{18}H_{16}O_4$: 296.1049 $[M]^+$; found: 296.1046.

Methyl (*Z*)-4-oxo-4-(2-methylphenyl)-2-[(2-methylphenyl)(trimethylsilyloxy)methyl]but-2-enoate (2b): ^1H NMR ($CDCl_3$): $\delta=-0.07$ (s, 9H), 2.29 (s, 3H), 2.61 (s, 3H), 3.41 (s, 3H), 5.82 (brs, 1H), 5.83 (d, $J=1.3$ Hz, 1H), 7.06–7.22 (m, 5H), 7.32 (t, $J=7.3$ Hz, 1H), 7.44 (d, $J=7.7$ Hz, 1H), 7.52 ppm (d, $J=7.7$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=-0.40$, 19.05, 21.54, 51.45, 72.72, 118.43, 125.09, 126.15, 127.78, 128.00, 130.52, 131.56, 131.59, 131.75, 135.25, 135.57, 137.88, 139.83, 159.85, 165.67, 198.56 ppm; IR (neat): $\tilde{\nu}=1725$, 1667 cm^{-1}; MS (EI): *m/z*: 396 $[M]^+$; HRMS: calcd for $C_{23}H_{28}O_4Si$: 396.1757 $[M]^+$; found: 396.1759.

Methyl (*Z*)-4-oxo-4-(3-methylphenyl)-2-[(3-methylphenyl)(trimethylsilyloxy)methyl]but-2-enoate (2c): ^1H NMR ($CDCl_3$): $\delta=-0.01$ (s, 9H), 2.25 (s, 3H), 2.29 (s, 3H), 3.45 (s, 3H), 5.51 (d, $J=1.7$ Hz, 1H), 6.15 (d, $J=$ 1.7 Hz, 1H), 6.99 (d, $J=7.3$ Hz, 1H), 7.04–7.12 (m, 3H), 7.18 (t, $J=$ 7.7 Hz, 1H), 7.24 (d, $J=7.3$ Hz, 1H), 7.45–7.47 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta=-0.27$, 21.17, 21.27, 51.54, 75.48, 117.15, 123.95, 125.84, 127.47, 127.92, 128.17, 128.83, 128.92, 133.68, 136.26, 137.73, 137.94, 139.57, 160.27, 165.63, 197.27 ppm; IR (neat): $\tilde{\nu}=1725$, 1668 cm^{-1}; MS (EI): *m/z*: 396 $[M]^+$; HRMS: calcd for $C_{23}H_{28}O_4Si$: 396.1757 $[M]^+$; found: 396.1759.

Methyl 2-(3-methylbenzoyl)-4-oxo-4-(3-methylphenyl)butyrate (3c): ^1H NMR ($CDCl_3$): $\delta=2.38$ (s, 6H), 3.08 (d, $J=6.8$ Hz, 2H), 3.70 (s, 3H), 5.77 (t, $J=6.8$ Hz, 1H), 7.33 (t, $J=7.7$ Hz, 2H), 7.39 (d, $J=7.7$ Hz, 2H), 7.76 (d, $J=7.7$ Hz, 2H), 7.79 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta=21.33$, 33.27, 52.19, 52.42, 125.83, 128.74, 129.16, 134.49, 134.52, 135.45, 138.81, 171.90, 195.33 ppm; IR (neat): $\tilde{\nu}=1738$, 1695 cm^{-1}; MS (EI): *m/z*: 324 $[M]^+$; HRMS: calcd for $C_{20}H_{20}O_4$: 324.1361 $[M]^+$; found: 324.1360.

Methyl (*Z*)-4-oxo-4-(4-methylphenyl)-2-[(4-methylphenyl)(trimethylsilyloxy)methyl]but-2-enoate (2d): ^1H NMR ($CDCl_3$): $\delta=-0.04$ (s, 9H), 2.28 (s, 3H), 2.35 (s, 3H), 3.43 (s, 3H), 5.52 (d, $J=1.7$ Hz, 1H), 6.09 (d, $J=$ 1.7 Hz, 1H), 7.05 (d, $J=8.1$ Hz, 2H), 7.12 (d, $J=8.1$ Hz, 2H), 7.15 (d, $J=$ 8.1 Hz, 2H), 7.60 ppm (d, $J=8.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta=0.00$, 21.37, 21.92, 51.79, 75.58, 117.61, 127.10, 128.93, 129.15, 129.29, 134.29, 137.02, 138.07, 143.91, 160.45, 165.92, 197.00 ppm; IR (neat): $\tilde{\nu}=1725$, 1667 cm^{-1}; MS (EI): *m/z*: 396 $[M]^+$; HRMS: calcd for $C_{23}H_{28}O_4Si$: 396.1757 $[M]^+$; found: 396.1756.

Methyl 2-(4-methylbenzoyl)-4-oxo-4-(4-methylphenyl)butyrate (3d): ^1H NMR ($CDCl_3$): $\delta=2.40$ (s, 6H), 3.08 (d, $J=6.9$ Hz, 2H), 3.69 (s, 3H), 5.75 (t, $J=6.9$ Hz, 1H), 7.25 (d, $J=8.2$ Hz, 4H), 7.88 ppm (d, $J=8.2$ Hz, 4H); ^{13}C NMR ($CDCl_3$): $\delta=21.63$, 33.25, 52.14, 128.74, 129.56, 132.86, 144.68, 171.90, 194.74 ppm; IR (neat): $\tilde{\nu}=1737$, 1692 cm^{-1}; MS (EI): *m/z*: 324 $[M]^+$; HRMS: calcd for $C_{20}H_{20}O_4$: 324.1361 $[M]^+$; found: 324.1361.

