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Efficient allylation of 4-silyloxyquinolinium triflates and other positively charged heteroaromatic systems

Uwe Beifuss,[a,*] Ursula Schniske[b] and Gerald Feder[a]

[a]*Institut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstr. 2, D-37077 Göttingen, Germany*
[b]*Laboratorium für Organische Chemie der Universität Bayreuth, Universitätsstr. 30, D-95447 Bayreuth, Germany*

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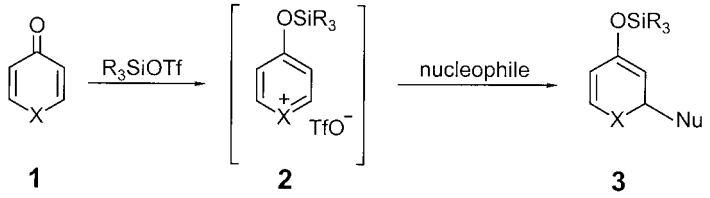
Abstract—The regioselective allylation of 4-silyloxyquinolinium triflates with allyltri-*n*-butyltin has been performed to give 2-allyl-4-silyloxy-1,2-dihydroquinolines with excellent yields. Similiar results have been obtained with 4-silyloxy-1-benzopyrylium triflates and 4-silyloxy-1-benzothiopyrylium triflates. © 2001 Elsevier Science Ltd. All rights reserved.

The 1,2-addition of allylic organometallic reagents to aldehydes, ketones and imines is one of the most important C—C bond-forming reactions as the allyl group represents a versatile functional carbon substituent.[1] This is why numerous protocols for this transformation have been developed. In most cases Lewis acids have been employed as activating reagents, because allylations without activation do not proceed under mild conditions.[2] In comparison, fewer conjugate additions of allylic organometallic reagents have been reported[1,3] and the conjugate addition to non activated vinylogous lactones, thiolactones and lactams remains almost unexplored.[4] An alternative is the use of double-activated Michael acceptors.[5] The allylation of azaaromatics is of great importance for the synthesis of biologically active nitrogen compounds, including alkaloids. Here the activation typically is achieved by use of the corresponding *N*-acyliminium salts that can be produced by reaction of the azaaromatics with acyl chlorides.[6] Using this approach, however, the allylation of vinylogous lactams like 4-quinolones cannot be achieved.

Our concept for the conjugate addition of nucleophiles to heterocyclic vinylogous carbonyl compounds **1** is based on the 1,2-addition of nucleophiles to the corresponding 4-silyloxy substituted positively charged heteroaromatic systems **2** (Scheme 1). They can be prepared in situ and exhibit both a reactive $C{=}X^+$ bond and a silyl enol ether. Due to the masking of the C=O group as a silyl enol ether, nucleophiles exclusively add to the $C{=}X^+$ bond to yield the 2-substituted silyl enol ethers **3** selectively. The silyl enol ethers can either be isolated or further transformed. Using this methodology the regioselective 1,2-addition of enamines,[7a] organolithium and organomagnesium reagents[7b] to 4-silyloxyquinolinium triflates has been reported to deliver the conjugate addition products without any side products. In addition it has been found that 4-silyloxyquinolinium triflates can be annulated in a highly regio- and diastereoselective manner employing 2-silyloxybuta-1,3-dienes[7c,d] and 2-aminobuta-1,3-dienes.[7a] Similar results have been obtained with 4-silyloxy-1-benzothiopyrylium triflates.[8] Here we report the regioselective allylation of several positively charged 4-silyloxy-substituted heteroaromatics corresponding to the conjugate allylation of vinylogous lactams, lactones and thiolactones (Scheme 2).



Scheme 1.

Keywords: allylation; quinolines; benzopyrans; sulfur heterocycles; tin and compounds; silicon and compounds.
* Corresponding author. Tel.: +49-551-39-3253; fax: +49-551-39-9660; e-mail: ubeifus@gwdg.de

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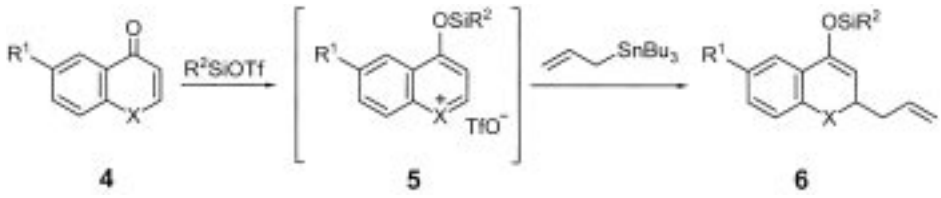


Scheme 2.

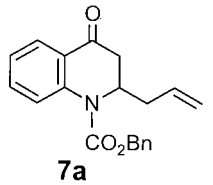
First the allylation of 4-silyloxyquinolinium triflates **5a–e** was investigated, easily obtained in situ by reaction of the *N*-protected 4-quinolones **4a,b** with a trifluoromethanesulfonic acid trialkylsilyl ester under mild conditions.[7] Treatment of the *N*-benzyloxycarbonyl- as well as the *N*-ethoxycarbonyl protected quinolinium triflates **5a–e** with 1.3 equiv. allyltri-*n*-butyltin at room temperature gave the 2-allyl-4-silyloxy-1,2-dihydroquinolines **6a–e** as single products in high yields (Table 1, Entries 1–5). It was found that this transformation can be performed with trifluoromethanesulfonic acid trialkyl silyl esters like trimethylsilyl trifluoromethanesulfonate (TMSOTf), triethylsilyl trifluoromethanesulfonate (TESOTf) and tri-*iso*-propylsilyl trifluoromethanesulfonate (TIPSOTf).[9] In almost all cases the addition products could be isolated and purified without any difficulties by flash chromatography. The only exception was the reaction of the trimethylsilyloxy derivative **5a**; here, the resulting trimethylsilyl enol ether **6a** undergoes partial hydrolysis to the corresponding 2-allyl tetrahydroquinolone **7a** upon isolation and purification (Table 1, Entry 1). Tetrahydroquinolones **7** can also be obtained by hydrolysis of the corresponding tri-*iso*-propylsilyl ethers. As an example, treatment of **6d** with **2** *N* sulfuric acid affords the tetrahydroquinolone **7a** in 70% yield. Allyltrimethylsilane, which has been widely used as an allylating reagent[1] does not react with **5a–i** under a variety of reaction conditions, indicating that allylic silicon reagents are not sufficiently nucleophilic to react with a 4-silyloxy quinoliniumtriflate.[10]

Also, exclusive α-functionalization and high yields were observed with the allylation of 4-silyloxy-1-benzopyrylium- and 4-silyloxy-1-benzothiopyrylium triflates **5j** and **5k** (Table 1, Entries 10, 11). These results show that this method is not restricted to the functionalization of 4-quinolones, but can be used for the selective allylation of vinylogous lactones and thiolactones like **4g** and **4h**, too. The structure of all products **6a–k** was established by NMR spectroscopy.

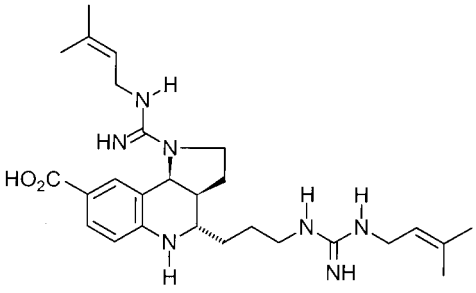
Table 1. The allylation of 4-silyloxy substituted positively charged heteroaromatics **5**

Entry	**4**	X	R^1	**5**	R^2	**6**	Yield **6** [%]
1	**a**	N-CO_2Bn	H	**a**	Me_3	**a**	52[a]
2	**a**	N-CO_2Bn	H	**b**	Et_3	**b**	88
3	**b**	N-CO_2Et	H	**c**	Et_3	**c**	94
4	**a**	N-CO_2Bn	H	**d**	$(i\text{-}Pr)_3$	**d**	80
5	**b**	N-CO_2Et	H	**e**	$(i\text{-}Pr)_3$	**e**	86
6	**c**	N-CO_2Bn	Br	**f**	$(i\text{-}Pr)_3$	**f**	84
7	**d**	N-CO_2Et	Br	**g**	$(i\text{-}Pr)_3$	**g**	90
8	**e**	N-CO_2Bn	CO_2Bn	**h**	$(i\text{-}Pr)_3$	**h**	78
9	**f**	N-CO_2Et	CO_2Bn	**i**	$(i\text{-}Pr)_3$	**i**	90
10	**g**	O	H	**j**	$(i\text{-}Pr)_3$	**j**	86
11	**h**	S	H	**k**	$(i\text{-}Pr)_3$	**k**	91

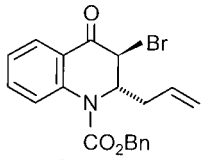
[a] Due to its hydrolytic instability, **6a** could not be obtained analytically pure. Besides **6a**, 28% of the corresponding tetrahydroquinolone **7a** was isolated.



