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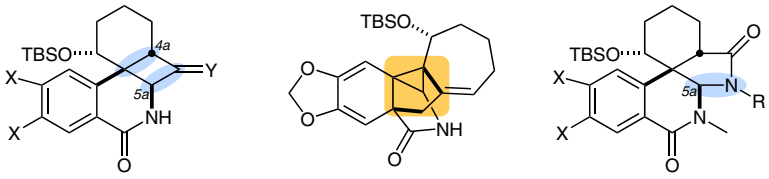
Photocycloaddition and Rearrangement Reactions in a Putative Route to the Skeleton of Plicamine-Type Alkaloids

Karl-Heinz Rimböck
Alexander Pöthig
Thorsten Bach*

Department Chemie and Catalysis Research Center (CRC),
Technische Universität München,
Lichtenbergstr. 4, 85747 Garching, Germany
thorsten.bach@ch.tum.de



[2+2] photocycloaddition products (Y = CH_2)

meta-photocycloaddition by-product

rearrangement: migration of C5a

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Abstract Two isoquinolones were prepared, to which an allenyl side chain was linked at position C4 via a stereogenic silyloxy-substituted carbon atom. Intramolecular [2+2] photocycloaddition reactions of these substrates proceeded with high diastereoselectivity and delivered the respective cyclobutanes with an exocyclic methylene group (83% and 49% yield). With the 5,6-dioxoloisoquinolone precursor an unprecedented *meta*-photocycloaddition was observed as a significant side reaction, which occurred at positions C4 and C8a of the isoquinolone skeleton. The cyclobutane products were, after N-alkylation and transformation into the respective cyclobutanones (22–57%), subjected to various rearrangement reactions. In detail, a direct photochemical rearrangement, thermal and photochemical Beckmann rearrangements, and Baeyer–Villiger oxidation reactions were studied. In all cases, products were found, which resulted from cleavage of the amino-substituted cyclobutane bond, but not from the desired cleavage of the alternative alkyl-substituted cyclobutane bond.

Key words alkaloids, cycloaddition, heterocycles, isoquinolones, photochemistry, rearrangements

Plicamine (**1**), first isolated from *Galanthus plicatus* ssp. *byzantinus* (Amaryllidaceae),[1] and structurally related natural products with a decahydroindolo[3,3a-*c*]isoquinoline skeleton (**A**)[2] are unique among the Amaryllidaceae alkaloids, because they contain two nitrogen atoms as opposed to the large majority of these alkaloids, which exhibit only a single nitrogen atom (Figure 1).

Biosynthetically, it is assumed that the second nitrogen atom stems from a tyramine, which intercepts a norbelladine-derived key intermediate,[3] which is known to lead to alkaloids of the crinine and tazettine type.[4] Extensive synthetic work on plicamine-type alkaloids has been performed by Ley and co-workers, who developed a concise access to skeleton **A** by an oxidative aromatic coupling between positions C12a and C12b.[5] Polymer-based reagents were mainly used in their work, which culminated in the first total syntheses of (+)-plicamine,[5a,b] (+)-plicane, and (–)-obliquine.[5c]

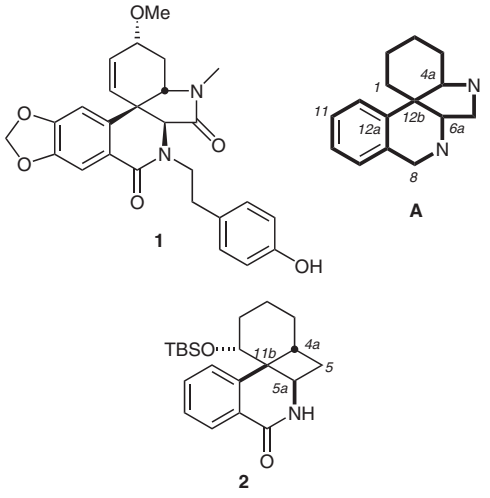
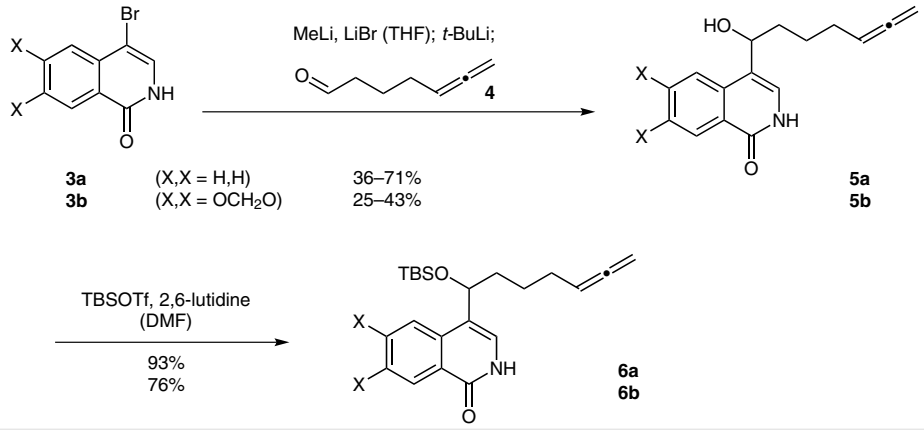


Figure 1 Structure of (+)-plicamine (**1**), the tetracyclic skeleton **A** of plicamine-type alkaloids, and the intramolecular [2+2] photocycloaddition product **2**

We became interested in plicamine-type alkaloids as synthetic targets in connection with recent work on the [2+2] photocycloaddition reaction of isoquinolones.[6] Most notably, we found that product **2** with an octahydro-1*H*-benzo[2,3]cyclobuta[1,2-*c*]isoquinoline core could be readily accessed by a diastereoselective intramolecular isoquinolone [2+2] photocycloaddition, in which the bonds between carbon atoms C4a/C11b and C5/C5a were established.[6a] It seemed promising to attempt a ring expansion of the cyclobutane to a pyrrolidine ring by 1,2-migration of carbon atom C4a to an electron-deficient nitrogen atom, which was to be installed at carbon atom C5.

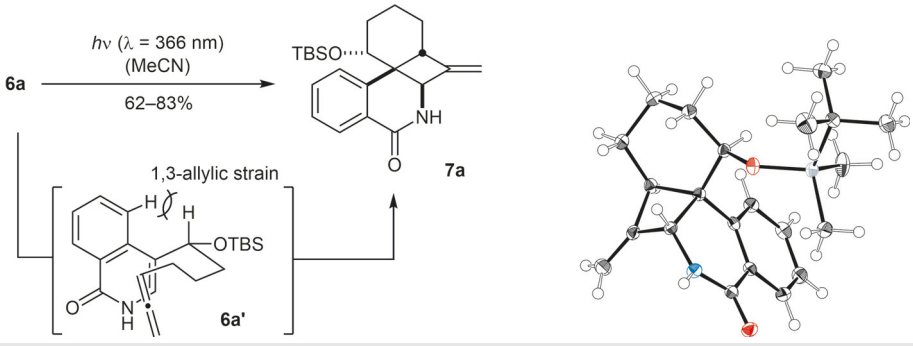


Scheme 1 Synthesis of allenic irradiation precursors **6** from 4-bromoisoquinolones **3**

In this paper, we provide full details on the synthesis of appropriate precursors for the attempted ring expansion reaction. For the [2+2] photocycloaddition, allenes were used to generate products with a functionalization at carbon atom C5. Unexpectedly, one of the allenyl-substituted precursors led to a photocycloaddition product, which formally resulted from a yet unprecedented *meta*-addition to the isoquinolone core. The attempted rearrangement reactions were performed thermally (Beckmann rearrangement) or photochemically. In all cases, a preference for migration of carbon atom C5a versus C4a was found resulting in the formation of the decahydroisoindolo[1,7a-*c*]isoquinoline skeleton, which is regioisomeric to skeleton **A**.

The synthetic work commenced with the preparation of the starting materials **6** from the respective 4-bromoisoquinolones **3**[7] (Scheme 1). In the first step, deprotonation and a subsequent bromine–lithium exchange reaction generate a putative dianion, which can be trapped with suitable electrophiles.[6a,7] While reactions with simple aldehydes and with DMF gave good results, the reaction with aldehyde **4**[8] turned out to be capricious and yields were variable. Protection of the resulting secondary alcohols with a *tert*-butyldimethylsilyl (TBS) group was facile if the respective triflate (OTf) was used as silylating agent. Although other methods for the construction of compounds **6** were tested, the brevity of the depicted route was considered a significant benefit and led us eventually to perform the synthesis of irradiation precursors **6** consistently by this route.[9]

In line with our previous work on the intramolecular [2+2] photocycloaddition of olefins to isoquinolones,[6a] the reaction of allenic substrate **6a** proceeded smoothly and delivered the expected product **7a** in good yields (Scheme 2). While the straight isomer clearly prevailed, minor amounts of the crossed regiosiosmer were detected. For solubility reasons the reaction was performed in acetonitrile as the solvent (c = 25 mM). At the chosen concentration, the product precipitated and could be easily separated from its regioisomer and from unreacted starting material by filtration. The diastereoselectivity of the [2+2] photocycloaddition was perfect and is explained by 1,3-allylic strain[10] operating between the aryl group and the substituents at the stereogenic center. The relative configuration of product **7a** was unambiguously established by its crystal structure.



Scheme 2 Diastereoselective intramolecular [2+2] photocycloaddition of isoquinolone **6a** to product **7a** (left); proof of relative configuration for **7a** by single-crystal X-ray crystallography (right)

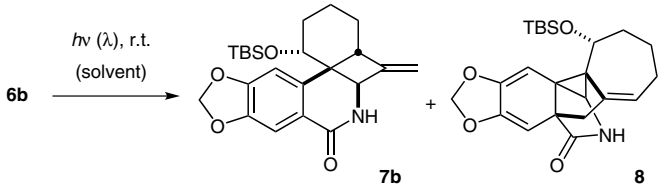
It has been shown for intermolecular [2+2] photocycloaddition reactions of isoquinolones that substituents at the isoquinolone do not alter the reaction course of the reaction with olefins.[6c] The substitution of the isoquinolone ring in substrate **6b** seemed therefore to be a minor modification and was not expected to influence the outcome of the photochemical reaction. It was the more surprising that – upon irradiation at λ = 366 nm – a second product accompanied the desired [2+2] photocycloaddition product **7b** in significant amounts. The formation of the by-product could be suppressed at the expense of total yield, if the reaction was performed in chlorinated solvents (Table 1, entries 1–3). These conditions allowed us to isolate the desired product essentially free from other isomers. In acetone (entry 4) and other solvents (entries 5–7), however, the undesired reaction pathway competed successfully with the [2+2] photocycloaddition reaction. The by-product **8** could be separated by column chromatography and was obtained in pure form. It was proven to be a constitutional isomer of **7b**, but the aromatic ring of the isoquinolone was no longer intact.