Methyl (*Z*)-4-oxo-4-(2-methoxyphenyl)-2-[hydroxy-(2-methoxyphenyl)-methyl]but-2-enoate (2e): ^1H NMR ($CDCl_3$): $\delta=3.47$ (s, 3H), 3.73 (s, 3H), 3.76 (s, 3H), 5.82 (d, $J=1.3$ Hz, 1H), 5.90 (d, $J=1.3$ Hz, 1H), 6.81 (d, $J=7.7$ Hz, 1H), 6.88–6.98 (m, 3H), 7.22–7.30 (m, 2H), 7.44 (ddd, $J=$ 9.0, 7.3, 2.1 Hz, 1H), 7.82 ppm (dd, $J=7.7$, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=51.41$, 55.12, 55.59, 71.39, 110.44, 112.02, 115.89, 120.56,

120.76, 125.91, 127.57, 128.13, 129.26, 131.20, 134.50, 156.48, 159.07, 161.56, 165.89, 194.82 ppm; IR (neat): $\tilde{\nu}$ = 3485, 1722, 1655 cm^{-1}; MS (EI): *m/z*: 356 $[M]^+$; HRMS: calcd for $C_{20}H_{20}O_6$: 356.1260 $[M]^+$; found: 356.1261.

Methyl (*Z*)-4-oxo-4-(3-methoxyphenyl)-2-[(3-methoxyphenyl)(trimethylsilyloxy)methyl]but-2-enoate (2f): ^{1}H NMR ($CDCl_3$): δ = 0.00 (s, 9H), 3.42 (s, 3H), 3.71 (s, 3H), 3.74 (s, 3H), 5.55 (d, *J* = 1.6 Hz, 1H), 6.15 (d, *J* = 1.6 Hz, 1H), 6.73 (dt, *J* = 7.4, 1.6 Hz, 1H), 6.83–6.86 (m, 2H), 6.99 (dt, *J* = 6.6, 2.7 Hz, 1H), 7.10–7.25 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): δ = −0.23, 51.62, 55.17, 55.27, 75.33, 111.81, 112.20, 113.75, 117.61, 119.20, 119.96, 121.62, 129.13, 129.43, 137.65, 141.33, 159.38, 159.58, 159.70, 165.59, 196.84 ppm; IR (neat): $\tilde{\nu}$ = 1725, 1671 cm^{-1}; MS (EI): *m/z*: 428 $[M]^+$; HRMS: calcd for $C_{23}H_{28}O_6Si$: 428.1656 $[M]^+$; found: 428.1652.

Methyl 2-(3-methoxybenzoyl)-4-oxo-4-(3-methoxyphenyl)butyrate (3f): ^{1}H NMR ($CDCl_3$): δ = 3.09 (d, *J* = 6.9 Hz, 2H), 3.70 (s, 3H), 3.80 (s, 6H), 5.76 (t, *J* = 6.9 Hz, 1H), 7.12 (ddd, *J* = 8.2, 2.4, 0.8 Hz, 2H), 7.36 (t, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 2.4 Hz, 2H), 7.55 ppm (ddd, *J* = 8.2, 2.4, 0.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 33.24, 52.18, 52.37, 55.32, 112.60, 120.51, 121.07, 129.87, 136.61, 159.97, 171.72, 194.81 ppm; IR (neat): 1738, 1696 cm^{-1}; MS (EI): *m/z*: 356 $[M]^+$; HRMS: calcd for $C_{20}H_{20}O_6$: 356.1260 $[M]^+$; found: 356.1252.

Methyl (*Z*)-4-oxo-4-(4-methoxyphenyl)-2-[(4-methoxyphenyl)-(trimethylsilyloxy)methyl]but-2-enoate (2g): ^{1}H NMR ($CDCl_3$): δ = −0.03 (s, 9H), 3.45 (s, 3H), 3.74 (s, 3H), 3.82 (s, 3H), 5.50 (d, *J* = 1.7 Hz, 1H), 6.11 (d, *J* = 1.7 Hz, 1H), 6.76 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.65 ppm (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = −0.23, 51.56, 55.18, 55.35, 75.08, 113.42, 113.72, 116.90, 128.14, 129.67, 130.88, 131.93, 159.32, 160.24, 163.30, 165.73, 195.71 ppm; IR (neat): $\tilde{\nu}$ = 1724, 1659 cm^{-1}; MS (EI): *m/z*: 428 $[M]^+$; HRMS: calcd for $C_{23}H_{28}O_6Si$: 428.1656 $[M]^+$; found: 428.1652.

Methyl 2-(4-methoxybenzoyl)-4-oxo-4-(4-methoxyphenyl)butyrate (3g): ^{1}H NMR ($CDCl_3$): δ = 3.07 (d, *J* = 6.8 Hz, 2H), 3.69 (s, 3H), 3.85 (s, 6H), 5.67 (t, *J* = 6.8 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 4H). 7.96 ppm (d, *J* = 9.0 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 33.40, 52.06, 52.17, 55.51, 114.08, 128.38, 131.04, 163.93, 172.08, 193.69 ppm; IR (neat): $\tilde{\nu}$ = 1735, 1686 cm^{-1}; MS (EI): *m/z*: 356 $[M]^+$; HRMS: calcd for $C_{20}H_{20}O_6$: 356.1260 $[M]^+$; found: 356.1258.