7a



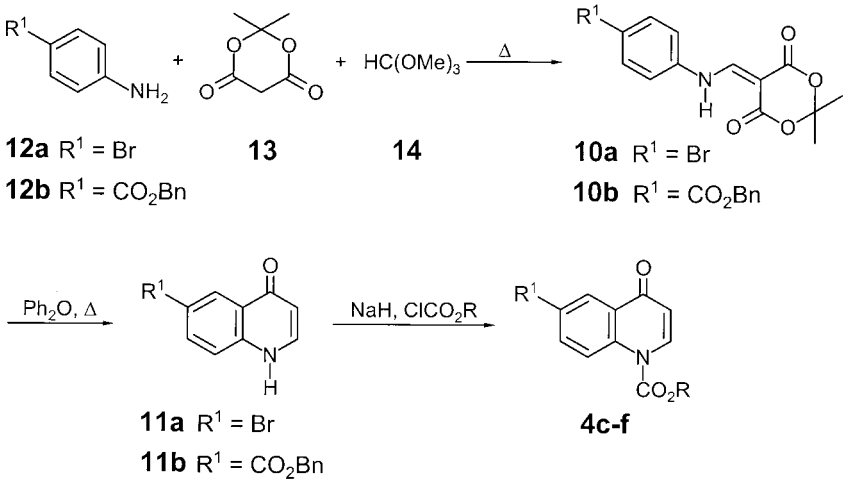
8



9

Martinellic acid (**8**) and related compounds are of great interest in the field of medicinal chemistry as they represent the first nonpeptide natural products that have been identified as bradykinin receptor antagonists.[11] In connection with studies towards the synthesis of **8** the allylation with 6-substituted 4-quinolones like **4c–f** was investigated. Again, the regioselective allylation occurred and the corresponding 2-allylated 1,2-dihydroquinolines **6f–i** could be isolated in yields from 78–90% (Table 1, Entries 6–9). The silyl enol ether functionality in **6** offers numerous perspectives for further functionalization at C-3 and C-4. Preliminary experiments show that treatment of **6a** and **6b** with *N*-bromosuccinimide (NBS) at −78°C proceeds diastereoselectively as only the 2,3-*trans*-disubstituted compound **9** was formed. With respect to the synthesis of **8** further studies will concentrate on radical transformations of **9** as well as reactions of silyl enol ethers **6** with *C*-electrophiles.

The assignment of the stereochemistry of **9** is mainly based on ^{1}H NMR spectroscopy. 3H resonates at δ=4.39 ppm as a



Scheme 3.

doublet with a coupling constant of J=2.0 Hz ($^3J_{2,3}$= 2.0 Hz): The small value for this vicinal coupling constant proves the *trans*-arrangement of the substituents at C-2 and C-3. The assignment finds support from the results of the X-ray crystal structure analysis of some related compounds.[12]

The *N*-protected 4-quinolones **4a,b** are easily accessible by protection of 4-quinolone **4i** (X=NH) using standard procedures.[13] 6-Bromo-4-quinolone (**11a**) and 6-benzyloxycarbonyl-4-quinolone (**11b**) were synthesized according to the procedure of *Valderrama* employing 4-bromoaniline (**12a**) and 4-benzyloxycarbonylaniline (**12b**) as starting materials.[14] The reaction of the *para*-substituted anilines **12** with Meldrum's acid (**13**) and methyl orthoformate (**14**) gave the corresponding arylaminomethylene Meldrum's derivatives **10a,b**, that in turn were heated in boiling diphenyl ether to deliver **11a** and **11b** with high yields. **11a** and **11b** were transformed into the *N*-protected 4-quinolones **4c–f** employing standard procedures (Scheme 3).[13]

To summarize, we have presented the first examples for the conjugate addition of allylstannanes to 4-quinolones. The new method relies on the efficient addition of allyltri-*n*-butyltin to 4-silyloxy quinolinium triflates, that are obtained from the corresponding 4-quinolones in situ. The allylation products are envisioned to be ideal building blocks for synthesizing biologically important molecules such as martinellic acid (**8**) and pumiliotoxin C. In addition it was shown, that the allylations are not restricted to 4-quinolones, but can be performed with 4-benzopyranones and 4-benzothiopyranones, too.

1. Experimental

1.1. Methods and materials

All solvents were distilled prior to use. CH_2Cl_2 was dried over basic alumina. Reagents and materials were either obtained from commercial suppliers and used without further purification or prepared by standard methods: flash chromatography, silica gel 60 (0.040–0.063 mm), Merck; TLC, silica gel 60 F_{254} glass plates, Merck [compounds were visualized by conc. H_2SO_4 (180°C, 5 min)]; melting points (uncorrected), Büchi 510; UV, Perkin–Elmer Lambda 9 or Shimadzu 160 A; IR, Perkin–Elmer Paragon 1000 FT IR spectrometer or Bruker IFS 25 FTIR spectrometer; ^{1}H and ^{13}C NMR, Jeol JNM-EX 270 or Bruker AM-500-FT; δ in ppm calibrated to residual solvent signal with chemical shifts referred to TMS (0.00 ppm); J in [Hz]; * assignments interchangeable; MS, MAT 312 mass spectrometer; combustion analyses, Microanalytical Laboratory of the Institut für Organische Chemie der Universität Göttingen.

1.1.1. General procedure for the allylation of 4. If not stated otherwise 1.3 equiv. TIPSOTf was added dropwise to 1.0 equiv. **4** and the mixture was held at room temperature for 1 h under argon. After the successive addition of dry dichloromethane (2 ml/1.0 mmol **4**), 1.3 equiv. 2,6-lutidine and 1.3 equiv. allyltri-*n*-butyltin at 0°C the resulting solution was stirred for 3 h at room temperature. The reaction mixture was poured into icecold 5% aqueous potassium hydrogen carbonate (20 ml/1.0 mmol **4**), and extracted with cold dichloromethane (3×30 ml/1.0 mmol **4**). The combined organic phases were dried over magnesium sulfate and the solvent was removed at reduced pressure on a rotary evaporator. Finally the crude product was purified by flash chromatography on silica gel.

1.1.2. 1-Benzyloxycarbonyl-2-(2-propenyl)-4-trimethyl silyloxy-2*H*-quinoline (6a). Reaction of 0.40 g (1.43 mmol) **4a** with 0.34 ml (1.76 mmol) TMSOTf, 0.22 ml (1.89 mmol) 2,6-lutidine and 0.58 ml (1.87 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=14:1) 0.13 g (28%) **7a** and 0.29 g (52%) **6a** as a colourless and sensitive oil. R_f=0.32 (cyclohexane/diethyl ether=9:1). ^{1}H NMR (270 MHz, $CDCl_3$): δ=0.24 [s, 9H, $Si(CH_3)_3$], 2.17 (t, ^3J=6.5 Hz, 2H, $CH_2CH{=}CH_2$), 4.85–5.00 (m, 2H, $CH_2CH{=}CH_2$), 5.06 (q, ^3J=6.5 Hz, 1H, 2H), 5.18 (d, ^3J=6.5 Hz, 1H, 3H), 5.19 (d, ^2J=12.0 Hz, 1H, $CO_2CH_aHC_6H_5$), 5.26 (d, ^2J=12.0 Hz, 1H, $CO_2CHH_bC_6H_5$),

5.70 (m_c, 1H, $CH_2CH{=}CH_2$), 7.08 (dt, ^4J=1.5 Hz, ^3J=7.5 Hz, 1H, 6H), 7.15–7.26 (m, 1H, 7H), 7.28–7.39 (m, 5H, 2′H, 3′H, 4′H, 5′H, 6′H), 7.42 (dd, ^4J=1.5 Hz, ^3J=7.5 Hz, 1H, 5H), 7.48–7.62 (br, 1H, 8H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=0.08 [$Si(CH_3)_3$], 38.73 ($CH_2CH{=}CH_2$), 52.23 (C-2), 67.55 ($CO_2CH_2C_6H_5$), 106.12 (C-3), 117.59 ($CH_2CH{=}CH_2$), 122.25 (C-8), 122.46 (C-6), 123.86 (C-5), 126.31 (C-4a), 127.82 (C-3′, C-5′)*, 127.91 (C-7), 128.01 (C-4′), 128.45 (C-2′, C-6′)*, 133.87 ($CH_2CH{=}CH_2$), 134.24 (C-4), 136.21 (C-1′), 145.82 (C-8a), 153.94 ($CO_2CH_2C_6H_5$).

1.1.3. 1-Benzyloxycarbonyl-2-(2-propenyl)-4-oxo-1,2,3,4-tetrahydroquinoline (7a). 0.84 ml (4.34 mmol) TMSOTf was added dropwise to 1.00 g (3.58 mmol) **4a** and the mixture was held at room temperature for 1 h under argon. After successive addition of 7.5 ml dry dichloromethane, 0.54 ml (4.64 mmol) 2,6-lutidine and 1.44 ml (4.64 mmol) allyltri-*n*-butyltin at 0°C the resulting solution was stirred for 3 h at room temperature. The reaction mixture was poured into 60 ml ice-cold 5% aqueous potassium hydrogen carbonate and extracted with cold dichloromethane (3×80 ml). The organic phases were combined and the solvent was removed at reduced pressure on a rotary evaporator. The combined organic phases were dried over magnesium sulfate and the solvent was removed. The residue was dissolved in 15 ml THF and treated with 10 ml 10% sulfuric acid. After stirring for 2 h at room temperature the reaction mixture was extracted with diethyl ether (3×80 ml). The combined organic phases were dried over magnesium sulfate and the solvent was removed. Purification of the crude product by flash chromatography on 95 g silica gel (cyclohexane/ethyl acetate=6:1) afforded 0.81 g (70%) **7a** as a colourless oil. R_f=0.31 (cyclohexane/ethyl acetate=4:1). IR (CCl_4): ν=3078 cm^{-1}, 3035 (arom. CH, C=CH); 2927, 2851 (CH); 1711 (C=O, carbamate); 1693 (C=O); 1603 (C=C); 1480; 1460; 1390; 1336; 1320; 1302; 1288; 1260; 1226. UV (acetonitrile): λ_{max} (log ϵ)=234 nm (4.49), 258 (4.03), 325 (3.56). ^{1}H NMR (270 MHz, $CDCl_3$): δ=2.14–2.40 (m, 2H, $CH_2CH{=}CH_2$), 2.66 (dd, ^3J=1.5 Hz, ^2J=17.5 Hz, 1H, $3H_a$), 3.01 (dd, ^3J=6.0 Hz, ^2J=17.5 Hz, 1H, $3H_b$), 4.86 (dd, ^2J=1.5 Hz, ^3J=17.0 Hz, 1H, $CH_2CH{=}CH_{(trans)}$), 4.96–5.10 (m, 2H, 2H, $CH_2CH{=}CH_{(cis)}$), 5.24–5.35 (m, 2H, $CO_2CH_2C_6H_5$), 5.69 (m_c, 1H, $CH_2CH{=}CH_2$), 7.16 (dt, ^4J=1.0 Hz, ^3J=8.0 Hz, 1H, 6H), 7.30–7.40 (m, 5H, 2′H, 3′H, 4′H, 5′H, 6′H), 7.49 (dt, ^4J=1.5 Hz, ^3J=8.0 Hz, 1H, 7H), 7.76 (d_{br}, ^3J=8.0 Hz, 1H, 8H), 7.97 (dd, ^4J=1.5 Hz, ^3J=8.0 Hz, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=36.07 ($CH_2CH{=}CH_2$), 42.52 (C-3), 53.39 (C-2), 68.19 ($CO_2CH_2C_6H_5$), 118.43 ($CH_2CH{=}CH_2$), 124.19, 124.66 (C-8, C-6), 124.87 (C-4a), 126.63 (C-5), 128.08 (C-3′, C-5′)*, 128.39 (C-4′), 128.63 (C-2′, C-6′)*, 133.37 ($CH_2CH{=}CH_2$), 134.47 (C-7), 135.73 (C-1′), 140.91 (C-8a), 153.94 ($CO_2CH_2C_6H_5$), 193.02 (C-4). MS (70 eV); *m/z* (%): 321 (4) [M^+], 280 (33) [M^+-C_3H_5], 236 (30) [280-CO_2], 146 (6), 91 (100) [$C_7H_7^+$], 65 (18) [$C_5H_5^+$]. Anal. calcd. for $C_{20}H_{19}NO_3$ (321.37): C, 74.75; H, 5.96; N, 4.36. Found: C, 74.60; H, 5.81; N 4.38.