NMR data suggested that compound **8** was the product of an intramolecular *meta*-photocycloaddition, but final proof for its constitution and relative configuration could only be obtained by single-crystal X-ray crystallography (Scheme 3). Apparently, the allene adds with its terminal double bond across the isoquinolone ring, forming carbon–carbon bonds to the former isoquinolone carbon atoms C4 and C8a, while the former carbon atoms C4a and C3 of the isoquinolone ring establish a cyclopropane bond. To the best of our knowledge, this type of *meta*-photocycloaddition[12] has not yet been reported. In order to illustrate the reaction course the reaction is depicted stepwise via **9** and **10** but it is mechanistically not clear whether it occurs on the singlet or triplet hypersurface.

Further exploratory experiments with other isoquinolone derivatives revealed that the isoquinolone *meta*-photocycloaddition reaction requires the presence of the 1,3-dioxole ring and of a tethered allene. If either one of them is absent the normal [2+2] photocycloaddition mode is observed.[13]

With the more readily accessible product **7a**, initial studies regarding a potential rearrangement were undertaken. The required *para*-hydroxyphenethyl chain was attached to the nitrogen atom by alkylation with bromide **11** (Scheme 4). The resulting product **12** was subjected to oxidative cleavage of the double bond. Dihydroxylation with *N*-methylmorpholine-*N*-oxide (NMO) was followed by oxidative diol cleavage[14] to generate the desired cyclobutanone **13** in moderate yields. There was no precedence for Beckmann rearrangement reactions[15,16] at cyclobutanones of this type. However, it had been reported that α,α-dichlorocyclobutanones underwent the desired rearrangement reaction upon treatment with the Tamura reagent,[17] *O*-mesitylenesulfonylhydroxylamine (MSH).[18] In these examples, it was not the chloro-substituted alkyl group, which underwent the migration but the other ketone substituent. We hoped that the amino-substituted alkyl group would behave similarly and would allow for a preferred migration of the secondary alkyl group. Initially, we were pleased to note that exposure of cyclobutanone **13** to MSH led in high yields to a single rearrangement product, which was shown to be a γ-lactam (pyrrolidinone).

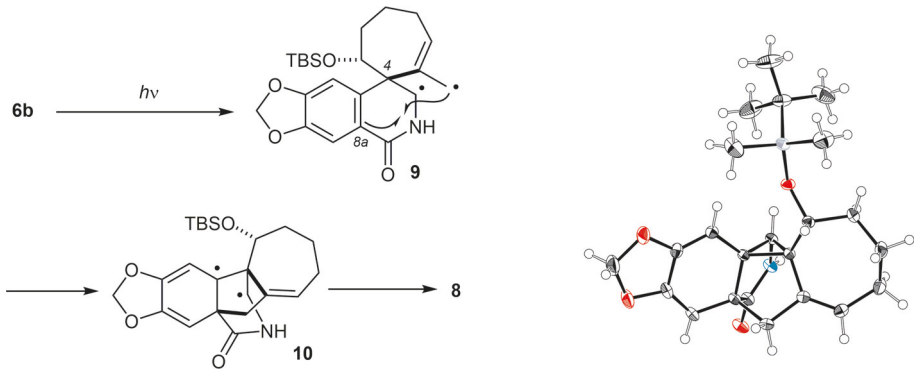
Table 1 Irradiation Products **7b** and **8** Obtained under Various Conditions from Isoquinolone **6b**



7b 8

Entry	Solvent	*c* (mM)	λ (nm)[a]	Time (h)[b]	Yield (%)[c]	**7b**/**8**	r.r.[d]
1	1,2-DCE[e]	5	366	16	41	89:11	>95:5
2	1,3-DCP[f]	5	366	17	49	>99:1	>95:5
3	1,3-DCP[f]	10	366	14	39	93:7	94:6
4	acetone	5	350	6	48	77:23	>95:5
5	benzene	5	366	18	65	58:42	85:15
6	toluene	5	366	19	58	60.40	84:16
7	Et_2O	5	366	17	60	61:39	87:13

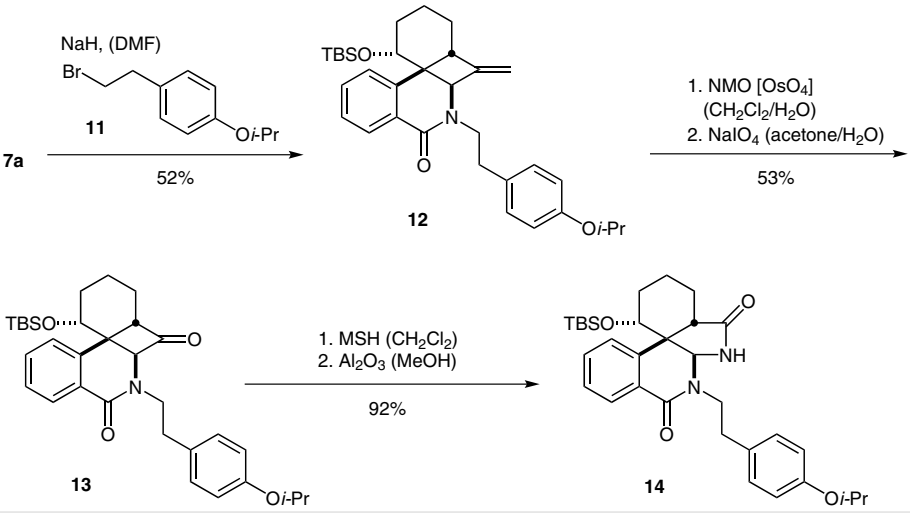
[a] Emission maximum of the fluorescent light source.[11]
[b] Time for complete conversion at the indicated conditions.
[c] Combined yield for isolated products **7b** and **8**.
[d] The regioisomeric ratio (r.r.) refers to the ratio of product **7b** to its regioisomer, which was formed in minor amounts and which was not separable from **7b**.
[e] 1,2-Dichloroethane.
[f] 1,3-Dichloropropane.



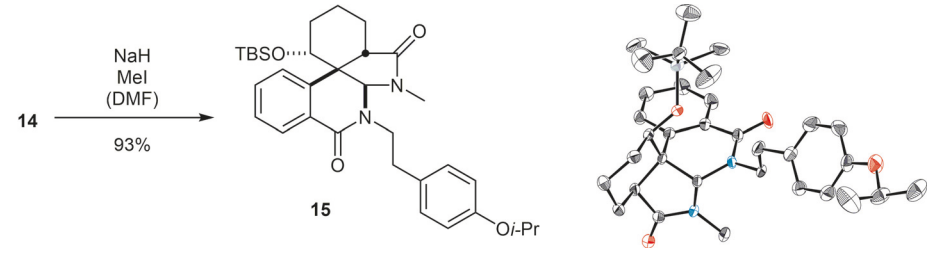
Scheme 3 Stepwise mechanism for the formation of product **8** from substrate **6b** (left); proof of constitution and configuration for **8** by single-crystal X-ray crystallography (right)

Attempts to elucidate the structure of rearrangement product **14** by NMR led to some ambiguities and we therefore strived to prove the structure by X-ray crystallography. After N-methylation of the γ-lactam core, a crystalline material was obtained, and its structure could be unequivocally elucidated (Scheme 5).

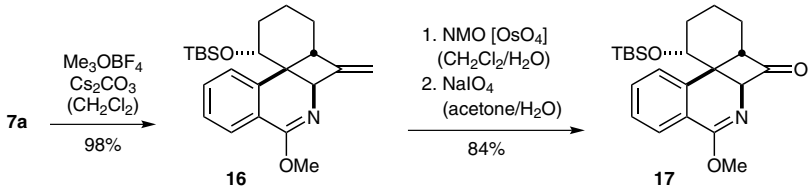
Disappointingly, the structure of product **15** revealed that the undesired migration pathway had been taken with the amino-substituted alkyl group migrating instead of the desired secondary alkyl group. We speculated that the observed migration was due to the fact that oxime formation at ketone **13** had for steric reasons occurred in favor of the *E*-diastereoisomer (relative to the amino-substituted alkyl



Scheme 4 Preparation of cyclobutanone **13** from [2+2] photocycloaddition product **7a** and Beckmann rearrangement to product **14**



Scheme 5 N-Methylation of amide **14** (left) and proof of constitution and configuration for **15** by single-crystal X-ray crystallography (right)

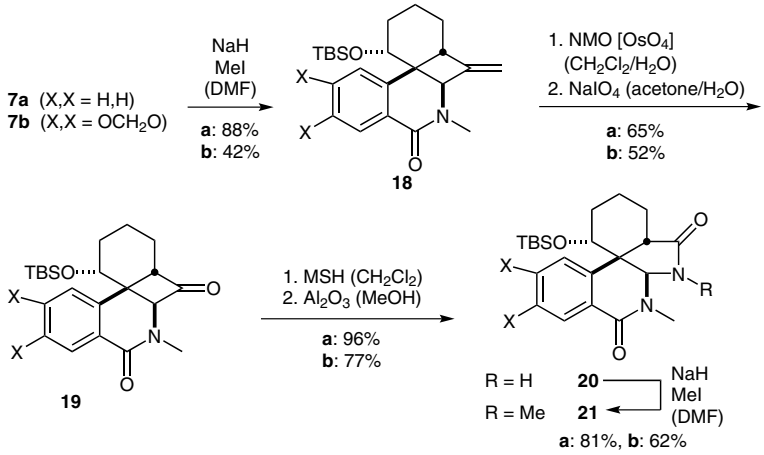


Scheme 6 Synthesis of cyclobutanone **17** from [2+2] photocycloaddition product **7a**

group). As a consequence, the typical *anti*-specific migration pathway invoked for the Beckmann rearrangement[16] would account for the observed regioselectivity. Attempts were therefore undertaken to minimize the steric bulk at the lactam site of the cyclobutanone. In a first set of experiments, lactam **7a** was converted into the respective imidate by treatment with Meerwein salt.[19] Product **16** was subsequently converted into cyclobutanone **17** by the established sequence of dihydroxylation/diol cleavage (Scheme 6). Application of the MSH protocol to this substrate did not provide any meaningful results and led only to unidentifiable products. It was possible to convert ketone **17** into the respective oxime by treatment with hydroxylamine and pyridine in CH_2Cl_2–MeOH (10:1). Despite extensive experimental efforts, conditions for a successful Beckmann rearrangement of the oxime could not be found.