Methyl (*Z*)-4-oxo-4-(2-bromo-4,5-dimethoxyphenyl)-2-[(2-bromo-4,5-dimethoxyphenyl)(trimethylsilyloxy)methyl]but-2-enoate (2h): ^{1}H NMR ($CDCl_3$): δ = −0.03 (s, 9H), 3.54 (s, 3H), 3.77 (s, 3H), 3.84 (s, 3H), 3.86 (s, 3H), 3.91 (s, 3H), 5.93 (s, 1H), 5.97 (s, 1H), 6.89 (s, 1H), 7.00 (s, 1H), 7.09 (s, 1H), 7.15 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = −0.20, 51.95, 55.98, 56.05, 56.11, 56.31, 74.02, 111.38, 112.66, 114.12, 114.64, 114.71, 117.20, 119.27, 128.55, 131.33, 147.44, 148.83, 149.45, 152.09, 165.58, 193.07 ppm; IR (neat): $\tilde{\nu}$ = 1724, 1675 cm^{-1}; MS (EI): *m/z*: 644 $[M]^+$; HRMS: calcd for $C_{25}H_{30}Br_2O_8Si$: 644.0077 $[M]^+$; found: 644.0049.

Methyl (*Z*)-4-oxo-4-(1-naphthyl)-2-[(1-naphthyl)(trimethylsilyloxy)methyl]but-2-enoate (2i): ^{1}H NMR ($CDCl_3$): δ = −0.08 (s, 9H), 3.15 (s, 3H), 5.87 (brs, 1H), 6.44 (brs, 1H), 7.26 (brs, 1H), 7.42–7.58 (m, 4H), 7.62–7.91 (m, 7H), 8.30 (brs, 1H), 9.08 ppm (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = −0.37, 51.55, 119.88, 123.88, 125.13, 125.70, 125.90, 126.06, 126.15, 126.34, 126.42, 128.21, 128.31, 128.69, 128.93, 130.41, 130.61, 131.72, 133.56, 133.70, 135.30, 159.64, 165.62, 198.66 ppm; IR (neat): $\tilde{\nu}$ = 1725, 1658 cm^{-1}; MS (EI): *m/z*: 468 $[M]^+$; HRMS: calcd for $C_{29}H_{28}O_4Si$: 468.1757 $[M]^+$; found: 468.1758.

Methyl (*Z*)-4-oxo-4-(2-naphthyl)-2-[(2-naphthyl)(trimethylsilyloxy)methyl]but-2-enoate (2j): ^{1}H NMR ($CDCl_3$): δ = −0.03 (s, 9H), 3.40 (s, 3H), 5.82 (d, *J* = 1.7 Hz, 1H), 6.23 (d, *J* = 1.7 Hz, 1H), 7.40–7.46 (m, 3H), 7.50–7.55 (m, 2H), 7.71–7.88 (m, 7H), 7.90 (dd, *J* = 8.5, 1.7 Hz, 1H), 8.08 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = −0.22, 51.64, 75.70, 118.19, 123.71, 124.56, 126.09, 126.13, 126.15, 126.40, 127.61, 127.91, 128.10, 128.29, 128.44, 129.54, 130.85, 132.19, 132.96, 133.17, 133.90, 135.46, 137.19, 159.96, 165.55, 197.07 ppm; IR (neat): $\tilde{\nu}$ = 1724, 1664 cm^{-1}; MS (EI): *m/z*: 468 $[M]^+$; HRMS: calcd for $C_{29}H_{28}O_4Si$: 468.1757 $[M]^+$; found: 468.1767.

Methyl 2-(2-naphthyloyl)-4-oxo-4-(2-naphthyl)butyrate (3j): ^{1}H NMR ($CDCl_3$): δ = 3.24 (d, *J* = 6.8 Hz, 2H), 3.74 (s, 3H), 6.11 (t, *J* = 6.8 Hz, 1H), 7.52–7.55 (m, 2H), 7.59–7.62 (m, 2H), 7.85–7.90 (m, 6H), 8.04 (dd, *J* = 8.5, 1.7 Hz, 2H), 8.58 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 33.53, 52.30, 52.58, 124.07, 126.97, 127.76, 128.92, 128.94, 129.71, 130.59, 132.43, 132.77, 135.80, 172.01, 195.09 ppm; IR (neat): $\tilde{\nu}$ = 1735, 1692 cm^{-1}; MS (EI): *m/z*: 396 $[M]^+$; HRMS: calcd for $C_{26}H_{20}O_4$: 396.1362 $[M]^+$; found: 396.1353.

Methyl (*Z*)-4-oxo-4-(4-chlorophenyl)-2-[(4-chlorophenyl)(trimethylsilyloxy)methyl]but-2-enoate (2k): ^{1}H NMR ($CDCl_3$): δ = −0.03 (s, 9H), 3.47 (s, 3H), 5.52 (d, *J* = 1.7 Hz, 1H), 6.06 (d, *J* = 1.7 Hz, 1H), 7.21 (d, *J* = 9.0 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 9.0 Hz, 2H), 7.62 ppm (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = −0.32, 51.79, 74.79, 118.12, 128.14, 128.64, 128.73, 129.79, 134.13, 134.73, 138.21, 139.52, 158.95, 165.29, 195.83 ppm; IR (neat): $\tilde{\nu}$ = 1725, 1673 cm^{-1}; MS (EI): *m/z*: 436 $[M]^+$; HRMS: calcd for $C_{21}H_{22}Cl_2O_4Si$: 436.0664 $[M]^+$; found: 436.0664.