1.1.4. 1-Benzyloxycarbonyl-2-(2-propenyl)-4-triethyl silyloxy-2*H*-quinoline (6b). Reaction of 0.40 g (1.43 mmol) **4a** with 0.42 ml (1.86 mmol) TESOTf, 0.22 ml (1.89 mmol) 2,6-lutidine and 0.58 ml (1.87 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=9:1) 0.55 g (88%) **6b** as a colourless oil. R_f=0.43 (cyclohexane/diethyl ether=9:1) IR (CCl_4): ν=3074 cm^{-1}, 3035 (arom. CH, C=CH); 2958, 2912, 2877 (CH); 1705 (C=O); 1646 (C=C); 1488; 1456; 1395; 1355; 1320; 1245. UV (acetonitrile): λ_{max} (log ϵ)=240 nm (4.39), 270 (3.76). ^{1}H NMR (270 MHz, $CDCl_3$): δ=0.73 (q, ^3J=8.0 Hz, 6H, 3×CH_2CH_3), 0.98 (t, ^3J=8.0 Hz, 9H, 3×CH_2CH_3), 2.16 (t, ^3J=7.0 Hz, 2H, $CH_2CH{=}CH_2$), 4.85–5.00 (m, 2H, $CH_2CH{=}CH_2$), 5.06 (q, ^3J=7.0 Hz, 1H, 2H), 5.17 (d, ^3J=7.0 Hz, 1H, 3H), 5.19 (d, ^2J=12.5 Hz, 1H, $CO_2CH_aHC_6H_5$), 5.26 (d, ^2J=12.5 Hz, 1H, $CO_2CHH_bC_6H_5$), 5.71 (m_c, 1H, $CH_2CH{=}CH_2$), 7.09 (dt, ^4J=1.0 Hz, ^3J=7.5 Hz, 1H, 6H), 7.22 (dt, ^4J=1.5 Hz, ^3J=7.5 Hz, 1H, 7H), 7.27–7.37 (m, 5H, 2′H, 3′H, 4′H, 5′H, 6′H), 7.48 (dd, ^4J=1.5 Hz, ^3J=7.5 Hz, 1H, 5H), 7.50–7.58 (br, 1H, 8H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=4.93 (3×CH_2CH_3), 6.68 (3×CH_2CH_3), 38.70 ($CH_2CH{=}CH_2$), 52.26 (C-2), 67.55 ($CO_2CH_2C_6H_5$), 105.37 (C-3), 117.55 ($CH_2CH{=}CH_2$), 122.25 (C-8), 123.94 (C-6), 124.37 (C-5), 126.46 (C-4a), 127.81 (C-3′, C-5′)*, 127.89 (C-7), 128.02 (C-4′), 128.47 (C-2′, C-6′)*, 133.98 ($CH_2CH{=}CH_2$), 134.96 (C-4), 136.28 (C-1′), 146.02 (C-8a), 153.98 ($CO_2CH_2C_6H_5$). MS (70 eV); *m/z* (%): 394 (53) [M^+-C_3H_5], 350 (83) [394-CO_2], 261 (12), 230 (12), 91 (100) [$C_7H_7^+$]. Anal. calcd. for $C_{26}H_{33}NO_3Si$ (435.64): C, 71.68; H, 7.63; N 3.22: Found: C, 71.87; H, 7.84; N, 3.14.

1.1.5. 1-Ethoxycarbonyl-2-(2-propenyl)-4-triethyl silyloxy-2*H*-quinoline (6c). Reaction of 1.2 g (5.52 mmol) **4b** with 1.62 ml (7.16 mmol) TESOTf, 0.84 ml (7.21 mmol) 2,6-lutidine and 2.23 ml (7.19 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=9:1) 1.93 g (94%) **6c** as a colourless oil. R_f=0.32 (cyclohexane/diethyl ether=9:1). IR (CCl_4): ν=3076 cm^{-1}, 3026 (arom. CH, C=CH); 2958, 2911, 2877 (CH); 1700 (C=O); 1646 (C=C); 1488; 1456; 1399; 1356; 1320; 1242. UV (acetonitrile): λ_{max} (log ϵ)=240 nm (4.42), 274 (3.79). ^{1}H NMR (270 MHz, $CDCl_3$): δ=0.73 (q, ^3J=8.0 Hz, 6H, 3× CH_2CH_3), 0.98 (t, ^3J=8.0 Hz, 9H, 3×CH_2CH_3), 1.28 (t, ^3J=7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.16 (t, ^3J=6.5 Hz, 2H, $CH_2CH{=}CH_2$), 4.12–4.32 (m, 2H, $CO_2CH_2CH_3$), 4.86–5.00 (m, 2H, $CH_2CH{=}CH_2$), 5.03 (q, ^3J=6.5 Hz, 1H, 2H), 5.17 (d, ^3J=6.5 Hz, 1H, 3H), 5.73 (m_c, 1H, $CH_2CH{=}CH_2$), 7.08 (dt, ^4J=1.0 Hz, ^3J=7.5 Hz, 1H, 6H), 7.22 (dt, ^4J=1.5 Hz, ^3J=7.5 Hz, 1H, 7H), 7.47 (dd, ^4J=1.5 Hz, ^3J=7.5 Hz, 1H, 5H), 7.42–7.57 (br, 1H, 8H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=4.95 (3×CH_2CH_3), 6.69 (3× CH_2CH_3), 14.46 ($CO_2CH_2CH_3$), 38.75 ($CH_2CH{=}CH_2$), 52.06 (C-2), 61.91 ($CO_2CH_2CH_3$), 105.42 (C-3), 117.43 ($CH_2CH{=}CH_2$), 122.22 (C-8), 123.72 (C-6), 124.31 (C-5), 126.40 (C-4a), 127.81 (C-7), 134.06 ($CH_2CH{=}CH_2$), 135.17 (C-4), 145.99 (C-8a), 154.18 ($CO_2CH_2CH_3$). MS (70 eV); *m/z* (%): 373 (1) [M^+], 332 (100) [M^+-C_3H_5], 288 (20) [332 CO_2], 260 (59) [288-C_2H_4], 230 (20), 172 (14), 87 (42), 59 (11), 32 (11). Anal. calcd. for $C_{21}H_{31}NO_3Si$ (373.57): C, 67.52; H, 8.36; N, 3.75. Found: C, 67.77; H, 8.51; N, 3.69.

1.1.6. 1-Benzyloxycarbonyl-2-(2-propenyl)-4-tri-*iso*-propyl silyloxy-2*H*-quinoline (6d). Reaction of 0.46 g (1.65 mmol) **4a** with 0.45 ml (1.67 mmol) TIPSOTf, 0.20 ml (1.72 mmol)

2,6-lutidine and 0.66 ml (2.13 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=9:1) 0.63 g (80%) **6d** as a colourless oil. R_f=0.38 (cyclohexane/diethyl ether=9:1). IR (CCl_4): ν=3075 cm^{-1}, 3035 (arom. CH, C=CH); 2945, 2893, 2867 (CH); 1705 (C=O); 1644 (C=C); 1488; 1463; 1455; 1395; 1353; 1320; 1245. UV (acetonitrile): λ_{max} (log ϵ)=240 nm (4.33), 274 (3.77). ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.10 [d, ^3J=7.0 Hz, 18H, 3×CH(CH_3)$_2$], 1.18–1.35 [m, 3H, 3×CH(CH$_3$)$_2$], 2.17 (t, ^3J=6.5 Hz, 2H, CH_2CH=CH$_2$), 4.86–5.00 (m, 2H, CH$_2$CH=CH_2), 5.07 (q, ^3J=6.5 Hz, 1H, 2H), 5.18 (d, ^3J=6.5 Hz, 1H, 3H), 5.21 (d, ^2J=12.5 Hz, 1H, CO$_2$CH_aHC$_6$H$_5$), 5.27 (d, ^2J=12.5 Hz, 1H, CO$_2$CHH_bC$_6$H$_5$), 5.72 (m$_c$, 1H, CH$_2$CH=CH$_2$), 7.10 (dt, ^4J=1.0 Hz, ^3J=7.5 Hz, 1H, 6H), 7.22 (dt, ^4J=1.5 Hz, ^3J=7.5 Hz, 1H, 7H), 7.27–7.38 (m, 5H, 2′H, 3′H, 4′H, 5′H, 6′H), 7.42–7.58 (br, 1H, 8H), 7.56 (dd, ^4J=1.5 Hz, ^3J=7.5 Hz, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=12.71 [3×CH(CH$_3$)$_2$], 18.02, 18.06 [3×CH(CH_3)$_2$], 38.66 (CH_2CH=CH$_2$), 52.27 (C-2), 67.53 (CO$_2$CH_2C$_6$H$_5$), 104.86 (C-3), 117.53 (CH$_2$CH=CH_2), 122.42 (C-8), 123.98 (C-6), 124.41 (C-5), 126.63 (C-4a), 127.78 (C-3′, C-5′)*, 127.99 (C-7), 128.46 (C-2′, C-4′, C-6′)*, 134.00 (CH$_2$CH=CH$_2$), 134.95 (C-4), 136.29 (C-1′), 146.26 (C-8a), 153.97 (CO_2CH$_2$C$_6$H$_5$). MS (70 eV); *m/z* (%): 436 (74) [M$^+$-C$_3$H$_5$], 392 (100) [436-CO$_2$], 258 (10), 202 (12), 188 (7), 172 (6), 91 (98) [C$_7$H$_7^+$]. Anal. calcd. for $C_{29}H_{39}NO_3Si$ (477.72): C, 72.91; H 8.23. Found: C, 73.07; H, 8.50.