Attempts to convert lactams **7a** and **7b** into the respective cyclobutanones without prior N-protection suffered from the instability of the products, which prohibited their isolation. Due to the reluctance of imidate **17** to undergo a Beckmann rearrangement, it was planned to attach a methyl group to the lactam nitrogen atom and study the regioselectivity of the Beckmann rearrangement with this substrate class. To this end, lactams **7a**,**b** were N-methylated (Scheme 7) under standard conditions.[20] The resulting products **18** were converted into cyclobutanones **19**, which in turn were submitted to the Tamura conditions of the Beckmann rearrangement. Disappointingly, the only isolable products in both cases were the undesired rearrangement products **20**. Their constitution was proven upon N-methylation of the pyrrolidinone nitrogen atom by comparison of their NMR spectra with the spectra of product **15**. In the Beckmann rearrangement of substrate **19b**, a second regioisomer was detected in the crude mixture in a ratio of 1:10 relative to the major product. It is likely that this product was the desired regioisomer but it could not be isolated. Starting from cyclobutanone **19a**, stoichiometric oxime formation was possible under the conditions given above for **17**. The oxime was formed as a 2:1 mixture of diastereoisomers but – like the former oxime – it could not be forced to undergo the desired rearrangement.

When preparing cyclobutanone **19b** under oxidative conditions from the respective diol (Scheme 7) we surprisingly found – apart from the desired product (52% yield) – the respective lactone **22b** (Figure 2) as a by-product (30% yield), which appears to be the product of a Baeyer–Villiger-type oxidation. Indeed, it could be shown that the more stable cyclobutanone **19a** underwent a clean Baeyer–Villiger oxidation[21,22] to lactone **22a** upon treatment with *meta*-chloroperbenzoic acid (*m*-CPBA) and sodium bicarbonate in CH_2Cl_2 (97% yield).[23] Expectedly, the more nucleophilic group migrated in the course of the rearrangement as proven by the crystal structure of γ-lactone **22a**.



Scheme 7 Synthesis of cyclobutanones **19** from [2+2] photocycloaddition products **7** and Beckmann rearrangement to products **20**

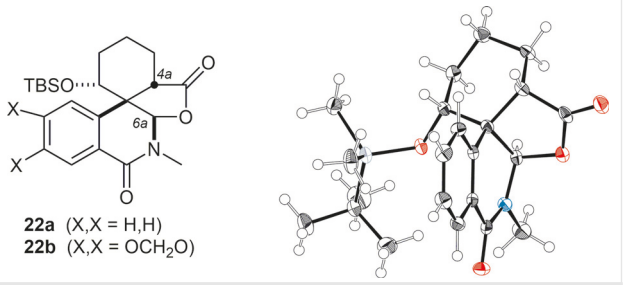
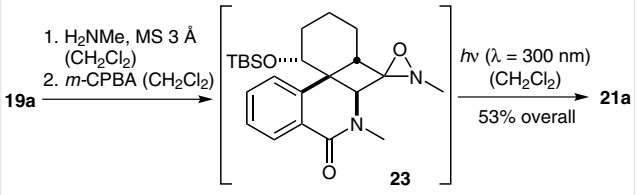


Figure 2 Structure of Baeyer–Villiger oxidation products **22** (left) and proof of constitution and configuration for **22a** by single-crystal X-ray crystallography (right)

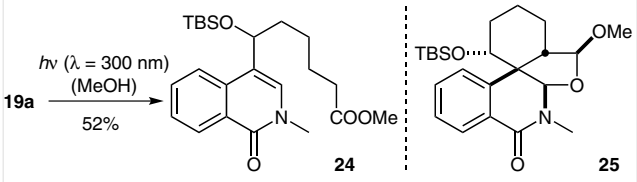
Since thermal variants of the Beckmann rearrangement had led either to the formation of the undesired regioisomer or had not proceeded at all, our interest shifted to a photochemical variant of the Beckmann rearrangement.[24,25] In this sequence, an oxaziridine is photochemically rearranged to the respective lactam. Consequently, cyclobutanone **19a** was first condensed with *N*-methylamine to the respective Schiff base. Without isolation, the solution of the imine was added at –40 °C to a solution of *m*-CPBA in CH_2Cl_2 to generate the required oxaziridine **23**. The reaction mixture was taken without workup into the photochemical step, which included a room temperature irradiation at λ = 300 nm. The three-step sequence delivered a single Beckmann-type rearrangement product, which turned out to be identical to the previous product **21a** (Scheme 8). In addition, indicating that the imine formation had been incomplete, lactone **22a** was isolated in 16% yield as result of a Baeyer–Villiger oxidation.



Scheme 8 Preparation of oxaziridine **23** and photochemical rearrangement to product **21a**

The outcome of the photochemical Beckmann rearrangement was surprising because the reaction has been employed previously to obtain products, which are regiochemically complimentary to the products of the thermal Beckmann rearrangement.[24a,e] Indeed, it has been shown that for stereoelectronic reasons there is a migration preference for the group which is *trans* to the free electron pair at the oxaziridine nitrogen atom.[26] In our case, the outcome of the rearrangement suggests that the oxaziridine is derived from a *Z*-configured imine, while the outcome of the thermal Beckmann rearrangement (Scheme 7) suggests that oxime formation occurred with *E*-selectivity. In the context of this work, further mechanistic studies were not undertaken but it appears – based on the results of stoichiometric oxime formation – that oxime formation from cyclobutanone **19a** is not selective (vide supra). Under the conditions of the MSH-initiated rearrangement *E*- and *Z*-oximes might equilibrate and eventually the higher migratory aptitude of the amino-substituted alkyl group (as seen in the Baeyer–Villiger oxidation, cf. Figure 2) could be decisive for selective product formation.

A final photochemical experiment was performed with cyclobutanone **19a**. A solution in methanol was irradiated at λ = 300 nm to initiate a Norrish type I cleavage. The reaction has been successfully applied to natural product total synthesis[27] and it was expected to lead to an acetal via an oxacarbene intermediate.[28] The major product, however, turned out to be ester **24**, which was isolated in 52% yield (Scheme 9). A by-product was obtained in 12% yield, to which acetal structure **25** was tentatively assigned based on its analytical data. In both cases, it is again the bond between carbon atoms C5a and C5, which is preferentially broken. Formation of compound **24** can be explained by Norrish type I cleavage of this bond and subsequent carbon–carbon bond fission between C4a and C11 (Figure 1) in the intermediate 1,4-diradical.[29] The resulting ketene is trapped by the solvent. Formation of acetal **25** can be explained by invoking the same intermediate, which closes to the five-membered oxacarbene, which in turn forms the acetal upon reaction with MeOH. The latter reaction has been suggested to occur on the singlet hypersurface.[28]



Scheme 9 Irradiation of cyclobutanone **19a** leads mainly to ester **24** as product of an α-cleavage with subsequent ketene formation; minor amounts of the oxacarbene rearrangement product **25** were obtained

In summary, we have shown in the first part of this study that intramolecular [2+2] photocycloaddition reactions of allenes to isoquinolones lead diastereoselectively to products with an octahydro-1*H*-benzo[2,3]cyclobuta[1,2-*c*]isoquinoline core. For substrate **6b** an unusual by-product was observed, which was shown to be the product of a yet unknown *meta*-photocycloaddition variant.

Attempts to rearrange the tetracyclic product skeleton to the decahydroindolo[3,3a-*c*]isoquinoline skeleton of plicamine-type alkaloids by migration of carbon atom C4a remained futile. Migration and carbon–carbon bond fission at the amino-substituted carbon atom C5a were preferred in all cases and led to the formation of undesired regioisomers. Baeyer–Villiger rearrangement product **22b** (Figure 2) could be of relevance to the synthesis of the plicamine-type

alkaloid *seco*-plicamine.[1] The latter compound exhibits a similar spiro skeleton but lacks the γ-lactam unit. Instead, it carries an amino group at C4a and a carbonyl group at C6a. It is apparent that these structural elements could be readily established from product **22b**.

General:[30] All reactions involving water-sensitive chemicals were carried out in flame-dried glassware under positive pressure of argon with magnetic stirring. Tetrahydrofuran, dichloromethane, and diethyl ether were purified using a SPS-800 solvent purification system (M. Braun). Triethylamine was distilled over calcium hydride. All other chemicals were either commercially available or prepared according to the cited references. For photochemical reactions, the reaction mixture was degassed by purging with argon in an ultrasonicating bath. Subsequently, the solution was transferred into Duran tubes (diameter: 1 cm, volume: 10 mL) and irradiated in a Rayonet RPR100 reactor, equipped with 16 fluorescent lamps (for emission spectra, see refs.[11] and the Supporting Information). The reactor was cooled with an internal fan, the operating temperature for photochemical reactions was ca. 35 °C. Thin-layer chromatography (TLC) was performed on silica-coated glass plates (silica gel 60 F_{254}) with detection by UV (λ = 254 nm) or $KMnO_4$ (0.5% in water) with subsequent heating. Flash chromatography was performed on silica gel 60 (Merck, 230–400 mesh) with the indicated eluent. Common solvents for chromatography [dichloromethane (CH_2Cl_2), pentane (P), ethyl acetate (EtOAc), methanol (MeOH)] were distilled prior to use. IR spectra were recorded on a JASCO IR-4100 (ATR) or Perkin-Elmer 1600 FT/IR. MS / HRMS measurements were performed on a Finnigan MAT 8200 or Thermo Fisher DFS (EI) / Finnigan LSQ classic or Thermo Fisher LTY Orbitrap XL (ESI). ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ at 303 K on a Bruker AV-250, Bruker AVHD-300, Bruker AV-360, Bruker AVHD-400, Bruker AV-500, or a Bruker AVHD-500 instrument. Chemical shifts are reported relative to $CHCl_3$ (δ = 7.26 ppm). Apparent multiplets that occur as a result of the accidental equality of coupling constants to those of magnetically non-equivalent protons are marked as virtual (*virt.*). The multiplicities of the ^{13}C NMR signal were determined by DEPT experiments, assignments are based on COSY, HMBC and HMQC experiments.

CAUTION: *O*-Mesitylenesulfonylhydroxylamine (MSH)[17] is a potential explosive and appropriate safety measures should be taken when working with this compound.