Methyl 2-(4-chlorobenzoyl)-4-oxo-4-(4-chlorophenyl)butyrate (3k): ^{1}H NMR ($CDCl_3$): δ = 3.09 (d, *J* = 6.8 Hz, 2H), 3.70 (s, 3H), 5.67 (t, *J* = 6.8 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 4H), 7.89 ppm (d, *J* = 8.5 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 33.10, 52.33, 52.35, 129.32, 129.97, 133.55, 140.48, 171.61, 193.70 ppm; IR (neat): $\tilde{\nu}$ = 1734, 1697 cm^{-1}; MS (EI): *m/z*: 364 $[M]^+$; HRMS: calcd for $C_{18}H_{14}Cl_2O_4$: 364.0269 $[M]^+$; found: 364.0271.

Methyl 4-(2,6-dimethylphenyl)-4-trimethylsilyloxy-2-butynoate (4n): ^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 9H), 2.51 (s, 6H), 3.76 (s, 3H), 5.96 (s, 1H), 7.02 (d, *J* = 7.7 Hz, 2H), 7.12 ppm (t, *J* = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = −0.11, 20.26, 52.58, 60.22, 76.18, 87.31, 128.25, 129.10, 135.31, 136.45, 153.81 ppm; IR (neat): $\tilde{\nu}$ = 2233, 1718, 1253 cm^{-1}; MS (EI): *m/z*: 290 $[M]^+$; HRMS: calcd for $C_{16}H_{22}O_3Si$: 290.1338 $[M]^+$; found: 290.1332.

Methyl 4-trimethylsilyloxy-2-heptynoate (4o): ^{1}H NMR ($CDCl_3$): δ = 0.17 (s, 9H), 0.92 (t, *J* = 7.2 Hz, 3H), 1.39–1.48 (m, 2H), 1.65–1.72 (m, 2H), 3.76 (s, 3H), 4.43 ppm (t, *J* = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = −0.05, 13.57, 18.29, 39.70, 52.66, 61.99, 75.67, 88.91, 153.88 ppm; IR (neat): $\tilde{\nu}$ = 2361, 1722, 1253 cm^{-1}; MS (EI): *m/z*: 228 $[M]^+$; HRMS: calcd for $C_{11}H_{20}O_3Si$: 228.1182 $[M]^+$; found: 228.1177.

Methyl 5-methyl-4-trimethylsilyloxy-2-hexynoate (4p): ^{1}H NMR ($CDCl_3$): δ = 0.16 (s, 9H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 1.84–1.89 (m, 1H), 3.76 (s, 3H), 4.18 ppm (d, *J* = 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = −0.10, 17.65, 17.94, 34.82, 52.64, 67.71, 76.38, 88.09, 153.88 ppm; IR (neat): $\tilde{\nu}$ = 2235, 1721, 1252 cm^{-1}; MS (EI): *m/z*: 228 $[M]^+$; HRMS: calcd for $C_{11}H_{20}O_3Si$: 228.1182 $[M]^+$; found: 228.1163.

Methyl 5,5-dimethyl-4-trimethylsilyloxy-2-hexynoate (4q): ^{1}H NMR ($CDCl_3$): δ = 0.16 (s, 9H), 0.96 (s, 9H), 3.76 (s, 3H), 4.03 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = −0.18, 25.26, 36.37, 52.59, 71.07, 76.63, 88.14, 153.88 ppm; IR (neat): $\tilde{\nu}$ = 2235, 1721, 1254 cm^{-1}; MS (EI): *m/z*: 242 $[M]^+$; HRMS: calcd for $C_{12}H_{22}O_3Si$: 242.1338 $[M]^+$; found: 242.1378.

Preparation of Methyl 4-(4-methylphenyl)-4-trimethylsilyloxy-2-butynoate (4d): A solution of methyl propiolate (840 mg, 10 mmol) in THF (5 mL) was added at −78 °C to a solution of lithium diisopropylamide (LDA) (10 mmol) in THF (15 mL), prepared from diisopropylamine and *n*-butyllithium, and the mixture was stirred for 20 min at the same temperature. After the addition of *p*-tolualdehyde (1.179 mL, 10 mmol) and further stirring for 0.5 h, chlorotrimethylsilane (1.4 mL, 11 mmol) was added dropwise. The mixture was then gradually warmed to room temperature, and continuously stirred for 0.5 h. After this time, the reaction was quenched with saturated NH_4Cl, extracted with CH_2Cl_2, and dried over $MgSO_4$. Finally, the solvent was evaporated to leave a residue, which was purified by chromatography on silica gel (CH_2Cl_2) to afford **4d** as a pale yellow oil (2.267 g, 82%). ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 9H), 2.35 (s, 3H), 3.76 (s, 3H), 5.53 (s, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.35 ppm (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 0.04, 21.10, 52.66, 64.19, 76.74, 87.60, 126.34, 129.23, 136.44, 138.23, 153.77 ppm; IR (neat): $\tilde{\nu}$ = 2237, 1719, 1253 cm^{-1}; MS (EI): *m/z*: 276 $[M]^+$; HRMS: calcd for $C_{15}H_{20}O_3Si$: 276.1182 $[M]^+$; found: 276.1170.