1.1.7. 1-Ethoxycarbonyl-2-(2-propenyl)-4-tri-*iso*-propyl silyloxy-2*H*-quinoline (6e). Reaction of 0.40 g (1.84 mmol) **4b** with 0.50 ml (1.85 mmol) TIPSOTf, 0.22 ml (1.89 mmol) 2,6-lutidine and 0.74 ml (2.39 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=9:1) 0.66 g (86%) **6e** as a colourless oil. R_f=0.29 (cyclohexane/diethyl ether=9:1). IR (CCl_4): ν=3077 cm^{-1} (arom. CH, C=CH); 2945, 2881, 2867 (CH); 1703 (C=O); 1644 (C=C); 1488; 1463; 1399; 1354; 1320; 1246. UV (acetonitrile): λ_{max} (log ϵ)=240 nm (4.33), 270 (3.69). ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.10 [d, ^3J=6.5 Hz, 18H, 3×CH(CH_3)$_2$], 1.18–1.33 [m, 6H, 3×CH(CH$_3$)$_2$, CH$_2$CH_3], 2.16 (t, ^3J=6.5 Hz, CH_2CH=CH$_2$), 4.16–4.35 (m, 2H, CH_2CH$_3$), 4.87–5.00 (m, 2H, CH$_2$CH=CH_2), 5.04 (q, ^3J=6.5 Hz, 1H, 2H), 5.17 (d, ^3J=6.5 Hz, 1H, 3H), 5.72 (m$_c$, 1H, CH$_2$CH=CH_2), 7.09 (dt, ^4J=1.0 Hz, ^3J=6.0 Hz, 1H, 6H), 7.22 (dt, ^4J=1.0 Hz, ^3J=6.0 Hz, 1H, 7H), 7.46–7.58 (br, 1H, 8H), 7.55 (dd, ^4J=1.0 Hz, ^3J=6.0 Hz, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=12.69 [3×CH(CH$_3$)$_2$], 14.42 (CO$_2$CH$_2$$CH_3$), 18.00, 18.04 [3×CH(C$H_3$)$_2$], 38.67 (C$H_2$CH=CH$_2$), 52.04 (C-2), 61.89 (CO$_2$CH_2CH$_3$), 104.85 (C-3), 117.38 (CH$_2$CH=CH_2), 122.36 (C-8), 123.76 (C-6), 124.35 (C-5), 126.54 (C-4a), 127.72 (C-7), 134.06 (CH$_2$CH=CH$_2$), 135.12 (C-4), 146.20 (C-8a), 154.15 (CO_2CH$_2$CH$_3$). MS (70 eV); *m/z* (%): 415 (3) [M$^+$], 374 (100) [M$^+$-C$_3$H$_5$], 330 (16) [374-CO$_2$], 302 (17) [330-C$_2$H$_4$], 258 (8) [M$^+$ C$_9$H$_{21}$Si], 202 (8), 172 (7), 115 (6) [C$_6$H$_{15}$Si$^+$], 87 (7), 73 (7) [C$_3$H$_9$Si$^+$], 59 (9). Anal. calcd. for $C_{24}H_{37}NO_3Si$ (415.65): C, 69.35; H, 8.97; N, 3.37. Found: C, 69.29; H, 8.89; N, 3.39.

1.1.8. 1-Benzyloxycarbonyl-6-bromo-2-(2-propenyl)-4-tri-*iso*-propyl silyloxy-2*H*-quinoline (6f). Reaction of 0.30 g (0.84 mmol) **4c** with 0.29 ml (1.08 mmol) TIPSOTf, 0.13 ml (1.12 mmol) 2,6-lutidine and 0.34 ml (1.10 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=14:1) 0.39 g (84%) **6f** as a colourless oil. R_f=0.45 (cyclohexane/diethyl ether=9:1). IR (CCl_4): ν=3072 cm^{-1}, 3030 (arom. CH, C=CH); 2946, 2881, 2867 (CH); 1710 (C=O); 1646 (C=C); 1482; 1394; 1342; 1310; 1244. UV (acetonitrile): λ_{max} (log ϵ)=247 nm (4.44). ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.09 [d, ^3J=6.5 Hz, 18H, 3×CH(CH_3)$_2$], 1.18–1.32 [m, 3H, 3×CH(CH$_3$)$_2$], 2.12–2.17 (m, 2H, CH_2CH=CH$_2$), 4.83–5.00 (m, 2H, CH$_2$CH=CH_2), 5.05 (q, ^3J=6.5 Hz, 1H, 2H), 5.18 (d, ^3J=6.5 Hz, 1H, 3H), 5.19–5.30 (m, 2H, CO$_2$CH_2C$_6$H$_5$), 5.68 (m$_c$, 1H, CH$_2$CH=CH$_2$), 7.26–7.46 (m, 7H, 2′H, 3′H, 4′H, 5′H, 6′H, 7H, 8H), 7.64 (d, ^4J=2.5 Hz, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=12.67 [3×CH(CH$_3$)$_2$], 18.00, 18.03 [3×CH(CH_3)$_2$], 38.80 (CH_2CH=CH$_2$), 52.29 (C-2), 67.78 (CO$_2$CH_2C$_6$H$_5$), 105.71 (C-3), 117.14 (C-6), 117.82 (CH$_2$CH=CH_2), 125.44 (C-8), 125.96 (C-5), 127.89 (C-3′, C-5′)*, 128.17 (C-4′), 128.44 (C-4a), 128.55 (C-2′, C-6′)*, 130.61 (C-7), 133.67 (CH$_2$CH=CH$_2$), 134.03 (C-4), 136.02 (C-1′), 145.25 (C-8a), 153.73 (CO_2CH$_2$C$_6$H$_5$). MS (70 eV); *m/z* (%): 516 (8) [M$^+$-C$_3$H$_5$], 514 (8) [M$^+$-C$_3$H$_5$], 472 (21) [516-CO$_2$], 470 (20) [514-CO$_2$], 186 (7), 91 (100) [C$_7$H$_7^+$]. Anal. calcd. for $C_{29}H_{38}BrNO_3Si$ (556.61): C, 62.58; H, 6.88. Found: C, 62.66; H, 6.85.

1.1.9. 6-Bromo-1-ethoxycarbonyl-2-(2-propenyl)-4-tri-*iso*-propyl silyloxy-2*H*-quinoline (6g). Reaction of 0.30 g (1.01 mmol) **4d** with 0.36 ml (1.34 mmol) TIPSOTf, 0.15 ml (1.29 mmol) 2,6-lutidine and 0.41 ml (1.32 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=9:1) 0.45 g (90%) **6g** as a colourless oil. R_f=0.38 (cyclohexane/diethyl ether=9:1). IR (CCl_4): ν=3078 cm^{-1} (arom. CH, C=CH); 2946, 2882, 2868 (CH); 1707 (C=O); 1642 (C=C); 1482; 1397; 1342; 1311; 1244. UV (acetonitrile): λ_{max} (log ϵ)=247 nm (4.35). ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.10 [d, ^3J=6.5 Hz, 18H, 3×CH(CH_3)$_2$], 1.18–1.35 [m, 6H, 3×CH(CH$_3$)$_2$, CH$_2$CH_3], 2.11–2.17 (m, 2H, CH_2CH=CH$_2$), 4.12–4.29 (m, 2H, CH_2CH$_3$), 4.84–5.09 (m, 3H, 2H, CH$_2$CH=CH_2), 5.19 (d, ^3J=6.5 Hz, 1H, 3H), 5.70 (m$_c$, 1H, CH$_2$CH=CH_2), 7.32 (dd, ^4J=2.0 Hz, ^3J=8.5 Hz, 1H, 7H), 7.36–7.46 (br, 1H, 8H), 7.64 (d, ^4J=2.0 Hz, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=12.63 [3×CH(CH$_3$)$_2$], 14.37 (CO$_2$CH$_2$$CH_3$), 17.94, 17.97 [3×CH(C$H_3$)$_2$], 38.78 (C$H_2$CH=CH$_2$), 52.04 (C-2), 62.05 (CO$_2$CH_2CH$_3$), 105.71 (C-3), 116.86 (C-6), 117.63 (CH$_2$CH=CH_2), 125.33 (C-8), 125.88 (C-5), 128.30 (C-4a), 130.48 (C-7), 133.66 (CH$_2$CH=CH$_2$), 134.20 (C-4), 145.17 (C-8a), 153.81 (CO_2CH$_2$CH$_3$). MS (70 eV); *m/z* (%): 454 (99) [M$^+$-C$_3$H$_5$], 452 (100) [M$^+$-C$_3$H$_5$], 410 (8) [454-CO$_2$], 408 (8) [452-CO$_2$], 382 (8) [410-C$_2$H$_4$], 380 (8) [408-C$_2$H$_4$], 338 (4) [M$^+$-C$_9$H$_{21}$Si], 336 (4) [M$^+$-C$_9$H$_{21}$Si], 286 (4), 258 (6), 214 (4), 186 (10), 172 (5), 115 (11) [C$_6$H$_{15}$Si$^+$], 87 (8), 73 (8) [C$_3$H$_9$Si$^+$], 59 (13). Anal. calcd. for $C_{24}H_{36}BrNO_3Si$ (494.54): C, 58.29; H, 7.34. Found: C, 58.57; H, 7.38.