4-(1-Hydroxyhepta-5,6-dien-1-yl)isoquinolin-1(2*H*)-one (5a)

To a suspension of 4-bromoisoquinolin-1(2*H*)-one (**3a**;[7] 407 mg, 1.82 mmol, 1.00 equiv) in THF (20 mL) at 0 °C was added dropwise a solution of MeLi·BrLi (2.2 M in Et_2O, 910 µL, 218 mg, 2.00 mmol, 1.10 equiv). After stirring for 10 min, the reaction mixture was cooled to –78 °C and a solution of *t*-BuLi (1.6 M in pentane, 2.50 mL, 256 mg, 4.00 mmol, 2.20 equiv) was added dropwise and the mixture stirred at –78 °C for 20 min. Subsequently hepta-5,6-dienal (**4**;[8] 400 mg, 3.63 mmol, 2.00 equiv) was added quickly in one portion whereupon the cooling bath was removed. The temperature was adjusted to –40 °C with another cooling bath. The mixture was stirred for 2 h at –40 °C. Subsequently, the reaction was quenched with sat. aq NH_4Cl (7 mL) and the resulting slurry was warmed to r.t. After addition of H_2O (7 mL) and CH_2Cl_2 (40 mL), the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 3 × 18 cm, CH_2Cl_2–MeOH, 95:5) to give **5a** as a colorless solid; yield: 315 mg (1.23 mmol, 68%); mp 129–130 °C; R_f <0.10 (CH_2Cl_2–MeOH, 95:5) [UV/CAM].

IR (ATR): 3423 (m), 3146 (w), 3050 (w), 2904 (m), 1959 (w), 1632 (vs), 1605 (s), 1070 (m), 801 (vs), 689 cm^{-1} (s).

^{1}H NMR (360 MHz, $CDCl_3$): δ = 10.00 (br s, 1 H, NH), 8.48 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1 H, C8-H), 7.87 (d, ^3J = 8.2 Hz, 1 H, C5-H), 7.73 (virt. td, $^3J \cong 7.7$ Hz, ^4J = 1.4 Hz, 1 H, C6-H), 7.55 (virt. t, $^3J \cong 7.7$ Hz, 1 H, C7-H), 7.24 (d, J = 4.0 Hz, 1 H, C3-H), 5.12 (virt. quint, $^3J \cong {}^4J$ = 6.7 Hz, 1 H, C5′-H), 5.04 (td, ^3J = 7.9 Hz, J = 4.0 Hz, 1H, C1′-H), 4.67 (dt, ^4J = 6.7 Hz, ^5J = 3.2 Hz, 2H, C7′-H), 2.10 (virt. qt, $^3J \cong 6.9$ Hz, ^5J = 3.2 Hz, 2 H, C4′-H_2), 2.05–1.83 (m, 2 H, C2′-H_2), 1.80–1.46 (m, 2 H, C3′-H_2).

^{13}C NMR (91 MHz, $CDCl_3$): δ = 208.5 (s, C6′), 163.8 (s, C1), 136.2 (s, C4a), 132.5 (d, C6), 127.9 (d, C8a), 126.6 (s, C8), 125.9 (d, C7), 124.9 (d, C3), 123.1 (s, C5), 119.5 (d, C4), 89.6 (d, C5′), 75.0 (d, C1′), 69.8 (t, C7′), 36.4 (t, C2′), 27.9 (t, C4′), 25.5 (t, C3′).

MS (EI, 70 eV): m/z (%) = 237 (100, [M$^+$ – H_2O]), 222 (65), 208 (27), 195 (12), 184 (25), 158 (21), 128 (11), 115 (10), 77 (12).

HRMS (EI): m/z [(M – H_2O)$^+$] calcd for $C_{16}H_{15}NO$: 237.1148; found: 237.1150.

4-{1-[(*tert*-Butyldimethylsilyl)oxy]hepta-5,6-dien-1-yl)isoquinolin-1(2*H*)-one (6a)

A solution of **5a** (1.02 g, 4.00 mmol, 1.00 equiv) in DMF (22 mL) was cooled to 0 °C. After addition of 2,6-lutidine (1.40 mL, 1.29 g, 12.0 mmol, 3.00 equiv) and stirring for 5 min, *t*-BuMe_2SiOTf (1.40 mL, 1.61 g, 6.09 mmol, 1.52 equiv) was added dropwise at 0 °C and the reaction mixture was warmed to r.t. overnight. Sat. aq NH_4Cl (35 mL) and CH_2Cl_2 (100 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were subsequently washed with H_2O (4 × 100 mL) and brine (50 mL), and dried (Na_2SO_4). After filtration, the solvent was removed in vacuo and the crude product was purified by flash chromatography (SiO_2, 3.5 × 20 cm, P–EtOAc, 1:1) to give **6a** as a colorless resin, which partially solidified upon storage in the refrigerator at 4 °C; yield: 1.38 g (3.72 mmol, 93%); mp 77–79 °C; R_f = 0.52 (P–EtOAc, 1:1) [UV/CAM].

IR (ATR): 3168 (w br), 3032 (w), 2926 (m), 2854 (m), 2360 (w), 2342 (w), 1955 (w), 1663 (vs), 1641 (s), 1607 (m), 1347 (m), 1248 (m), 1076 (m), 831 (vs), 767 (vs), 541 cm^{-1} (m).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.67 (br s, 1 H, NH), 8.48 (dd, ^3J = 8.1 Hz, ^4J = 1.0 Hz, 1 H, C8-H), 7.88 (d, ^3J = 8.1 Hz, 1 H, C5-H), 7.70 (virt. t, $^3J \cong 7.7$ Hz, 1 H, C6-H), 7.52 (virt. t, $^3J \cong 7.7$ Hz, 1 H, C7-H), 7.14 (d, J = 4.8 Hz, 1 H, C3-H), 5.05 (virt. quint, $^3J \cong {}^4J$ = 6.6 Hz, 1 H, C5′-H), 4.92 (t, ^3J = 6.0 Hz, 1 H, C1′-H), 4.61 (dt, ^4J = 6.6 Hz, ^5J = 3.2 Hz, 2 H, C7′-H_2), 2.00 (virt. qt, $^3J \cong 6.8$ Hz, ^5J = 3.2 Hz, 2 H, C4′-H_2), 1.89–1.82 (m, 2 H, C2′-H_2), 1.61–1.40 (m, 2 H, C3′-H_2), 0.90 [s, 9 H, SiC(CH_3)$_3$], 0.09 (s, 3 H, $SiCH_3$), –0.10 (s, 3 H, $SiCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 208.6 (s, C6′), 162.5 (s, C1), 136.9 (s, C4a), 132.7 (d, C6), 132.5 (s, C8a), 127.8 (d, C8), 126.9 (d, C7), 123.8 (d, C3), 123.4 (d, C5), 117.0 (s, C4), 89.2 (d, C5′), 77.2 (d, C1′), 75.3 (t, C7′), 32.5 (t, C2′), 27.9 (t, C4′), 25.64 (t, C3′), 25.63 [q, SiC(CH_3)$_3$], 18.0 [s, SiC(CH_3)$_3$], –3.6 (q, $SiCH_3$).

MS (EI, 70 eV): m/z (%) = 369 (5, [M$^+$]), 312 (28, [M$^+$ – *t*-Bu]), 294 (11, [M$^+$ – C_2H_7OSi]), 288 (46, [M$^+$ – C_6H_9]), 241 (11), 185 (10), 167 (18), 149 (44), 75 (100, [$C_2H_7OSi^+$]), 57 (42, [*t*-Bu$^+$]), 43 (43).

HRMS (EI): m/z [M$^+$] calcd for $C_{22}H_{31}NO_2Si$: 369.2119; found: 369.2125.

1-[(*tert*-Butyldimethylsilyl)oxy]-5-methylene-1,2,3,4,4a,5,5a,6-octahydro-7*H*-benzo[2,3]cyclobuta[1,2-*c*]isoquinolin-7-one (7a)

A solution of **6a** (1.74 g, 4.72 mmol) in anhydrous MeCN (189 mL) was purged with argon in an ultrasound bath for 20 min. After irradiation (λ = 366 nm) at r.t. for 26 h, the crystalline product was collected by filtration and successive concentration of the filtrate gave **7a** as a colorless crystalline solid; total yield: 1.45 g (3.92 mmol, 83%); mp 186–189 °C; R_f = 0.20 (CH_2Cl_2–MeOH, 99:1) [UV/CAM].

IR (ATR): 3189 (w br), 3071 (w), 2935 (s), 2879 (m), 2853 (m), 1673 (s), 1600 (m), 1460 (m), 1353 (s), 1085 (s), 857 (vs), 780 (vs), 751 cm^{-1} (s).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1 H, C8-H), 7.54 (virt. td, $^3J \cong$ 7.6 Hz, ^4J = 1.4 Hz, 1 H, C10-H), 7.34 (virt. td, $^3J \cong$ 7.6 Hz, ^4J = 1.2 Hz, 1 H, C9-H), 7.28 (dd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, 1 H, C11-H), 6.30 (br s, 1 H, NH), 4.93 (s, 1 H, C5-C*H*H), 4.78–4.70 (m, 1 H, C5a-H), 4.73 (s, 1 H, C5-CH*H*), 3.84 (dd, ^3J = 10.9 Hz, ^3J = 5.8 Hz, 1 H, C1-H), 2.83 (virt. t, $^3J \cong$ 9.0 Hz, 1 H, C4a-H), 2.18–2.05 (m, 1 H, C4-*H*H), 1.99–1.94 (m, 1 H, C2-*H*H)), 1.86–1.76 (m, 1 H, C3-*H*H), 1.56–1.44 (m, 1 H, C2-H*H*), 1.41–1.28 (m, 2 H, C3-H*H*, C4-H*H*), 0.69 [s, 9 H, $SiC(CH_3)_3$], –0.24 (s, 3 H, $SiCH_3$), –0.65 (s, 3 H, $SiCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.2 (s, C7), 152.7 (s, C5), 145.8 (s, C11a), 132.6 (d, C10), 129.1 (s, C7a), 127.3 (d, C8), 127.2 (d, C11), 126.7 (d, C9), 104.4 (t, C5=CH_2), 76.5 (d, C1), 52.6 (d, C5a), 51.0 (d, C4a), 46.3 (s, C11b), 32.0 (t, C2), 28.8 (t, C4), 25.5 [q, $SiC(CH_3)_3$], 22.4 (t, C3), 17.6 [s, $SiC(CH_3)_3$], –5.1 (q, $SiCH_3$), –5.9 (q, $SiCH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 354 (3, [M^+ – CH_3]), 312 (100, [M^+ – *t*-Bu]), 294 (7, [M^+ – C_2H_7OSi]), 236 (5), 209 (4), 147 (4), 115 (4, [$C_6H_{15}Si^+$]), 84 (14), 75 (19, [$C_2H_7OSi^+$]).