Reaction of propiolate (1a) with benz[D]aldehyde: Benz[D]aldehyde was purchased from Aldrich (98 atom% D) and used as received. A solution of methyl 3-trimethylsilylpropiolate (156 mg, 1 mmol), benz[D]aldehyde (54 mg, 0.5 mmol), and DABCO (112 mg, 1 mmol) in anhydrous benzene (1 mL) was refluxed for 40 min. After this time, the mixture was cooled to room temperature and diluted with CH_2Cl_2 (20 mL). This solu-

tion was then washed with hydrochloric acid (10%) and brine successively, and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica-gel column chromatography (CH_2Cl_2) to afford compound [D]**2a** (57 mg, 62%). Only a trace amount of the product [D]**3a** could be detected by TLC. A solution of [D]**2a** (40 mg, 0.11 mmol) and DABCO (24 mg, 0.22 mmol) in anhydrous benzene (0.5 mL) was refluxed for 14 h. After this time, the same workup procedure as that described above was utilized and compound [D]**3a** (11 mg, 34%) and the starting material [D]**2a** (24 mg, 60%) were isolated.

The experiment in the presence of MeOH was performed as follows: A solution of methyl 3-trimethylsilylpropiolate (156 mg, 1 mmol), benz[-D]aldehyde (54 mg, 0.5 mmol), DABCO (112 mg, 1 mmol), and MeOH (100 µl) in anhydrous benzene (1 mL) was refluxed for 40 min. After this time, the mixture was cooled to room temperature and diluted with CH_2Cl_2 (20 mL). This solution was then washed with hydrochloric acid (10%) and brine successively, and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica-gel column chromatography (CH_2Cl_2) to afford compound [D]**2a** (48 mg, 52%). The ^{1}H NMR spectrum showed that 100% of the deuterium was incorporated into the product.

Product [D]2a: ^{1}H NMR ($CDCl_3$): $\delta = -0.01$ (s, 9H), 3.45 (s, 3H), 7.17–7.31 (m, 7H), 7.46 (t, $J = 7.3$ Hz, 1H), 7.68 ppm (d, $J = 8.1$ Hz, 2H); MS (EI) *m/z*: 370 $[M]^+$; HRMS calcd for $C_{21}H_{22}D_2O_4Si$: 370.1567 $[M]^+$; found: 370.1578. In the ^{1}H NMR spectrum, the peaks $\delta = 5.56$ (d, $J = 1.7$ Hz, 1H) and $\delta = 6.12$ ppm (d, $J = 1.7$ Hz, 1H), which were observed in the ^{1}H NMR spectrum of compound **2a**, were found to have disappeared.

Product [D]3a: ^{1}H NMR ($CDCl_3$): $\delta = 3.70$ (s, 3H), 5.79 (s, 1H), 7.46 (t, $J = 7.3$ Hz, 4H), 7.58 (t, $J = 7.3$ Hz, 2H), 7.97 (d, $J = 7.3$ Hz, 4H); MS (EI) *m/z*: 298 $[M]^+$; HRMS calcd for $C_{18}H_{14}D_2O_4$: 298.1174 $[M]^+$; found: 298.1183. In the ^{1}H NMR spectrum, the peak $\delta = 3.10$ ppm (d, $J = 6.4$ Hz, 2H), which was observed in the ^{1}H NMR spectrum of compound **3a**, was found to have disappeared, and the peak $\delta = 5.80$ (t, $J = 6.4$ Hz, 1H) in **3a** was simplified to a singlet.

General procedure for the preparation of the 3-trimethylsilylpropiolic esters of salicylaldehydes 10a–f: 4-Dimethylaminopyridine (24 mg, 0.2 mmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (575 mg, 3 mmol) were added successively to a solution of salicylaldehyde (2 mmol) and 3-trimethylsilylpropiolic acid (284 mg, 2 mmol) in anhydrous CH_2Cl_2 (10 mL) at room temperature. The resulting mixture was then stirred for 1 h at room temperature. The order of the addition of the reagents, the concentration of the solution, and the reaction time were very important factors for the reproducibility of the reaction. Alternative procedures or a prolonged reaction time resulted in the formation of salicylaldehyde trimethylsilyl ethers, which could not be removed from the desired esters. The reaction mixture was concentrated to about 4 mL, which was directly purified by silica-gel column chromatography (CH_2Cl_2) to afford a mixture of the ester **10** and the starting salicylaldehyde. After evaporation of the solvent, the residue was dissolved in Et_2O (50 mL), washed with K_2CO_3 (10%, 4×30 mL), and dried over $MgSO_4$. The aqueous layer was then acidified with HCl (10%), and extracted with CH_2Cl_2 to give the recovered salicylaldehyde (20–40%). Evaporation of the organic layer afforded the pure ester as a colorless oil in 52–88% yield based on the consumed salicylaldehyde.