1.1.10. 1,6-Dibenzyloxycarbonyl-2-(2-propenyl)-4-tri-*iso*-propyl silyloxy-2*H*-quinoline (6h). Reaction of 0.40 g (0.97 mmol) **4e** with 0.34 ml (1.26 mmol) TIPSOTf,

0.15 ml (1.29 mmol) 2,6-lutidine and 0.39 ml (1.26 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=9:1) 0.46 g (78%) **6h** as a colourless oil. R_f=0.26 (cyclohexane/diethyl ether=9:1). IR (CCl_4): ν= 3067 cm^{-1}, 3034 (arom. CH, C=CH); 2946, 2892, 2867 (CH); 1717 (C=O); 1652 (C=C); 1491; 1456; 1394; 1351; 1302; 1280; 1232. UV (acetonitrile): λ_{max} (log ϵ)=261 nm (4.66), 293 (3.95). ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.07 [d, ^3J=7.5 Hz, 18H, 3×CH(CH_3)$_2$], 1.20–1.30 [m, 3H, 3×CH(CH$_3$)$_2$], 2.11–2.21 (m, 2H, CH_2CH=CH$_2$), 4.90 (ddd, ^4J=1.5 Hz, ^2J=2.0 Hz, ^3J=17.0 Hz, 1H, CH$_2$CH=CH$H_{(trans)}$), 4.96 (ddd, ^4J= 1.0 Hz, ^2J=2.0 Hz, ^3J=10.0 Hz, 1H, CH$_2$CH=CH$H_{(cis)}$), 5.07 (q, ^3J=6.5 Hz, 1H, 2H), 5.19 (d, ^3J=6.5 Hz, 1H, 3H), 5.22 (d, ^2J=12.5 Hz, 1H, NCO$_2$CH_aHC$_6$H$_5$), 5.26 (d, ^2J=12.5 Hz, 1H, NCO$_2$CHH_bC$_6$H$_5$), 5.31 (d, ^2J=12.5 Hz, 1H, CO$_2$CH_aHC$_6$H$_5$), 5.35 (d, ^2J=12.5 Hz, 1H, CO$_2$CHH_bC$_6$H$_5$), 5.68 (m$_c$, 1H, CH$_2$CH=C$H$$_2$), 7.29–7.43 (m, 10H, 2′H, 3′H, 4′H, 5′H, 6′H, 2″H, 3″H, 4″H, 5″H, 6″H), 7.62–7.71 (br, 1H, 8H), 7.94 (dd, ^4J=2.0 Hz, ^3J=8.5 Hz, 1H, 7H), 8.29 (d, ^4J=2.0 Hz, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=12.67 [3×CH(CH$_3$)$_2$], 17.97, 18.00 [3×CH(CH$_3$)$_2$], 39.25 (CH$_2$CH=CH$_2$), 52.64 (C-2), 66.65 (CO$_2$$CH_2C_6H_5$), 67.95 (NCO$_2$$CH_2C_6H_5$), 105.04 (C-3), 117.93 (CH$_2$CH=CH$_2$), 123.91 (C-8), 124.24 (C-5), 125.36 (C-6), 126.28 (C-4a), 127.96 (C-3″, C-5″)*, 128.14 (C-4″)*, 128.18 (C-2″, C-6″)*, 128.24 (C-4′)*, 128.53 (C-3′, C-5′)*, 128.57 (C-2′, C-6′)*, 129.44 (C-7), 133.52 (CH$_2$$C$H=CH$_2$), 135.84 (C-1′)*, 136.03 (C-1″)*, 139.43 (C-4), 145.66 (C-8a), 153.68 (NCO$_2$CH$_2$C$_6$H$_5$), 165.99 (CO$_2$CH$_2$C$_6$H$_5$). MS (70 eV); *m/z* (%): 570 (17) [M$^+$-C$_3$H$_5$], 526 (67) [570-CO$_2$], 392 (8), 91 (100) [C$_7$H$_7^+$]. Anal. calcd. for $C_{37}H_{45}NO_5Si$ (611.85): C, 72.63; H, 7.41. Found: C, 72.55; H, 7.33.

1.1.11. 6-Benzyloxycarbonyl-1-ethoxycarbonyl-2-(2-propenyl)-4-tri-*iso*-propyl silyloxy-2*H*-quinoline (6i). Reaction of 0.30 g (0.85 mmol) **4f** with 0.30 ml (1.12 mmol) TIPSOTf, 0.13 ml (1.12 mmol) 2,6-lutidine and 0.34 ml (1.10 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=9:1) 0.42 g (90%) **6i** as a colourless oil. R_f=0.21 (cyclohexane/diethyl ether=9:1) IR (CCl_4): ν=3068 cm^{-1}, 3034 (arom. CH, C=CH); 2945, 2881, 2867 (CH); 1719 (C=O); 1649 (C=C); 1492; 1463; 1385; 1351; 1304; 1243. UV (acetonitrile): λ_{max} (log ϵ)=261 nm (4.61). ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.07 [d, ^3J=7.0 Hz, 18H, 3×CH(CH_3)$_2$], 1.16–1.33 [m, 6H, 3×CH(CH$_3$)$_2$, CH$_2$CH_3], 2.06–2.26 (m, 2H, CH_2CH=CH$_2$), 4.16–4.31 (m, 2H, CH_2CH$_3$), 4.85–5.00 (m, 2H, CH$_2$CH=CH_2), 5.05 (q, ^3J=6.5 Hz, 1H, 2H), 5.19 (d, ^3J=6.5 Hz, 1H, 3H), 5.25–5.34 (m, 2H, CO$_2$CH_2C$_6$H$_5$), 5.70 (m$_c$, 1H, CH$_2$CH=C$H$$_2$), 7.26–7.45 (m, 5H, 2″H, 3″H, 4″H, 5″H, 6″H), 7.63 (d, ^3J=8.5 Hz, 1H, 8H), 7.94 (dd, ^4J=2.0 Hz, ^3J=8.5 Hz, 1H, 7H), 8.28 (d, ^4J=2.0 Hz, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=12.64 [3×CH(CH$_3$)$_2$], 14.38 (CO$_2$CH$_2$$CH_3$), 17.96, 17.99 [3×CH($CH_3$)$_2$], 39.27 ($CH_2$CH=CH$_2$), 52.46 (C-2), 62.32 (CO$_2$$CH_2CH_3$), 66.63 ($CO_2CH_2C_6H_5$), 105.06 (C-3), 117.81 (CH$_2$CH=CH$_2$), 123.81 (C-8), 124.21 (C-5), 125.16 (C-6), 126.20 (C-4a), 128.13 (C-4″), 128.16 (C-3″, C-5″)*, 128.52 (C-2″, C-6″)*, 129.36 (C-7), 133.59 (CH$_2$$C$H=CH$_2$), 136.04 (C-1″), 139.65 (C-4), 145.63 (C-8a), 153.85 (CO$_2$CH$_2$CH$_3$), 166.03 (CO$_2$CH$_2$C$_6$H$_5$). MS (70 eV); *m/z* (%): 549 (1) [M$^+$], 508 (100) [M$^+$-C$_3$H$_5$], 464 (5) [508-CO$_2$], 436 (6) [464-C$_2$H$_4$], 392 (5) [M$^+$-C$_9$H$_{21}$Si], 374 (4), 91 (62) [C$_7$H$_7^+$], 59 (6). Anal. calcd. for $C_{32}H_{43}NO_5Si$ (549.78): C, 69.91; H, 7.88; N, 2.55. Found: C, 70.19; H, 7.95; N, 2.54.

1.1.12. 2-(2-Propenyl)-4-tri-*iso*-propylsilyloxy-2*H*-chromene (6j). Reaction of 0.31 g (2.12 mmol) **4g** with 0.58 ml (2.16 mmol) TIPSOTf, 0.25 ml (2.15 mmol) 2,6-lutidine and 0.85 ml (2.74 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=80:1) 0.63 g (86%) **6j** as a colourless oil. R_f=0.41 (cyclohexane/diethyl ether=80:1). IR (CCl_4): ν=3078 cm^{-1}, 3040 (arom. CH, C=CH); 2945, 2893, 2867 (CH); 1646 (C=C); 1606; 1484; 1454; 1356; 1231. UV (acetonitrile): λ_{max} (log ϵ)=215 nm (4.27), 269 (3.51), 306 (3.62). ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.11 [d, ^3J=7.0 Hz, 18H, 3× CH(CH_3)$_2$], 1.18–1.32 [m, 3H, 3×CH(CH$_3$)$_2$], 2.34–2.61 (m, 2H, CH_2CH=CH$_2$), 4.81 (d, ^3J=3.5 Hz, 1H, 3H), 4.95 (dt, ^3J=3.5 Hz, ^3J=6.5 Hz, 1H, 2H), 5.06–5.15 (m, 2H, CH$_2$CH=CH_2), 5.77–5.94 (m, 1H, CH$_2$CH=C$H$$_2$), 6.76 (dd, ^4J=1.0 Hz, ^3J=7.5 Hz, 1H, 8H), 6.87 (dt, ^4J=1.0 Hz, ^3J=7.5 Hz, 1H, 6H), 7.12 (dt, ^4J=1.5 Hz, ^3J=7.5 Hz, 1H, 7H), 7.39 (dd, ^4J=1.5 Hz, ^3J=7.5 Hz, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=12.73 [3×CH(CH$_3$)$_2$], 18.04, 18.05 [3×CH(CH$_3$)$_2$], 40.72 (CH$_2$CH=CH$_2$), 75.35 (C-2), 100.78 (C-3), 115.69 (C-8), 117.71 (CH$_2$CH=CH$_2$), 120.64 (C-6)*, 121.69 (C-4a), 122.47 (C-5)*, 129.49 (C-7), 133.65 (CH$_2$$C$H=CH$_2$), 145.92 (C-4), 154.66 (C-8a). MS (70 eV); *m/z* (%): 344 (1) [M$^+$], 303 (100) [M$^+$-C$_3$H$_5$], 259 (8), 173 (5), 157 (5) [C$_9$H$_{21}$Si$^+$], 131 (6), 115 (37) [C$_6$H$_{15}$Si$^+$], 102 (18), 87 (10), 73 (9) [C$_3$H$_9$Si$^+$], 59 (10). Anal. calcd. for $C_{21}H_{32}O_2Si$ (344.57): C, 73.20; H, 9.36. Found: C, 73.10; H, 9.49.