HRMS (EI): *m*/*z* [(M – CH_3)$^+$] calcd for $C_{21}H_{28}NO_2Si$: 354.1884; found: 354.1885.

X-ray Crystal Data[31]

Formula: $C_{22}H_{31}NO_2Si$; M_r = 369.57; crystal color and shape: colorless prism, crystal dimensions = 0.11 × 0.22 × 0.35 mm; crystal system: triclinic; space group *P*-1 (no. 2); *a* = 7.8533(1), *b* = 9.8450(2), *c* = 13.2681(2) Å, *α* = 94.7210(8), *β* = 101.3000(7), *γ* = 90.7474(8); *V* = 1002.09(3) Å^3; $\mu(Mo_{K\alpha})$ = 0.133 mm^{-1}; ρ_{calcd}=1.225 g cm^{-3}; *θ*-range = 1.57–25.51°; data collected: 42364; independent data [$I_o > 2\sigma(I_o)$/all data/R_{int}]: 3193/3706/0.0311; data/restraints/parameters: 3706/0/240; *R*1 [$I_o > 2\sigma(I_o)$/all data]: 0.0324/0.0405; *wR*2 [$I_o > 2\sigma(I_o)$/all data]: 0.0804/0.0850; GOF = 1.026; $\Delta\rho_{max/min}$: 0.33/–0.26 e Å^{-3}.

8-(1-Hydroxyhepta-5,6-dien-1-yl)[1,3]dioxolo[4,5-*g*]isoquinolin-5(6*H*)-one (5b)

To a suspension of 8-bromo[1,3]dioxolo[4,5-*g*]isoquinolin-5(6*H*)-one (**3b**;[7,32] 276 mg, 1.03 mmol, 1.00 equiv) in THF (12 mL) at 0 °C was added dropwise a solution of MeLi·BrLi complex (2.2 M in Et_2O, 520 µL, 123 mg, 1.13 mmol, 1.10 equiv). After stirring for 10 min, the reaction mixture was cooled to –78 °C and a solution of *t*-BuLi (1.6 M in pentane, 1.12 mL, 146 mg, 2.28 mmol, 2.20 equiv) was added dropwise and the mixture was stirred at –78 °C for 20 min. Subsequently hepta-5,6-dienal (**4**;[8] 228 mg, 2.07 mmol, 2.00 equiv) was added dropwise whereupon the cooling bath was removed and the mixture slowly warmed to r.t. The reaction was quenched with sat. aq NH_4Cl (5 mL). After addition of H_2O (5 mL) and CH_2Cl_2 (30 mL), the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (30 mL) and brine (30 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 3.5 × 19 cm, EtOAc) to give **5b** as a colorless solid; yield: 133 mg (443 µmol, 43%); mp 192–194 °C; R_f = 0.27 (CH_2Cl_2–MeOH, 95:5) [UV/CAM].

IR (ATR): 3401 (m), 2911 (m), 1953 (w), 1645 (vs), 1461 (s), 1262 (s), 1038 (s), 852 cm^{-1} (s).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.11 (d, ^3J = 5.9 Hz, 1 H, NH), 7.55 (s, 1 H, C4-H), 7.33 (s, 1 H, C-9H), 6.98 (d, ^3J = 5.9 Hz, 1 H, C7-H), 6.16 (s, 2 H, OCH_2O), 5.22–5.09 (m, 1 H, OH), 5.16 (virt. quint, $^3J \cong {}^4J$ = 6.5 Hz, 1 H, C5′-H), 4.74–4.67 (m, 3 H, C1′-H, C7′-H_2), 1.97 (virt. tdd, $^3J \cong$ 9.8 Hz, ^3J = 6.1 Hz, ^5J = 2.6 Hz, 2 H, C4′-H_2), 1.79–1.68 (m, 1 H, C2′-*H*H), 1.68–1.59 (m, 1 H, C2′-H*H*), 1.56–1.38 (m, 2 H, C3′-H_2).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 207.9 (s, C6′), 160.7 (s, C5), 151.3 (s, C9a), 146.7 (s, C3a), 133.3 (s, C8a), 124.2 (d, C7), 121.4 (s, C4a), 118.4 (s, C8), 104.6 (d, C4), 101.9 (d, C9), 101.8 (t, C2), 89.8 (d, C5′), 75.3 (d, C1′), 68.1 (t, C7′), 36.4 (t, C2′), 27.5 (t, C4′), 25.2 (t, C3′).

MS (EI, 70 eV): *m*/*z* (%) = 299 (2, [M^+]), 281 (14), 266 (6), 218 (11), 202 (7), 189 (100, [M^+ – $C_7H_{10}O$]), 131 (17), 103 (9), 76 (12).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{17}NO_4$: 299.1158; found: 299.1152.

8-{1-[(*tert*-Butyldimethylsilyl)oxy]hepta-5,6-dien-1-yl}[1,3]dioxolo[4,5-*g*]isoquinolin-5(6*H*)-one (6b)

A solution of **5b** (61.3 mg, 205 µmol, 1.00 equiv) in DMF (2 mL) was cooled to 0 °C. After addition of 2,6-lutidine (94.5 µL, 87.2 mg, 814 µmol, 3.97 equiv) and stirring for 5 min, *t*-$BuMe_2SiOTf$ (94.3 µL, 108 mg, 409 µmol, 2.00 equiv) was added dropwise at 0 °C and the reaction mixture was warmed to r.t. overnight. Sat. aq NH_4Cl (15 mL), H_2O (10 mL), and Et_2O (40 mL) were added, and the layers were separated. The aqueous layer was extracted with Et_2O (5 × 50 mL) and the combined organic layers were dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 3 × 10 cm, EtOAc) to give **6b** as a colorless solid; yield: 66.9 mg (162 µmol, 79%); mp 178–180 °C (dec.); R_f = 0.78 (CH_2Cl_2–MeOH, 9:1) [UV/CAM].

IR (ATR): 2924 (w), 2853 (m), 1955 (w), 1655 (vs), 1476 (s), 1258 (s), 1035 (s), 831 (s), 772 cm^{-1} (m).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.13 (d, ^3J = 5.8 Hz, 1 H, NH), 7.54 (s, 1 H, C9-H), 7.44 (s, 1 H, C4-H), 7.02 (d, ^3J = 5.8 Hz, 1 H, C7-H), 6.18 (d, ^2J = 1.0 Hz, 1 H, OC*H*HO), 6.15 (d, ^2J = 1.0 Hz, 1 H, OCH*H*O), 5.14 (virt. quint, $^3J \cong {}^4J$ = 6.7 Hz, 1 H, C5′-H), 4.86 (t, ^3J = 6.2 Hz, 1 H, C1′-H), 4.69 (dt, ^4J = 6.7 Hz, ^2J = 3.3 Hz, 2 H, C7′-H_2), 1.95 (m, 2 H, C4′-H_2), 1.82–1.65 (m, 2 H, C2′-H_2), 1.52–1.42 (m, 1 H, C3′-*H*H), 1.41–1.30 (m, 1 H, C3′-H*H*), 0.84 [s, 9 H, $SiC(CH_3)_3$], 0.06 [s, 3 H, $Si(CH_3)(CH_3)$], –0.14 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, DMSO-d_6): δ = 207.9 (s, C6′), 160.7 (s, C5), 151.2 (s, C9a), 146.7 (s, C3a), 132.8 (s, C8a), 124.8 (d, C7), 121.5 (s, C4a), 117.5 (s, C8), 104.6 (d, C4), 102.1 (d, C9), 101.9 (t, OCH_2O), 89.7 (d, C5′), 75.3 (t, C7′), 37.5 (t, C2′), 27.2 (t, C4′), 25.7 [q, $SiC(CH_3)_3$], 25.0 (t, C3′), 17.8 [s, $SiC(CH_3)_3$], –4.8 [q, $Si(CH_3)(CH_3)$], –5.0 [q, $Si(CH_3)(CH_3)$].

MS (EI, 70 eV): *m*/*z* (%) = 413 (7, [M^+]), 356 (11), 332 (36), 281 (10), 189 (100, [M^+ – $C_{13}H_{25}OSi$]), 131 (18), 75 (61).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{23}H_{31}NO_4Si$: 413.2022; found: 413.2019.

1-[(*tert*-Butyldimethylsilyl)oxy]-5-methylene-1,2,3,4,4a,5,5a,6-octahydro-7*H*-benzo[2,3]cyclobuta[1,2-*c*][1,3]dioxolo[4,5-*g*]isoquinolin-7-one (7b) and 5-[(*tert*-Butyldimethylsilyl)oxy]-6,7,8,10-tetrahydro-4a*H*,5*H*-4b,10a-(methanoiminomethano)cyclohepta[1,2]indeno[5,6-*d*][1,3]dioxol-12-one (8)

A solution of **6b** (18.0 mg, 43.5 µmol) in anhydrous benzene (8.7 mL) was purged with argon in an ultrasound bath for 20 min. After irradiation (λ = 366 nm) at r.t. for 18 h, the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 2 × 10 cm, P–EtOAc, 5:1 → 4:1 → 3:1) to give the [2+2] photocycloaddition product **7b** and the *meta*-photocycloaddition product **8** as colorless solids.

[2+2] Photocycloaddition Product 7b

Yield: 6.8 mg (16.4 µmol, 38%); mp 158–160 °C; R_f = 0.74 (P–EtOAc, 1:1) [UV/CAM].

IR (ATR): 3203 (w), 3076 (w), 2929 (vs), 2856 (s), 1671 (vs), 1471 (m), 1247 (m), 835 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (s, 1 H, C8-H), 6.66 (s, 1 H, C12-H), 6.53 (d, ^3J = 5.3 Hz, 1 H, NH), 6.00 (d, ^2J = 1.4 Hz, 1 H, OC*H*HO), 5.97 (d, ^2J = 1.4 Hz, 1 H, OCH*H*O), 4.92–4.89 (m, 1 H, C5-C*H*H), 4.74–4.71 (m, 1 H, C5-CH*H*), 4.69 (virt. dq, ^3J = 5.3 Hz, ^4J = 2.4 Hz, 1 H, C5a-H), 3.75 (dd, ^3J = 10.9 Hz, ^3J = 5.8 Hz, 1 H, C1-H), 2.77 (virt. t, ^3J ≅ 8.5 Hz, 1 H, C4a-H), 2.13–2.04 (m, 1 H, C4-*H*H), 1.97–1.88 (m, 1 H, C2-*H*H), 1.81–1.72 (m, 1 H, C3-*H*H), 1.52–1.40 (m, 1 H, C2-H*H*), 1.28 (m, 2 H, C3-H*H*, C4-H*H*), 0.70 [s, 9 H, SiC$(CH_3)_3$], –0.22 [s, 3 H, Si(CH_3)(CH_3)], –0.55 [s, 3 H, Si(CH_3)(CH_3)].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.0 (s, C7), 153.0 (s, C5), 151.3 (s, C11a), 146.8 (s, C8a), 141.3 (s, C12a), 124.0 (s, C7a), 107.0 (d, C8), 106.7 (d, C12), 104.3 (t, C5=CH_2), 101.6 (t, OCH_2O), 76.2 (d, C1), 52.6 (d, C5a), 51.1 (d, C4a), 46.7 (s, C12b), 32.1 (t, C2), 28.9 (t, C4), 25.6 [q, SiC(CH_3)$_3$], 22.5 (t, C3), 17.7 [s, SiC$(CH_3)_3$], –4.9 [q, Si(CH_3)(CH_3)], –5.5 (q, Si(CH_3)(CH_3)].