2-Formylphenyl 3-trimethylsilylpropiolate (10a): Yield 52%; ^{1}H NMR ($CDCl_3$): $\delta = 0.30$ (s, 9H), 7.24 (dd, $J = 1.3$, 8.1 Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 1H), 7.65 (ddd, $J = 1.3$, 7.7, 8.1 Hz, 1H), 7.92 (dd, $J = 1.3$, 7.7 Hz, 1H), 10.18 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -0.62$, 93.33, 98.36, 123.23, 127.10, 127.89, 130.53, 135.46, 150.70, 150.91, 188.13 ppm; IR (neat): $\tilde{\nu} = 2178$, 1734, 1703 cm^{-1}; MS (EI): *m/z*: 246 $[M]^+$; HRMS: calcd for $C_{13}H_{14}O_3Si$: 246.0712 $[M]^+$; found: 246.0688.

2-Formyl-4-methylphenyl 3-trimethylsilylpropiolate (10b): Yield 59%; ^{1}H NMR ($CDCl_3$): $\delta = 0.30$ (s, 9H), 2.41 (s, 3H), 7.12 (d, $J = 8.2$ Hz, 1H), 7.44 (dd, $J = 2.2$, 8.2 Hz, 1H), 7.70 (d, $J = 2.2$ Hz, 1H), 10.14 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -0.66$, 20.99, 93.40, 98.08, 122.93, 127.43, 130.63, 136.08, 137.10, 148.76, 150.93, 188.27 ppm; IR (neat): $\tilde{\nu} = 2177$, 1728, 1697 cm^{-1}; MS (EI): *m/z*: 260 $[M]^+$; HRMS: calcd for $C_{14}H_{16}O_3Si$: 260.0868 $[M]^+$; found: 260.0853.

2-Formyl-4-methoxyphenyl 3-trimethylsilylpropiolate (10c): Yield 56%; ^{1}H NMR ($CDCl_3$): $\delta = 0.29$ (s, 9H), 3.84 (s, 3H), 7.14 (d, $J = 9.0$ Hz, 1H), 7.16 (dd, $J = 2.6$, 9.0 Hz, 1H), 7.36 (d, $J = 2.6$ Hz, 1H), 10.14 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -0.99$, 55.81, 93.16, 98.19, 112.17, 122.21, 124.15, 128.20, 144.91, 151.15, 157.93, 187.79 ppm; IR (neat): $\tilde{\nu} = 2178$, 1733 cm^{-1}; MS (EI): *m/z*: 276 $[M]^+$; HRMS: calcd for $C_{14}H_{16}O_4Si$: 276.0818 $[M]^+$; found: 276.0825.

2-Formyl-5-methoxyphenyl 3-trimethylsilylpropiolate (10d): Yield 88%; ^{1}H NMR ($CDCl_3$): $\delta = 0.31$ (s, 9H), 3.88 (s, 3H), 6.71 (d, $J = 2.2$ Hz, 1H), 6.91 (dd, $J = 2.2$, 8.8 Hz, 1H), 7.85 (d, $J = 8.8$ Hz, 1H), 10.02 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -0.66$, 56.13, 93.32, 98.21, 108.53, 112.99, 121.39, 132.42, 150.51, 152.50, 165.20, 186.96 ppm; IR (neat): $\tilde{\nu} = 2179$, 1735, 1693 cm^{-1}; MS (EI): *m/z*: 276 $[M]^+$; HRMS: calcd for $C_{14}H_{16}O_4Si$: 276.0818 $[M]^+$; found: 276.0788.

1-Formyl-2-naphthyl 3-trimethylsilylpropiolate (10e): Yield 69%; ^{1}H NMR ($CDCl_3$): $\delta = 0.32$ (s, 9H), 7.31 (d, $J = 8.8$ Hz, 1H), 7.58 (ddd, $J = 1.1$, 6.9, 8.2 Hz, 1H), 7.70 (ddd, $J = 1.3$, 6.9, 8.5 Hz, 1H), 7.88 (d, $J = 8.2$ Hz, 1H), 8.12 (d, $J = 8.8$ Hz, 1H), 9.18 (d, $J = 8.5$ Hz, 1H), 10.73 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -0.66$, 93.19, 98.95, 121.08, 121.36, 125.40, 126.99, 128.49, 129.87, 130.97, 132.02, 136.66, 150.72, 153.60, 189.84 ppm; IR (neat): $\tilde{\nu} = 2172$, 1728, 1684 cm^{-1}; MS (EI): *m/z*: 296 $[M]^+$; HRMS: calcd for $C_{17}H_{16}O_3Si$: 296.0869 $[M]^+$; found: 296.0858.

4-Chloro-2-formylphenyl 3-trimethylsilylpropiolate (10f): Yield 64%; ^{1}H NMR ($CDCl_3$): $\delta = 0.31$ (s, 9H), 7.22 (d, $J = 8.8$ Hz, 1H), 7.60 (dd, $J = 2.2$, 8.8 Hz, 1H), 7.88 (d, $J = 2.2$ Hz, 1H), 10.13 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = -0.66$, 92.98, 99.15, 124.76, 128.85, 129.74, 133.04, 135.19, 149.43, 150.37, 186.70 ppm; IR (neat): $\tilde{\nu} = 2178$, 1736 cm^{-1}; MS (EI): *m/z*: 280 $[M]^+$; HRMS: calcd for $C_{13}H_{13}ClO_3Si$: 280.0323 $[M]^+$; found: 280.0274.

General procedure for the formation of the 3-formylcoumarins 11a–f: A mixture of the propiolic ester **10** (0.125 mmol), and DABCO (28 mg, 0.25 mmol) or quinuclidine (28 mg, 0.25 mmol) in a suitable solvent (1 mL) was refluxed under an Ar atmosphere. After completion of the reaction, the mixture was diluted with CH_2Cl_2, washed with HCl (10%) and brine, and dried over $MgSO_4$. The solvent was evaporated to leave a residue, which was purified by silica-gel chromatography (CH_2Cl_2) to afford the 3-formylcoumarin as a colorless solid. The yields from all these reactions are listed in Table 4.