1.1.13. 2-(2-Propenyl)-4-tri-*iso*-propyl silyloxy-2*H*-thiochromene (6k). Reaction of 0.30 g (1.85 mmol) 4h with 0.50 ml (1.86 mmol) TIPSOTf, 0.22 ml (1.89 mmol) 2,6-lutidine and 0.75 ml (2.42 mmol) allyltri-*n*-butyltin according to the *General Procedure* yielded after flash chromatography on 95 g silica gel (cyclohexane/diethyl ether=80:1) 0.61 g (91%) **6k** as a yellow oil. R_f=0.43 (cyclohexane/diethyl ether=80:1). IR (CCl_4): ν= 3063 cm^{-1}, 3030 (arom. CH, C=CH); 2945, 2892, 2867 (CH); 1634 (C=C); 1468; 1346; 1259. UV (acetonitrile): λ_{max} (log ϵ)=225 nm (4.14), 255 (4.06), 325 (3.29). ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.10 [d, ^3J=7.0 Hz, 18H, 3×CH(CH_3)$_2$], 1.18–1.32 [m, 3H, 3×CH(CH$_3$)$_2$], 2.39 (t, ^3J=6.5 Hz, 2H, CH_2CH=CH$_2$), 3.63 (q, ^3J=6.5 Hz, 1H, 2H), 5.00–5.10 (m, 2H, CH$_2$CH=CH_2), 5.19 (d, ^3J= 6.5 Hz, 1H, 3H), 5.78 (m$_c$, 1H, CH$_2$CH=C$H$$_2$), 7.06–7.14 (m, 2H, 6H, 8H), 7.18–7.23 (m, 1H, 7H), 7.58–7.63 (m, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=12.78 [3×CH(CH$_3$)$_2$], 18.07, 18.09 [3×CH(CH$_3$)$_2$], 38.51 (C-2), 40.79 (CH$_2$CH=CH$_2$), 104.26 (C-3), 117.47 (CH$_2$CH=CH$_2$), 124.14 (C-6), 125.09 (C-8), 127.13 (C-7), 128.12 (C-5), 131.63 (C-4a), 132.67 (C-8a), 134.71 (CH$_2$$C$H=CH$_2$), 149.06 (C-4). MS (70 eV); *m/z* (%): 360 (5) [M$^+$], 319 (100) [M$^+$-C$_3$H$_5$], 275 (6), 189 (5), 157 (4) [C$_9$H$_{21}$Si$^+$], 115 (22) [C$_6$H$_{15}$Si$^+$], 110 (24), 102 (17), 87 (10), 73 (11)

[$C_3H_9Si^+$], 59 (13). Anal. calcd. for $C_{21}H_{32}OSSi$ (360.63): C, 69.94; H, 8.94. Found: C, 69.87; H 8.84.

1.1.14. (2*SR*,3*SR*)-1-Benzyloxycarbonyl-3-bromo-2-(2-propenyl)-4-oxo-1,2,3,4-tetrahydroquinoline (9). 0.18 ml (0.93 mmol) TMSOTf was added dropwise to 0.20 g (0.72 mmol) **4a** and the mixture was held at room temperature for 1 h under argon. After the successive addition of 1.5 ml dry dichloromethane, 0.11 ml (0.94 mmol) 2,6-lutidine and 0.29 ml (0.94 mmol) allyltri-*n*-butyltin at 0°C the resulting solution was stirred for 3 h at room temperature. The reaction mixture was cooled to −78°C, treated with 0.14 g (0.79 mmol) NBS, warmed to room temperature, poured into 20 ml saturated potassium hydrogen carbonate solution and extracted with dichloromethane (3×20 ml). The combined organic phases were dried over sodium sulfate and the solvent was removed at reduced pressure on a rotary evaporator. Finally the crude product was purified by flash chromatography on 95 g silica gel (cyclohexane/ethyl acetate=6:1) to yield 138 mg (48%) **9** as a yellow oil. R_f=0.27 (cyclohexane/ethyl acetate=6:1) IR (CCl_4): ν= 3080 cm^{-1}, 3035 (arom. CH, C=CH); 2979 (CH); 1721 (C=O, carbamate); 1693 (C=O); 1602 (C=C); 1481; 1461; 1388; 1335; 1300; 1238; 1225. UV (acetonitrile): λ_{max} (log ϵ)=237 nm (4.40), 268 (3.89), 346 (3.52). ^{1}H NMR (270 MHz, $CDCl_3$): δ=2.20–2.40 (m, 2H, CH_2CH=CH_2), 4.39 (d, ^3J=2.0 Hz, 1H, 3H), 4.90 (dd, ^2J=1.5 Hz, ^3J=17.0 Hz, 1H, CH_2CH=C$H_{(trans)}$), 5.04 (dd, ^2J=1.5 Hz, ^3J=10.0 Hz, 1H, CH_2CH=C$H_{(cis)}$), 5.13 (dt, ^3J=2.0 Hz, ^3J=7.0 Hz, 1H, 2H), 5.27 (d, ^2J=12.5 Hz, 1H, $CO_2CH_aHC_6H_5$), 5.36 (d, ^2J=12.5 Hz, 1H, $CO_2CH_bHC_6H_5$), 5.68 (tdd, ^3J=7.0 Hz, ^3J=10.0 Hz, ^3J= 17.0 Hz, 1H, CH_2CH=CH_2), 7.20 (dt, ^4J=1.0 Hz, ^3J= 8.0 Hz, 1H, 6H), 7.30–7.44 (m, 5H, 2′H, 3′H, 4′H, 5′H, 6′H), 7.56 (dt, ^4J=1.5 Hz, ^3J=8.0 Hz, 1H, 7H), 7.81 (d_{br}, ^3J=8.0 Hz, 1H, 8H), 8.04 (dd, ^4J=1.5 Hz, ^3J=8.0 Hz, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=34.69 (CH_2CH=CH_2), 48.16 (C-3), 59.71 (C-2), 68.47 ($CO_2CH_2C_6H_5$), 119.30 (CH_2CH=CH_2), 121.59 (C-4a), 124.48, 124.59 (C-8, C-6), 128.14, 128.39, 128.55 (C-5, C-2′, C-3′, C-4′, C-5′, C-6′), 132.05 (CH_2CH=CH_2), 135.17 (C-7), 135.48 (C-1′), 140.02 (C-8a), 154.28 ($CO_2CH_2C_6H_5$), 186.13 (C-4). MS (70 eV); *m/z* (%): 401 (1) [M^+], 399 (1) [M^+], 360 (5) [M^+-C_3H_5], 358 (5) [M^+-C_3H_5], 316 (5) [360-CO_2], 314 (5) [358-CO_2], 226 (30), 224 (29), 145 (10), 91 (100) [$C_7H_7^+$], 84 (40). Anal. calcd. for $C_{20}H_{18}BrNO_3$ (400.27): C, 60.01; H, 4.53. Found: C, 60.23; H, 4.73.

1.1.15. 2,2-Dimethyl-5-(4-bromo-phenylamino-methylene)-[1.3]dioxan-4,6-dione (10a). A solution of 4.6 g (31.9 mmol) Meldrum′s acid (**13**) and 60 ml (547.9 mmol) methyl orthoformate (**14**) was heated to reflux for 2 h under argon. At room temperature 3.8 g (22.1 mmol) 4-bromoaniline (**12a**) were added and the reaction mixture was heated for another 6 h under reflux. The precipitate was collected after cooling followed by recrystallization from methanol to yield 6.11 g (85%) **10a** as yellow crystals. Mp.: 208–209°C (methanol). R_f=0.42 (cyclohexane/ethyl acetate=2:1). IR (KBr): ν=3258 cm^{-1} (NH); 3100 (arom. CH, C=CH); 2993, 2925 (CH); 1719, 1674 (C=O); 1627 (C=C); 1578; 1483; 1407; 1391; 1337; 1289; 1269; 1204. ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.74 (s, 6H, 2×CH_3), 7.11 (d, ^3J=9.0 Hz, 2H, 2′H, 6′H), 7.54 (d, ^3J=9.0 Hz, 2H, 3′H, 5′H), 8.57 (d, ^3J=14.5 Hz, 1H, =CH), 11.20 (d_{br}, ^3J=14.5 Hz, 1H, NH, D_2O exchangeable). ^{13}C NMR (68 MHz, $CDCl_3$): δ=27.05 (2×CH_3), 87.81 (C-2), 105.32 (C-5), 119.47 (C-2′, C-6′), 119.93 (C-4′), 133.15 (C-3′, C-5′), 136.89 (C-1′), 152.28 (CH), 163.27 (C=O), 165.48 (C=O). MS (70 eV); *m/z* (%): 327 (38) [M^+], 325 (40) [M^+], 312 (2) [M^+-CH_3], 310 (1) [M^+-CH_3], 269 (92) [M^+-C_3H_6O], 267 (88) [M^+-C_3H_6O], 252 (10), 250 (12), 241 (6) [269-CO], 239 (7) [267-CO], 225 (58) [269-CO_2], 224 (100), 223 (60) [267-CO_2], 222 (99), 197 (75) [225-CO], 195 (78) [223-CO], 182 (12), 173 (14), 171 (16), 169 (14), 157 (22) [$C_6H_4Br^+$], 155 (20) [$C_6H_4Br^+$], 144 (87), 116 (97), 89 (48), 76 (22), 63 (20), 53 (18).