MS (ESI): *m*/*z* = 414 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{32}NO_4Si$: 414.2101; found: 414.2099.

***meta*-Photocycloaddition Product 8**

Yield: 4.9 mg (11.9 µmol, 27%); mp 168 °C (dec.); R_f = 0.20 (CH_2Cl_2–MeOH, 99:1) [UV/CAM].

IR (ATR): 3204 (w), 3073 (w), 2927 (vs), 2855 (s), 1666 (s), 1470 (s), 1252 (m), 1039 (m), 835 (w), 775 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.59 (s, 1 H, NH), 5.90 (ddd, ^3J = 6.6 Hz, ^3J = 4.4 Hz, ^4J = 2.5 Hz, 1 H, C5-H), 5.55 (d, ^2J = 0.8 Hz, 1 H, OC*H*HO), 5.49 (d, ^2J = 0.8 Hz, 1 H, OCH*H*O), 5.32 (d, ^5J = 0.9 Hz, 1 H, C11-H), 5.15 (d, ^5J = 0.9 Hz, 1 H, C7-H), 4.23 (dd, ^3J = 8.7 Hz, ^3J = 4.1 Hz, 1 H, C1-H), 3.61 (s, 1 H, C12-H), 2.91 (virt. dq, ^2J = 13.4 Hz, ^4J ≅ 2.5 Hz, 1 H, C6-*H*H), 2.72 (d, ^2J = 13.4 Hz, 1 H, C6-H*H*), 2.14–1.96 (m, 3 H, C4-*H*H, C4-H*H*, C2-*H*H), 1.83–1.60 (m, 2 H, C2-H*H*, C3-*H*H), 1.54–1.39 (m, 1 H, C3-H*H*), 0.90 [s, 9 H, SiC$(CH_3)_3$], 0.10 [s, 3 H, Si(CH_3)(CH_3)], 0.10 [s, 3 H, Si(CH_3)(CH_3)].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 183.1 (s, C14), 145.2 (s, C10a), 144.3 (s, C7a), 133.6 (s, C5a), 126.7 (d, C5), 99.0 (t, OCH_2O), 91.5 (d, C11), 90.2 (d, C7), 70.7 (d, C1), 59.1 (t, C6), 54.7 (s, C6a), 50.6 (s, C12a), 45.9 (s, C11a), 45.8 (d, C12), 39.4 (t, C2), 28.4 (t, C4), 26.2 [q, SiC(CH_3)$_3$], 23.3 (t, C3), 18.2 [s, SiC$(CH_3)_3$], –3.8 [q, Si(CH_3)(CH_3)], –3.8 [q, Si(CH_3)(CH_3)].

MS (ESI): *m*/*z* = 414 [(M + H)$^+$]

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{32}NO_4Si$: 414.2101; found: 414.2099.

X-ray Crystal Data[31]

Formula: $C_{23}H_{31}NO_4Si$; M_r = 413.58; crystal color and shape: yellow fragment, crystal dimensions = 0.23 × 0.33 × 0.64 mm; crystal system: trigonal; space group *R* –3 (no. 148); *a* = *b* = 26.8583(10), *c* = 17.0912(7) Å; *V* = 10677.3(10) Å^3; $\mu(Mo_{K\alpha})$ = 0.125 mm^{-1}; ρ_{calcd} = 1.158 g cm^{-3}; θ-range = 1.48–25.35°; data collected: 34010; independent data [$I_o>2\sigma(I_o)$/all data/R_{int}]: 3668/4347/0.0497; data/restraints/parameters: 4347/0/267; *R*1 [$I_o>2\sigma(I_o)$/all data]: 0.0402/0.0501; *wR*2 [$I_o>2\sigma(I_o)$/all data]: 0.0934/0.0990; GOF = 1.036; $\Delta\rho_{max/min}$: 0.32/–0.35 e Å^{-3}.

1-[(*tert*-Butyldimethylsilyl)oxy]-6-(4-isopropoxyphenethyl)-5-methylene-1,2,3,4,4a,5,5a,6-octahydro-7*H*-benzo[2,3]cyclobuta[1,2-*c*]isoquinolin-7-one (12)

NaH (60% dispersion in mineral oil, 32.7 mg, 818 µmol, 1.20 equiv) was added to a solution of isoquinolone **7a** (252 mg, 682 µmol, 1.00 equiv) in DMF (10 mL) and the resulting suspension was stirred for 45 min. A solution of 1-(2-bromoethyl)-4-isopropoxybenzene (**11**;[33] 348 mg, 1.43 mmol, 2.10 equiv) in DMF (2 mL) was added and the reaction mixture was stirred at r.t. for 24 h. H_2O (20 mL) and EtOAc (25 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (5 × 25 mL) and the combined organic layers were subsequently washed with H_2O (5 × 15 mL) and brine (2 × 15 mL), and dried (Na_2SO_4). After filtration, the solvent was removed in vacuo and the crude product was purified by flash chromatography (SiO_2, 2 × 20 cm, P–EtOAc, 10:1 → 5:1) to give the N-alkylated isoquinolone **12** as a colorless resin; yield: 187 mg (352 µmol, 52%); R_f = 0.63 (P–EtOAc, 5:1) [UV/CAM].

IR (ATR): 2928 (br s), 2855 (m), 1659 (m), 1509 (vs), 1477 (s), 1242 (s), 1036 cm^{-1} (s).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, ^3J = 7.8 Hz, 1 H, C8-H), 7.51 (virt. t, ^3J ≅ 7.5 Hz, 1 H, C10-H), 7.34 (virt. t, ^3J ≅ 7.6 Hz, 1 H, C9-H), 7.24 (virt. d, *J* = 8.3 Hz, 2 H, C2″-H, C6″-H), 6.86 (virt. d, *J* = 8.3 Hz, 2 H, C3″-H, C5″-H), 4.85 (s, 1 H, C5-C*H*H), 4.75 (s, 1 H, C5a-H), 4.67 (s, 1 H, C5-CH*H*), 4.53 [sept, ^3J = 6.1 Hz, 1 H, OC*H*$(CH_3)_2$], 3.84 (dd, ^3J = 11.1 Hz, ^3J = 5.8 Hz, 1 H, C1-H), 3.82–3.68 (m, 2 H, C1′-H_2), 3.01–2.88 (m, 2 H, C1′-H_2), 2.80 (virt. t, ^3J ≅ 8.7 Hz, 1 H, C4a-H), 2.12 (virt. t, ^3J ≅ 9.1 Hz, 1 H, C4-*H*H), 2.02–1.92 (m, 1 H, C2-*H*H), 1.87–1.77 (m, 1 H, C3-*H*H), 1.62–1.48 (m, 1 H, C2-H*H*), 1.34 [d, ^3J = 6.1 Hz, 6 H, OCH$(CH_3)_2$], 1.43–1.21 (m, 2 H, C3-H*H*, C4-H*H*), 0.65 [s, 9 H, SiC$(CH_3)_3$], –0.28 (s, 3 H, $SiCH_3$), –0.62 (s, 3 H, $SiCH_3$).

The ^{1}H NMR signal for C11-H was covered by the residual proton signal of the solvent. Measurement in CD_3OD resulted in the following ^{1}H NMR signal:

^{1}H NMR (500 MHz, CD_3OD): δ = 7.45 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1 H, C11-H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.5 (s, C7), 156.4 (s, C4″), 152.4 (s, C5), 144.7 (s, C11a), 131.9 (d, C10), 131.0 (s, C1″), 130.2 (s, C7a), 129.8 (d, C2″, C6″), 127.6 (d, C8), 126.8 (d, C11), 126.7 (d, C9), 115.9 (d, C3″, C5″), 104.0 (t, C5-CH_2), 76.5 (d, C1), 69.9 [d, OCH$(CH_3)_2$], 58.4 (d, C5a), 50.6 (d, C4a), 49.8 (t, C1′), 46.4 (s, C11b), 34.1 (t, C2′), 31.9 (t, C2), 28.6 (t, C4), 25.6 [q, SiC(CH_3)$_3$], 22.5 (t, C3), 22.1 [q, OCH$(CH_3)_2$], 17.7 [s, SiC$(CH_3)_3$], –5.3 (q, $SiCH_3$), –5.7 (q, $SiCH_3$).

MS (ESI): *m*/*z* = 532 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{33}H_{46}NO_3Si$: 532.3247; found: 532.3238.