3-Formylcoumarin (11a): Yield 64%; m.p. 134–135 °C (lit.[36] m.p. 132–133 °C); ^{1}H NMR ($CDCl_3$): $\delta = 7.36$–7.42 (m, 2H), 7.68–7.72 (m, 2H), 8.43 (s, 1H), 10.27 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 117.15$, 118.13, 121.69, 125.33, 130.81, 135.06, 145.67, 155.50, 160.14, 187.78 ppm.

3-Formyl-6-methylcoumarin (11b): Yield 81%; m.p. 123–124 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.44$ (s, 3H), 7.30 (d, $J = 8.6$ Hz, 1H), 7.46–7.51 (m, 2H), 8.37 (s, 1H), 10.26 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 20.69$, 116.86, 117.89, 121.55, 130.37, 135.23, 136.27, 145.66, 153.72, 160.40, 187.94 ppm; IR (KBr): $\tilde{\nu} = 1733$, 1691 cm^{-1}; MS (EI): *m/z*: 188 $[M]^+$; HRMS: calcd for $C_{11}H_8O_3$: 188.0474 $[M]^+$; found: 188.0448.

3-Formyl-6-methoxycoumarin (11c): Yield 47%; m.p. 176–178 °C (lit.[37] m.p. 170 °C); ^{1}H NMR ($CDCl_3$): $\delta = 3.87$ (s, 3H), 7.07 (d, $J = 2.7$ Hz, 1H), 7.25–7.35 (m, 2H), 8.37 (s, 1H), 10.25 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 56.15$, 111.68, 118.33, 118.53, 121.88, 123.64, 145.48, 150.19, 156.58, 187.88 ppm; MS (EI): *m/z*: 204 $[M]^+$; HRMS: calcd for $C_{11}H_8O_4$: 204.0423 $[M]^+$; found: 204.0378.

3-Formyl-7-methoxycoumarin (11d): Yield 46%; m.p. 236–238 °C (lit.[37] m.p. 238 °C); ^{1}H NMR ([D$_6$]DMSO): $\delta = 3.92$ (s, 3H), 7.05 (dd, $J = 2.6$, 8.5 Hz, 1H), 7.11 (d, $J = 2.6$ Hz, 1H), 7.92 (d, $J = 8.5$ Hz, 1H), 8.65 (s, 1H), 9.99 ppm (s, 1H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 56.03$, 111.64, 113.18, 113.53, 117.99, 132.48, 146.98, 157.16, 159.07, 165.20, 186.59 ppm; MS (EI): *m/z*: 204 $[M]^+$; HRMS: calcd for $C_{11}H_8O_4$: 204.0423 $[M]^+$; found: 204.0387.

3-Formylbenzo[*d*]coumarin (11e): Yield 50%; m.p. 226–228 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.50$ (d, $J = 9.1$ Hz, 1H), 7.64 (ddd, $J = 1.1$, 7.1, 8.0 Hz, 1H), 7.78 (ddd, $J = 1.4$, 7.1, 8.5 Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 8.15 (d, $J = 9.1$ Hz, 1H), 8.36 (d, $J = 8.5$ Hz, 1H), 9.20 (s, 1H), 10.33 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 112.93$, 116.86, 120.03, 121.70, 126.99, 129.42, 129.58, 130.03, 130.34, 137.07, 141.16, 156.64, 160.30, 187.80 ppm; IR

(KBr): $\tilde{\nu}=1724\ cm^{-1}$; MS (EI): *m/z*: 224 $[M]^+$; HRMS: calcd for $C_{14}H_8O_3$: 224.0473 $[M]^+$; found: 224.0405.

6-Chloro-3-formylcoumarin (11f): Yield 26%; m.p. 180–182°C (lit.[37] m.p. 179°C); ^1H NMR ($CDCl_3$): $\delta=7.36$ (d, $J=8.8$ Hz, 1H), 7.64 (dd, $J=2.5$, 8.8 Hz, 1H), 7.68 (d, $J=2.5$ Hz, 1H), 8.34 (s, 1H), 10.25 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta=118.71$, 119.17, 122.57, 129.72, 130.76, 134.92, 144.28, 153.84, 159.80, 187.30 ppm; MS (EI): *m/z*: 208 $[M]^+$; HRMS: calcd for $C_{10}H_5ClO_3$: 207.9927 $[M]^+$; found: 207.9905.