1.1.16. 2,2-Dimethyl-5-(4-benzyloxycarbonyl-phenylamino-methylene)-[1.3]dioxan-4,6-dione (10b). A solution of 4.6 g (31.9 mmol) Meldrum′s acid (**13**) and 30 ml (273.9 mmol) methyl orthoformate (**14**) was heated to reflux for 2 h under argon. At room temperature 4.99 g (22.0 mmol) benzyl 4-amino benzoate (**12b**) were added and the reaction mixture was heated for another 6 h under reflux. The precipitate was collected after cooling followed by recrystallization from methanol to yield 7.56 g (90%) **10b** as pale yellow crystals. Mp.: 194.5–196°C (methanol). R_f=0.20 (toluene/ethyl acetate=9:1). IR (KBr): ν= 3164 cm^{-1} (NH); 3031, 3008 (arom. CH, C=CH); 2993 (CH); 1723, 1683 (C=O); 1634 (C=C); 1605; 1581; 1461; 1414; 1379; 1310; 1282. UV (acetonitrile): λ_{max} (log ϵ)=223 nm (4.19), 335 (4.59). ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.74 (s, 6H, 2×CH_3), 5.35 (s, 2H, $CO_2CH_2C_6H_5$), 7.27 (d, ^3J=9.0 Hz, 2H, 2′H, 6′H), 7.28–7.41 (m, 5H, $CO_2CH_2C_6H_5$), 8.13 (d, ^3J=9.0 Hz, 2H, 3′H, 5′H), 8.67 (d, ^3J=14.0 Hz, 1H, =CH), 11.29 (d_{br}, ^3J=14.0 Hz, 1H, NH, D_2O exchangeable). ^{13}C NMR (68 MHz, $CDCl_3$): δ=27.12 (2×CH_3), 67.04 ($CO_2CH_2C_6H_5$), 88.65 (C-2), 105.48 (C-5), 117.33 (C-2′, C-6′), 128.18 (C-4′), 128.33 (C-3″, C-5″)*, 128.43 (C-4″), 128.65 (C-2″, C-6″)*, 131.89 (C-3′, C-5′), 135.69 (C-1″), 141.38 (C-1′), 151.94 (CH), 163.17 (C=O), 165.20, 165.39 ($CO_2CH_2C_6H_5$, C=O). MS (70 eV); *m/z* (%): 381 (18) [M^+], 323 (86) [M^+ C_3H_6O], 278 (53), 172 (21), 144 (100), 91 (86) [$C_7H_7^+$], 65 (5) [$C_5H_5^+$]. Anal. calcd. for $C_{21}H_{19}NO_6$ (381.38): C, 66.14; H, 5.02. Found: C, 66.31; H, 4.91.

1.1.17. 6-Bromo-4-oxo-4*H*-quinoline (11a). 5.75 g (17.6 mmol) **10a** were dissolved in 91 ml hot diphenyl ether and refluxed until the formation of gaseous products ceased. The product was precipitated by cooling and subsequent mixing with 91 ml pentane. After 48 h at room temperature the precipitate was isolated by filtration followed by washing with 68 ml pentane and drying under vacuum (1.33×10^{-3} mbar). Purification of the crude product by sublimation (200°C, 1.33×10^{-3} mbar) delivered 2.82 g (72%) **11a** as a colourless solid. Mp.: 286–291°C. R_f=0.47 (ethyl acetate/ethanol=7:3). IR (KBr): ν=3300–2500 cm^{-1} (NH); 3061 (arom. CH, C=CH); 1625 (C=O); 1603 (C=C); 1552; 1510; 1465; 1346; 1304; 1198. UV (acetonitrile): λ_{max} (log ϵ)=212 nm (4.33), 236 (4.03), 292 (3.52), 326 (3.72), 339 (3.74). ^{1}H NMR (270 MHz, CD_3OD / [D_6] DMSO): δ=6.32 (d, ^3J=7.5 Hz, 1H, 3H), 7.52 (d, ^3J=9.0 Hz, 1H, 8H), 7.80 (dd, ^4J=2.5 Hz, ^3J=9.0 Hz, 1H, 7H), 7.98 (d, ^3J=7.5 Hz, 1H, 2H), 8.35 (d, ^4J=2.5 Hz, 1H, 5H). ^{13}C NMR (68 MHz, CD_3OD / [D_6] DMSO): δ=110.23 (C-3), 118.47

(C-6), 121.75 (C-8), 128.11 (C-4a), 128.69 (C-5), 136.43 (C-7), 140.30 (C-8a), 141.74 (C-2), 179.26 (C-4). MS (70 eV); *m/z* (%): 225 (99) [M^+], 223 (100) [M^+], 197 (17) [M^+-CO], 195 (18) [M^+-CO], 169 (8), 144 (12) [M^+-Br], 116 (37), 89 (17). Anal. calcd. for C_9H_6BrNO (224.06): C, 48.25; H, 2.70. Found: C, 48.10; H, 2.82.

1.1.18. 6-Benzyloxycarbonyl-4-oxo-4*H*-quinoline (11b). 4.68 g (12.3 mmol) **10b** were dissolved in 74 ml hot diphenyl ether and refluxed until the formation of gaseous products ceased. The product was precipitated by cooling and subsequent mixing with 74 ml pentane. After 18 h at room temperature the precipitate was isolated by filtration followed by washing with 150 ml pentane and drying under vacuum (1.33×10^{-3} mbar). Flash chromatography of the crude product on 95 g silica gel (ethyl acetate/ethanol=4:1) gave 2.53 g (74%) **11b** as a pale yellow solid. Mp.: 244–247°C. R_f=0.44 (ethyl acetate/ethanol=4:1). IR (KBr): ν=3300–2700 cm^{-1} (N—H); 3061 (arom. CH, C=CH); 2970, 2885, 2835 (CH); 1717 (C=O, ester); 1635 (C=O); 1559; 1498; 1280; 1246. UV (acetonitrile): λ_{max} (log ϵ)=221 nm (3.97), 250 (3.47), 258 (3.47), 305 (3.20), 325 (3.31), 335 (3.33). ^{1}H NMR (270 MHz, CD_3OD/[D_6] DMSO): δ=5.44 (s, 2H, $CO_2CH_2C_6H_5$), 6.33 (d, ^3J=7.5 Hz, 1H, 3H), 7.38–7.55 (m, 5H, $CO_2CH_2C_6H_5$), 7.68 (d, ^3J=9.0 Hz, 1H, 8H), 8.02 (d, ^3J=7.5 Hz, 1H, 2H), 8.30 (dd, ^4J=2.0 Hz, ^3J=9.0 Hz, 1H, 7H), 8.94 (d, ^4J=2.0 Hz, 1H, 5H). ^{13}C NMR (68 MHz, CD_3OD/[D_6] DMSO): δ=67.96 ($CO_2CH_2C_6H_5$), 111.08 (C-3), 120.16 (C-8), 126.18 (C-6)*, 126.61 (C-4a)*, 129.10 (C-4′), 129.45 (C-5, C-3′, C-5′)*, 129.79 (C-2′, C-6′)*, 133.27 (C-7), 137.63 (C-1′), 142.03 (C-2), 144.28 (C-8a), 166.81 ($CO_2CH_2C_6H_5$), 180.19 (C-4). MS (70 eV); *m/z* (%): 279 (26) [M^+], 172 (100) [M^+-C_7H_7O], 145 (18), 116 (10), 91 (64) [$C_7H_7^+$], 65 (7) [$C_5H_5^+$].

1.1.19. 1-Benzyloxycarbonyl-6-bromo-4-oxo-4*H*-quinoline (4c). 1.00 g (4.5 mmol) **11a** was added to a suspension of 0.30 g (12.5 mmol) sodium hydride in 20 ml dry THF under argon. At 60°C 1.15 g (6.7 mmol) benzyl chloroformate was added dropwise and the reaction mixture was stirred for 24 h at room temperature. After quenching with 13 ml water the mixture was neutralized with 2N hydrochloric acid and extracted with dichloromethane (3×15 ml). The combined organic phases were dried over sodium sulfate and the solvent was removed at reduced pressure on a rotary evaporator. Finally the crude product was purified by crystallization from cyclohexane/ethyl acetate=1:2 to yield 1.23 g (77%) **4c** as pale yellow crystals. Mp.: 134–137°C (cyclohexane/ethyl acetate=1:2). R_f=0.27 (cyclohexane/ethyl acetate=2:1). IR (KBr): ν=3067 cm^{-1} (arom. CH, C=CH); 2985 (CH); 1754 (C=O, carbamate); 1644 (C=O); 1592; 1468; 1373; 1350; 1266; 1211. UV (acetonitrile): λ_{max} (log ϵ)=240 nm (4.40), 328 (4.10). ^{1}H NMR (270 MHz, $CDCl_3$): δ=5.45 (s, 2H, $CO_2CH_2C_6H_5$), 6.25 (d, ^3J=8.5 Hz, 1H, 3H), 7.40–7.44 (m, 5H, 2′H, 3′H, 4′H, 5′H, 6′H), 7.72 (dd, ^4J=2.5 Hz, ^3J=9.5 Hz, 1H, 7H), 8.35 (d, ^3J=8.5 Hz, 1H, 2H), 8.47 (d, ^4J=2.5 Hz, 1H, 5H), 8.59 (d, ^3J=9.5 Hz, 1H, 8H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=70.76 ($CO_2CH_2C_6H_5$), 112.60 (C-3), 119.51 (C-6), 122.03 (C-8), 127.96 (C-4a), 128.91 (C-3′, C-5′)*, 128.98 (C-2′, C-6′)*, 129.11, 129.37 (C-4′, C-5), 133.67 (C-1′), 135.72 (C-7), 137.21 (C-8a), 138.34 (C-2), 150.97 ($CO_2CH_2C_6H_5$), 177.47 (C-4). MS (70 eV); *m/z* (%): 359 (2) [M^+], 357 (2) [M^+], 315 (1) [M^+-CO_2], 313 (3) [M^+-CO_2], 150 (3), 147 (9), 119 (3), 116 (3), 91 (100) [$C_7H_7^+$], 65 (5) [$C_5H_5^+$]. Anal. calcd. for $C_{17}H_{12}BrNO_3$ (358.19): C, 57.01; H, 3.38. Found: C, 56.74; H, 3.60.