1-[(*tert*-Butyldimethylsilyl)oxy]-7-(4-isopropoxyphenethyl)-2,3,4,4a,6a,7-hexahydroisoindolo[1,7a-*c*]isoquinoline-5,8(1*H*,6*H*)-dione (14) via 1-[(*tert*-Butyldimethylsilyl)oxy]-6-(4-isopropoxyphenethyl)-2,3,4,4a,5a,6-hexahydro-1*H*-benzo[2,3]cyclobuta[1,2-*c*]isoquinoline-5,7-dione (13)

A solution of the N-alkylated isoquinolone **12** (184 mg, 345 µmol, 1.00 equiv) in CH_2Cl_2 (10 mL) was treated with NMO monohydrate (140 mg, 1.04 mmol, 3.00 equiv) and aq 4% OsO_4 (110 µL, 4.39 mg, 17.3 µmol, 0.05 equiv). The reaction mixture was stirred for 37 h at r.t. The reaction was quenched by the addition of sat. aq $Na_2S_2O_3$ (5 mL) and stirred for 1 h. The solvents were removed in vacuo and the remaining residue was extracted with EtOAc (5 × 25 mL). The EtOAc solution of the crude product was dried (Na_2SO_4) and filtered over a short pad of silica gel. Removal of the solvent in vacuo furnished the respective diol of modest purity. The crude diol (158 mg, 279 µmol, 1.00 equiv) was dissolved in acetone (16 mL) and treated with aq $NaIO_4$ (0.21 M, 179 mg, 837 µmol, 3.00 equiv). The reaction mixture was stirred for 12 h at r.t. and then filtered through a short pad of Celite. The solvent was removed in vacuo and the residue was redissolved in a mixture of EtOAc (40 mL) and H_2O (20 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography [SiO_2, 2 × 20 cm, P–EtOAc, 5:1 (2% Et_3N)] to give **13** as a colorless resin; yield: 97.6 mg (183 µmol, 53% over two steps); R_f = 0.83 [P–EtOAc, 5:1 (2% Et_3N)] [UV/CAM]. Due to the high reactivity of the cyclobutanone only NMR spectra were recorded.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1 H, C8-H), 7.54 (virt. td, $^3J \cong$ 7.6 Hz, ^4J = 1.4 Hz, 1 H, C10-H), 7.38 (virt. td, $^3J \cong$ 7.6 Hz, ^4J = 1.2 Hz, 1 H, C9-H), 7.30 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1 H, C11-H), 7.22 (virt. d, J = 8.5 Hz, 2 H, C2″-H, C-6″-H), 6.85 (virt. d, J = 8.5 Hz, 2 H, C3″-H, C5″-H), 5.07 (d, ^4J = 2.3 Hz, 1 H, C5a-H), 4.52 [sept, ^3J = 6.1 Hz, 1 H, OC*H*$(CH_3)_2$], 4.12 (dd, ^3J = 10.5 Hz, ^3J = 5.5 Hz, 1 H, C1-H), 4.04 (ddd, ^2J = 13.4 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 1 H, C1′-*H*H), 3.45 (ddd, ^2J = 13.4 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 1 H, C1′-H*H*), 3.13 (virt. td, $^3J_1 \cong$ 10.0 Hz, ^4J = 2.3 Hz, 1 H, C4a-H), 3.04–2.90 (m, 2 H, C2′-H_2), 2.13–2.08 (m, 1 H, C4-*H*H), 2.09–2.00 (m, 1 H, C2-*H*H), 1.99–1.90 (m, 1 H, C3-*H*H), 1.62–1.50 (m, 1 H, C2-H*H*), 1.51–1.40 (m, 2 H, C3-H*H*, C4-H*H*), 1.33 [d, ^3J = 6.1 Hz, 6 H, OCH$(CH_3)_2$], 0.67 [s, 9 H, SiC$(CH_3)_3$], –0.23 (s, 3 H, $SiCH_3$), –0.62 (s, 3 H, $SiCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 204.3 (s, C5), 161.6 (s, C7), 156.4 (s, C4″), 142.3 (s, C11a), 132.5 (d, C10), 131.0 (s, C7a), 129.8 (s, C1″), 129.8 (d, C2″, C6″), 128.4 (d, C8), 127.7 (d, C9), 126.9 (d, C11), 115.9 (d, C3″, C5″), 76.0 (d, C1), 69.9 [d, OCH$(CH_3)_2$], 69.6 (d, C5a), 64.5 (d, C4a), 49.8 (t, C1′), 41.4 (s, C11b), 33.6 (t, C2′), 31.2 (t, C2), 25.5 [q, SiC$(CH_3)_3$], 23.3 (t, C4), 22.9 (t, C3), 22.1 [q, OCH$(CH_3)_2$], 17.6 [s, SiC$(CH_3)_3$], –5.2 (s, $SiCH_3$), –5.8 (s, $SiCH_3$).

A solution of the cyclobutanone **13** (97.6 mg, 183 µmol, 1.00 equiv) in CH_2Cl_2 (2 mL) was treated with a solution of MSH[17] (41.2 mg, 192 µmol, 1.05 equiv) in CH_2Cl_2 (2 mL) at 0 °C (**CAUTION!** For precautions when working with MSH, see the general remarks section and the literature[17b]). The resulting mixture was stirred for 1 h at 0 °C whereupon the solvent was removed in vacuo at r.t. (!). The residue was redissolved in a mixture of benzene (3.6 mL) and MeOH (1.2 mL) and added to a suspension of activated basic Al_2O_3 (activity I, 1.15 g) in MeOH (3 mL). The suspension was stirred for 14 h and then filtered through a pad of Celite. After removal of the solvents in vacuo, the crude product was purified by flash chromatography [SiO_2, 3.5 × 15 cm, P–EtOAc, 1:1 (1% Et_3N) → 0:1 (1% Et_3N)] to give the γ-lactam **14** as a colorless solid; yield. 92.8 mg (169 µmol, 92%); mp 210 °C; R_f = 0.59 [EtOAc (1% Et_3N)] [UV/CAM].

IR (ATR): 3229 (br w), 2928 (vs), 2856 (s), 1708 (s), 1654 (s), 1508 (m), 1479 (w), 1462 (w), 1241 (s), 1095 (m), 836 cm^{-1} (s).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1 H, C9-H), 7.53 (virt. td, $^3J \cong$ 7.6 Hz, ^4J = 1.5 Hz, 1 H, C11-H), 7.37 (virt. td, $^3J \cong$ 7.5 Hz, ^4J = 1.1 Hz, 1 H, C10-H), 7.31 (dd, ^3J = 7.9, ^4J = 1.1 Hz, 1 H, C12-H), 7.20 (virt. d, J = 8.6 Hz, 2 H, C2″-H, C6″-H), 6.87 (virt. d, J = 8.6 Hz, 2 H, C3″-H, C5″-H), 5.25 (s, 1 H, C6a-H), 5.10 (s, 1 H, NH), 4.52 [sept, ^3J = 6.1 Hz, 1 H, OC*H*$(CH_3)_2$], 4.27–4.16 (m, 1 H, C1′-*H*H), 3.77 (dd, ^3J = 11.3 Hz, ^3J = 4.6 Hz, 1 H, C1-H), 3.54–3.34 (m, 1 H, C1′-H*H*), 3.07 (virt. dt, ^2J = 13.7 Hz, $^3J \cong$ 8.2 Hz, 1 H, C2′-*H*H), 2.93 (ddd, ^2J = 13.7 Hz, ^3J = 8.0 Hz, ^3J = 4.7 Hz, 1 H, C2′-H*H*), 2.81 (dd, ^3J = 12.2 Hz, ^3J = 6.4 Hz, 1 H, C4a-H), 2.18–2.08 (m, 1 H, C4-*H*H), 1.99–1.84 (m, 2 H, C2-*H*H, C3-*H*H), 1.67–1.53 (m, 1 H, C2-H*H*), 1.55–1.42 (m, 1 H, C3-H*H*), 1.32 [d, ^3J = 6.1 Hz, 6 H, OCH$(CH_3)_2$], 1.32–1.27 (m, 1 H, C4-H*H*), 0.67 [s, 9 H, SiC(CH_3)], –0.32 (s, 3 H, $SiCH_3$), –0.67 (s, 3 H, $SiCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 175.1 (s, C5), 162.5 (s, C8), 156.8 (s, C4″), 141.0 (s, C12a), 132.7 (d, C11), 130.6 (s, C8a), 129.8 (d, C2″, C6″), 129.8 (s, C1″), 128.0 (d, C9), 127.6 (d, C10), 125.8 (d, C12), 116.3 (d, C3″, C5″), 77.7 (d, C1), 70.5 (d, C6a), 70.0 [d, OCH$(CH_3)_2$], 51.5 (t, C1′), 50.9 (s, C12b), 50.4 (d, C4a), 34.0 (t, C2′), 31.9 (t, C2), 26.6 (t, C4), 25.6 [q, SiC$(CH_3)_3$], 22.7 (t, C3), 22.03 [q, OCH$(CH_3)_2$], 17.7 [s, SiC$(CH_3)_3$], –5.8 (q, $SiCH_3$).

MS (ESI): m/z = 549 [(M + H)$^+$].

HRMS (ESI): m/z [(M + H)$^+$] calcd for $C_{32}H_{45}N_2O_4Si$: 549.3149; found: 549.3145.

1-[(*tert*-Butyldimethylsilyl)oxy]-7-(4-isopropoxyphenethyl)-6-methyl-2,3,4,4a,6a,7-hexahydroisoindolo[1,7a-*c*]isoquinoline-5,8(1*H*,6*H*)-dione (15)

NaH (60% dispersion in mineral oil, 3.0 mg, 74.8 µmol, 1.20 equiv) was added to a solution of γ-lactam **14** (34.2 mg, 62.3 µmol, 1.00 equiv) in DMF (2 mL) and the resulting suspension was stirred for 45 min. MeI (12 µL, 26.5 mg, 187 µmol, 3.00 equiv) was added and the reaction mixture was stirred at r.t. for 13 h. Sat. aq NH_4Cl (10 mL), H_2O (5 mL), Et_2O (20 mL) were added and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (40 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography [SiO_2, 2 × 10 cm, EtOAc (2% Et_3N)] to give the N-alkylated γ-lactam **15** as a colorless solid; yield: 32.5 mg (57.7 µmol, 93%); mp 184 °C; R_f = 0.59 (P–EtOAc, 1:1) [UV/CAM].

IR (ATR): 2930 (br s), 2857 (s), 1698 (s), 1653 (vs), 1508 (m), 1478 (m), 1462 (m), 1239 (s), 1089 (s), 835 cm^{-1} (s).

^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.14 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1 H, C9a-H), 7.54 (virt. td, $^3J \cong$ 7.8 Hz, ^4J = 1.6 Hz, 1 H, C11-H), 7.43–7.33 (m, 2 H, C10-H, C12-H), 7.23–7.17 (m, 2 H, C2″-H, C6″-H), 6.94–6.81 (m, 2 H, C3″-H, C5″-H), 5.44 (s, 1 H, C6a-H), 4.62–4.52 (m, 1 H, C1′-*H*H), 4.52 [sept, ^3J = 6.1 Hz, 1 H, OC*H*$(CH_3)_2$], 3.87 (dd, ^3J = 11.4 Hz, ^3J = 4.5 Hz, 1 H, C1-H), 3.27–3.07 (m, 2 H, C1′-H*H*, C2′-*H*H), 2.96 (dd, ^3J = 12.2 Hz, ^3J = 6.3 Hz, 1 H, C4a-H), 2.92–2.83 (m, 1 H, C2′-H*H*), 2.70 (s, 3 H, NCH_3), 2.26–2.11 (m, 1 H, C4-*H*H), 2.10–1.92 (m, 2 H, C2-*H*H, C3-*H*H), 1.71 (virt. qd, $^2J \cong ^3J$ = 11.4 Hz, ^3J = 2.7 Hz, 1 H, C2-H*H*), 1.63–1.47 (m, 1 H, C3-H*H*), 1.43–1.25 (m, 1 H, C4-H*H*), 1.33 [d, ^3J = 6.1 Hz, 6 H, OCH$(CH_3)_2$], 0.65 [s, 9 H, SiC$(CH_3)_3$], –0.37 [s, 3 H, Si$(CH_3)(CH_3)$], –0.47 [s, 3 H, Si$(CH_3)(CH_3)$].