Preparation of compound 17: A mixture of allylpalladium chloride dimer (27 mg, 0.15 mmol), triethyl phosphite (50 mg, 0.3 mmol), and hexamethyldisilane (0.64 mL, 3.2 mmol) was stirred at room temperature for 5 min. Coumarin 3-carboxylic acid chloride (314 mg, 1.5 mmol) in anhydrous toluene (0.5 mL) was then added to this solution, and the resulting reaction mixture was refluxed for 16 h (coumarin 3-carboxylic acid chloride was prepared by the treatment of coumarin 3-carboxylic acid with thionyl chloride). After this time, the reaction mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$, dried over $MgSO_4$, and then the solvent removed by evaporation. Purification of the residue was achieved by silica-gel chromatography (20% AcOEt/hexane) affording compound **17** (17 mg, 5%) as a pale yellow solid. M.p. 117–119°C; ^1H NMR ($CDCl_3$): $\delta=0.32$ (s, 9H), 7.33 (dt, $J=1.3$, 7.7 Hz, 1H), 7.38 (d, $J=8.1$ Hz, 1H), 7.61–7.66 (m, 2H), 8.04 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta=-2.39$, 116.80, 118.58, 124.96, 128.53, 130.51, 133.75, 142.06, 155.04, 160.71 ppm; IR (KBr): $\tilde{\nu}=1719$, 1631, 1608, 1554 cm^{-1}; MS (EI): *m/z*: 246 $[M]^+$; HRMS: calcd for $C_{13}H_{14}O_3Si$: 246.0712 $[M]^+$; found: 246.0740.

Preparation of the deuterated substrate [D]10a: Following the reported procedure,[38] salicylaldehyde was protected as a methoxymethyl ether. This compound was then transformed into a cyanohydrin trimethylsilyl ether as follows (see reference [39]). Trimethylsilyl cyanide (104 mg, 1 mmol) and triethylamine (1 drop) were added to a solution of the methoxymethyl ether (166 mg, 1 mmol) in anhydrous CH_2Cl_2 (4 mL). After continuous stirring at room temperature for 4 h the reaction mixture was evaporated and dried under reduced pressure by a vacuum pump to afford the cyanohydrin trimethylsilyl ether (254 mg, 96%) in an almost entirely pure form (this was determined from the ^1H NMR spectrum). ^1H NMR ($CDCl_3$): $\delta=0.25$ (s, 9H), 3.51 (s, 3H), 5.24 (d, $J=6.8$ Hz, 1H), 5.29 (d, $J=6.8$ Hz, 1H), 5.81 (s, 1H), 7.07 (dt, $J=1.3$, 7.7 Hz, 1H), 7.14 (dd, $J=1.3$, 7.7 Hz, 1H), 7.33 (dt, $J=1.7$, 7.7 Hz, 1H), 7.60 ppm (dd, $J=1.7$, 7.7 Hz, 1H).

The deuterium-rich salicylaldehyde and the propiolic ester [D]**10a** were prepared by the following procedure: The cyanohydrin trimethylsilyl ether (254 mg, 0.96 mmol) was dissolved in THF (2 mL) and added to an equimolar amount of LDA in THF (2 mL) at −78°C. The mixture was then stirred at −78°C for 15 min and D_2O (1 mL) was added. The mixture was then diluted with aqueous NH_4Cl, extracted with CH_2Cl_2, and dried over $MgSO_4$. Evaporation of the solvent produced a residue, which was dissolved in MeOH (3 mL), treated with K_2CO_3 (138 mg, 1 mmol), and then stirred at room temperature for 0.5 h. After this time, the reaction mixture was diluted with H_2O, extracted with CH_2Cl_2, and then dried over $MgSO_4$. Evaporation of the solvent afforded the deuterium-rich salicylaldehyde methoxymethyl ether. The deuterium incorporation of this compound was estimated as approximately 60% from the ^1H NMR spectrum. Aqueous H_2SO_4 (5 mol%, 1 mL) was then added to a solution of this crude product in MeOH (5 mL), and the resulting mixture was heated at 60°C for 12 h. After dilution with H_2O, the aqueous solution was extracted with CH_2Cl_2 and dried over $MgSO_4$. Finally, the solvent was evaporated to leave a residue, which was purified by silica-gel chromatography (CH_2Cl_2) affording salicyl[D]aldehyde (71 mg, 60%). The deuterium-rich propiolic ester [D]**10a** was synthesized according to the general procedure mentioned above. The 60% D incorporation of these products was confirmed by their ^1H NMR spectra.

The coumarin-forming reaction of compound [D]10a: A mixture of the propiolic ester [D]**10a** (30 mg, 0.125 mmol) and DABCO (28 mg, 0.25 mmol) in benzene (1 mL) was refluxed for 8 h. After completion of the reaction, the mixture was diluted with CH_2Cl_2, washed with HCl (10%) and brine, and dried over $MgSO_4$. Removal of the solvent by evaporation produced a residue, which was purified by silica-gel chromatography (CH_2Cl_2) affording the 3-formylcoumarin [D_a]**11a** as a colorless solid (9 mg, 41%). The ^1H NMR spectrum was identical to that obtained for **11a** with one exception. The integration value for the proton at C-4 on the coumarin nucleus ($\delta=8.43$ ppm) suggested 60% D incorporation.

Formation of compound [D_b]11a: A mixture of the propiolic ester **10a** (31 mg, 0.125 mmol), DABCO (28 mg, 0.25 mmol), and [D_4]MeOH (1 drop) in benzene (1 mL) was refluxed for 1 h. After this time, the mixture was diluted with CH_2Cl_2, washed with HCl (10%) and brine, and dried over $MgSO_4$. The solvent was then removed by evaporation, and the residue produced was purified by silica-gel chromatography (CH_2Cl_2) affording 3-formylcoumarin [D_b]**11a** as a colorless solid (3 mg, 14%). The other major product obtained was salicylaldehyde, which was probably formed by methanolysis. The ^1H NMR spectrum of [D_b]**11a** was identical to that obtained for **11a**, with the exception of the integration value of the formyl proton (10.27 ppm), which suggested 60% D incorporation.

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