1.1.20. 6-Bromo-1-ethoxycarbonyl-4-oxo-4*H*-quinoline (4d). 1.00 g (4.5 mmol) **11a** was added to a suspension of 0.28 g (11.7 mmol) sodium hydride in 20 ml dry THF under argon. At 50°C 1.25 g (11.5 mmol) ethyl chloroformate was added dropwise and the reaction mixture was stirred for 48 h at room temperature. After quenching with 7.1 ml water the mixture was neutralized with 2N hydrochloric acid and extracted with dichloromethane (3×20 ml). The combined organic phases were dried over sodium sulfate and the solvent was removed at reduced pressure on a rotary evaporator. Finally the crude product was purified by flash chromatography on 95 g silica gel (cyclohexane/ethyl acetate=1.9:1) to yield 0.96 g (73%) **4d** as a colourless solid. Mp.: 104–105°C. R_f=0.18 (cyclohexane/ethyl acetate=2:1). IR (CCl_4): ν=3130 cm^{-1} (arom. CH, C=CH); 2985 (CH); 1758 (C=O, carbamate); 1659 (C=O); 1621 (C=C); 1594; 1468; 1444; 1370; 1345; 1270; 1216. UV (acetonitrile): λ_{max} (log ϵ)=216 nm (4.17), 240 (4.37), 328 (4.06). ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.47 (t, ^3J=7.0 Hz, 3H, $CO_2CH_2CH_3$), 4.52 (q, ^3J=7.0 Hz, 2H, $CO_2CH_2CH_3$), 6.28 (d, ^3J=8.5 Hz, 1H, 3H), 7.74 (dd, ^4J=2.5 Hz, ^3J=9.5 Hz, 1H, 7H), 8.37 (d, ^3J=8.5 Hz, 1H, 2H), 8.48 (d, ^4J=2.5 Hz, 1H, 5H), 8.58 (d, ^3J=9.5 Hz, 1H, 8H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=14.16 ($CO_2CH_2CH_3$), 65.36 ($CO_2CH_2CH_3$), 112.47 (C-3), 119.44 (C-6), 122.03 (C-8), 127.99 (C-4a), 129.13 (C-5), 135.71 (C-7), 137.28 (C-8a), 138.46 (C-2), 151.10 ($CO_2CH_2CH_3$), 177.56 (C-4). MS (70 eV); *m/z* (%): 297 (97) [M^+], 295 (96) [M^+], 253 (5), 251 (5), 238 (20), 236 (19), 225 (70), 223 (100), 197 (10), 196 (10), 195 (10), 194 (10), 172 (5), 170 (5), 147 (5), 144 (19), 116 (21), 115 (23), 89 (10), 88 (10), 29 (97) [$C_2H_5^+$]. Anal. calcd. for $C_{12}H_{10}BrNO_3$ (296.12): C, 48.67; H, 3.40. Found: C, 48.97; H, 3.56.

1.1.21. 1,6-Dibenzyloxycarbonyl-4-oxo-4*H*-quinoline (4e). 20.00 g (71.6 mmol) **11b** was added to a suspension of 2.23 g (93.1 mmol) sodium hydride in 143 ml dry THF and the mixture was refluxed for 1 h under argon. 15.8 g (93.1 mmol) benzyl chloroformate was added dropwise and the reaction mixture was stirred for 1 h at room temperature. After quenching with 72 ml water the mixture was extracted with dichloromethane (3×70 ml). The combined organic phases were dried over sodium sulfate and the solvent was removed at reduced pressure on a rotary evaporator. Finally the crude product was purified by flash chromatography on 500 g silica gel (diethyl ether/light petroleum=1:1) to give 26.6 g (90%) **4e** as a colourless solid. Mp.: 110–111°C. R_f=0.20 (cyclohexane/ethyl acetate=2:1). IR (KBr): ν=3052 cm^{-1}, 3030 (arom. CH, C=CH); 2952 (CH); 1760 (C=O, carbamate); 1715 (C=O, ester); 1649 (C=O); 1610 (C=C); 1456; 1353; 1266; 1213. UV (acetonitrile): λ_{max} (log ϵ)=210 nm (4.46), 253 (4.41), 260 (4.44), 287 (3.40), 307 (4.05), 319 (4.12). ^{1}H NMR (270 MHz, $CDCl_3$): δ=5.38 (s, 2H, $CO_2CH_2C_6H_5$), 5.46 (s, 2H, $NCO_2CH_2C_6H_5$), 6.27 (d, ^3J=9.0 Hz, 1H, 3H), 7.32–7.46 (m, 10H, 2′H, 3′H, 4′H, 5′H, 6′H, 2″H, 3″H, 4″H, 5″H, 6″H), 8.30 (dd, ^4J=2.5 Hz, ^3J=9.0 Hz, 1H, 7H), 8.35 (d, ^3J=9.0 Hz, 1H, 2H), 8.72 (d, ^3J=9.0 Hz, 1H, 8H), 9.02 (d, ^4J=2.5 Hz, 1H, 5H). ^{13}C NMR

(68 MHz, $CDCl_3$): δ=67.09 ($CO_2CH_2C_6H_5$), 70.89 ($NCO_2CH_2C_6H_5$), 113.13 (C-3), 120.33 (C-8), 126.30 (C-6), 127.20 (C-4a), 128.37 (C-5), 128.42 (C-3″, C-5″)*, 128.63 (C-2″, C-6″)*, 128.75 (C-4″)*, 128.96 (C-3′, C-5′)*, 129.02 (C-2′, C-6′)*, 129.44 (C-4′)*, 133.41 (C-7), 133.65 (C-1′), 135.71 (C-1″), 138.47 (C-2), 141.31 (C-8a), 151.07 ($NCO_2CH_2C_6H_5$), 165.26 ($CO_2CH_2C_6H_5$), 178.27 (C-4). MS (70 eV); *m/z* (%): 413 (5) [M^+], 369 (60), 262 (5), 172 (4), 91 (100) [$C_7H_7^+$], 65 (7) [$C_5H_5^+$], 44 (44). HRMS calcd. for $C_{25}H_{19}NO_5$: 413.1263. Found: 413.1263.

1.1.22. 6-Benzyloxycarbonyl-1-ethoxycarbonyl-4-oxo-4*H*-quinoline (4f). 3.00 g (10.7 mmol) **11b** was added to a suspension of 0.33 g (13.9 mmol) sodium hydride in 21 ml dry THF and the mixture was refluxed for 1 h under argon. 1.51 g (13.9 mmol) ethyl chloroformate was added dropwise and the reaction mixture was stirred for 2 h at room temperature. After quenching with 11 ml water the mixture was extracted with dichloromethane (3×10 ml). The combined organic phases were dried over sodium sulfate and the solvent was removed at reduced pressure on a rotary evaporator. Finally the crude product was purified by flash chromatography on silica gel (ethyl acetate/light petroleum=2:1) to yield 3.52 g (94%) **4f** as a colourless solid. Mp.: 132–134°C. R_f=0.13 (cyclohexane/ethyl acetate=2:1). IR (KBr): ν=3116 cm^{-1}, 3059 (arom. CH, C=CH); 2999 (CH); 1744 (C=O, carbamate); 1721 (C=O, ester); 1657 (C=O); 1610 (C=C); 1480; 1448; 1387; 1365; 1332; 1294; 1282; 1223. UV (acetonitrile): λ_{max} (log ϵ)=224 nm (4.40), 252 (4.37), 260 (4.40), 287 (3.98), 308 (4.03), 320 (4.09). ^{1}H NMR (270 MHz, $CDCl_3$): δ=1.48 (t, ^3J=7.0 Hz, 3H, $CO_2CH_2CH_3$), 4.54 (q, ^3J=7.0 Hz, 2H, $CO_2CH_2CH_3$), 5.39 (s, 2H, $CO_2CH_2C_6H_5$), 6.30 (d, ^3J=8.5 Hz, 1H, 3H), 7.35–7.46 (m, 5H, 2″H, 3″H, 4″H, 5″H, 6″H), 8.31 (dd, ^4J=2.0 Hz, ^3J=9.0 Hz, 1H, 7H), 8.37 (d, ^3J=8.5 Hz, 1H, 2H), 8.71 (d, ^3J=9.0 Hz, 1H, 8H), 9.03 (d, ^4J=2.0 Hz, 1H, 5H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=14.16 ($CO_2CH_2CH_3$), 65.48 ($CO_2CH_2CH_3$), 67.08 ($CO_2CH_2C_6H_5$), 112.96 (C-3), 120.31 (C-8), 126.29 (C-6), 127.10 (C-4a), 128.37 (C-5), 128.41 (C-3″, C-5″)*, 128.63 (C-2″, C-6″)*, 128.76 (C-4″), 133.36 (C-7), 135.71 (C-1″), 138.60 (C-2), 141.33 (C-8a), 151.16 ($CO_2CH_2CH_3$), 165.28 ($CO_2CH_2C_6H_5$), 178.34 (C-4). MS (70 eV); *m/z* (%): 351 (20) [M^+], 244 (44) [M^+-C_7H_7O], 234 (5), 217 (12), 200 (12), 172 (22), 144 (5), 116 (5), 91 (100) [$C_7H_7^+$], 65 (5) [$C_5H_5^+$]. Anal. calcd. for $C_{20}H_{17}NO_5$ (351.36): C, 68.37; H, 4.88. Found: C, 68.43; H, 5.04.

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