^{13}C NMR (91 MHz, $CDCl_3$): δ = 173.1 (s, C5), 162.9 (s, C8), 156.6 (s, C4″), 141.1 (s, C12a), 132.7 (d, C11), 130.5 (s, C2″, C6″), 129.9 (s, C1″), 129.6 (s, C8a), 128.1 (d, C9), 127.6 (d, C10), 125.4 (d, C12), 116.0 (d, C3″, C5″), 78.0 (d, C1), 73.2 (d, C6a), 69.9 [d, OCH$(CH_3)_2$], 51.4 (t, C1′),

50.1 (d, C4a), 49.5 (s, C12b), 33.9 (t, C2′), 31.9 (t, C2), 26.3 (t, C4), 26.1 (q, NCH_3), 25.8 [q, $SiC(CH_3)_3$], 23.0 (t, C3), 22.1 [q, $OCH(CH_3)_2$], 18.0 [s, $SiC(CH_3)_3$], –5.3 [q, $Si(CH_3)(CH_3)$], –5.7 [q, $Si(CH_3)(CH_3)$].

MS (ESI): m/z = 563 [$(M + H)^+$].

HRMS (ESI): m/z [$(M + H)^+$] calcd for $C_{33}H_{47}N_2O_4Si$: 563.3305; found: 563.3301.

X-ray Crystal Data[31]

Formula: $C_{33}H_{46}N_2O_4Si$; M_r = 562.81; crystal color and shape: colorless fragment, crystal dimensions = 0.05 × 0.12 × 0.46 mm; crystal system: orthorhombic; space group *P b c a* (no. 61); a = 13.8133(12), b = 9.9083(9), c = 46.649(4) Å; V = 6384.7(10) Å^3; $\mu(Mo_{K\alpha})$ = 0.111 mm^{-1}; ρ_{calcd} = 1.171 g cm^{-3}; θ-range = 1.71–25.34°; data collected: 15738; independent data [$I_o > 2\sigma(I_o)$/all data/R_{int}]: 3580/5754/0.0669; data/restraints/parameters: 5754/0/369; $R1$ [$I_o > 2\sigma(I_o)$/all data]: 0.0567/0.1054; $wR2$ [$I_o > 2\sigma(I_o)$/all data]: 0.1167/0.1359; GOF = 1.014; $\Delta\rho_{max/min}$: 0.38/–0.28 e Å^{-3}.

1-[(*tert*-Butyldimethylsilyl)oxy]-7-methoxy-5-methylene-2,3,4,4a,5,5a-hexahydro-1*H*-benzo[2,3]cyclobuta[1,2-*c*]isoquinoline (16)

Cs_2CO_3 (8.39 g, 25.8 mmol, 25.0 equiv) was added to a solution of [2+2] photocycloaddition product **7a** (380 mg, 1.03 mmol, 1.00 equiv) in CH_2Cl_2 (30 mL) at 0 °C and the solution stirred for 5 min. Subsequently, Me_3OBF_4 (762 mg, 5.15 mmol, 5.00 equiv) was added at 0 °C in portions (ca. 100 mg every 2 min). After the addition was complete, the reaction mixture was warmed to r.t. over 3.5 h. Ice-water (80 mL) was added to quench the reaction. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 60 mL). The combined organic layers were washed with brine (60 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 3.5 × 10 cm, P–EtOAc, 5:1) to give the methyl imidate **16** as a colorless resin; yield: 386 mg (1.01 mmol, 98%); R_f = 0.90 (P–EtOAc, 5:1) [UV/CAM].

IR (ATR): 2930 (br vs), 2856 (s), 1658 (m), 1460 (w), 1438 (w), 1308 (w), 1255 (w), 1088 cm^{-1} (m).

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.71 (dd, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1 H, C8-H), 7.45 (virt. td, $^3J \cong$ 7.5 Hz, ^4J = 1.3 Hz, 1 H, C10-H), 7.27 (dd, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1 H, C11-H), 7.23 (virt. td, $^3J \cong$ 7.5 Hz, ^4J = 1.2 Hz, 1 H, C9-H), 5.18 (virt. q, $^2J \cong {}^4J$ = 2.7 Hz, 1 H, C5=C*H*H), 4.86 (virt. t, $^4J \cong$ 2.1 Hz, 1 H, C5a-H), 4.64 (dd, ^2J = 2.7 Hz, ^4J = 1.2 Hz, 1 H, C5=CH*H*), 3.85 (s, 3 H, OCH_3), 3.72 (dd, ^3J = 11.0 Hz, ^3J = 5.8 Hz, 1 H, C1-H), 2.85 (virt. t, $^3J \cong$ 9.1 Hz, 1 H, C4a-H), 2.16–2.05 (m, 1 H, C4-*H*H), 1.96–1.70 (m, 2 H, C2-*H*H, C3-*H*H) 1.56 (virt. qd, $^2J \cong {}^3J$ = 11.0 Hz, ^3J = 2.5 Hz, 1 H, C2-H*H*), 1.48–1.27 (m, 2 H, C3-H*H*, C4-H*H*), 0.66 [s, 9 H, $SiC(CH_3)_3$], –0.23 [s, 3 H, $Si(CH_3)(CH_3)$], –0.72 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.3 (s, C7), 155.0 (s, C5), 145.9 (s, C7a), 131.5 (s, C11a), 127.5 (d, C10), 126.2 (d, C8), 125.9 (d, C11), 124.1 (d, C9), 103.1 (t, C5=CH_2), 76.9 (d, C1), 57.9 (d, C5a), 52.9 (s, C11b), 52.2 (d, C4a), 43.9 (q, OCH_3), 31.4 (t, C2), 29.4 (t, C4), 25.4 [q, $SiC(CH_3)_3$], 22.5 (t, C3), 17.5 [s, $SiC(CH_3)_3$], –4.8 [q, $Si(CH_3)(CH_3)$], –6.2 [q, $Si(CH_3)(CH_3)$].

MS (ESI): m/z = 384 [$(M + H)^+$].

HRMS (ESI): m/z [$(M + H)^+$] calcd for $C_{23}H_{34}NO_2Si$: 384.2359; found: 384.2356.

1-[(*tert*-Butyldimethylsilyl)oxy]-7-methoxy-2,3,4,4a-tetrahydro-1*H*-benzo[2,3]cyclobuta[1,2-*c*]isoquinolin-5(5a*H*)-one (17)

A solution of the methyl imidate **16** (323 mg, 842 µmol, 1.00 equiv) in CH_2Cl_2 (24 mL) was treated with NMO monohydrate (341 mg, 2.53 mmol, 3.00 equiv) and aq 4% OsO_4 (326 µL, 12.9 mg, 50.2 µmol, 0.06 equiv). The reaction mixture was stirred for 23 h at r.t. The reaction was quenched by the addition of sat. aq $Na_2S_2O_3$ (2 mL) and the resulting mixture was stirred for 1 h. The solvents were removed in vacuo and the remaining residue was washed with CH_2Cl_2 (3 × 30 mL) and the combined CH_2Cl_2 solution of the crude product was dried (Na_2SO_4). Filtration and removal of the solvent in vacuo furnished the respective crude diol. The crude diol was dissolved in acetone (10 mL) and treated with aq $NaIO_4$ (0.67 M, 360 mg, 1.68 mmol, 2.00 equiv). The reaction mixture was stirred for 30 min at r.t. and then filtered over a short pad of Celite. The solvent was removed in vacuo and the residue was partitioned between CH_2Cl_2 (100 mL) and brine (40 mL). The layers were separated and the organic layer was washed with brine (40 mL), dried (Na_2SO_4), filtered and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 3.5 × 13 cm, P–EtOAc, 5:1) to give the cyclobutanone **17** as a colorless resin; yield: 272 mg (705 µmol, 84%); R_f = 0.92 (CH_2Cl_2–MeOH, 95:5) [UV/CAM].

IR (ATR): 2946 (vs), 2931 (vs), 2855 (s), 1783 (s), 1652 (s), 1462 (w), 1438 (w), 1313 (s), 1087 cm^{-1} (s).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, ^3J = 7.8 Hz, 1 H, C8-H), 7.48 (virt. td, $^3J \cong$ 7.8 Hz, ^4J = 1.3 Hz, 1 H, C10-H), 7.34 (d, ^3J = 7.8 Hz, 1 H, C11-H), 7.27 (virt. t, $^3J \cong$ 7.8 Hz, 1 H, C9-H), 5.64 (d, ^4J = 1.6 Hz, 1 H, C5a-H), 4.01 (dd, ^3J = 10.9 Hz, ^3J = 5.4 Hz, 1 H, C1-H), 3.85 (s, 3 H, OCH_3), 3.15 (virt. td, $^3J \cong$ 10.2 Hz, ^4J = 1.6 Hz, 1 H, C4a-H), 2.16–2.04 (m, 1 H, C4-*H*H), 1.99–1.85 (m, 2 H, C2-*H*H, C3-*H*H), 1.69–1.37 (m, 3 H, C2-H*H*, C3-H*H*, C4-H*H*), 0.67 [s, 9 H, $SiC(CH_3)_3$], –0.20 [s, 3 H, $Si(CH_3)(CH_3)$], –0.68 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 207.3 (s, C5), 160.2 (s, C7), 143.5 (s, C11a), 132.1 (d, C10), 127.7 (s, C7a), 127.3 (d, C8), 126.1 (d, C11), 124.9 (d, C9), 76.5 (d, C1), 71.3 (d, C5a), 66.7 (d, C4a), 53.2 (q, OCH_3), 39.4 (s, C11b), 30.9 (t, C2), 25.5 [q, $SiC(CH_3)_3$], 23.9 (t, C4), 23.0 (t, C3), 17.7 [s, $SiC(CH_3)_3$], –4.6 [q, $Si(CH_3)(CH_3)$], –6.1 [q, $Si(CH_3)(CH_3)$].

MS (ESI): m/z = 386 [$(M + H)^+$].

HRMS (ESI): m/z [$(M + H)^+$] calcd for $C_{22}H_{32}NO_3Si$: 386.2152; found: 386.2150.

1-[(*tert*-Butyldimethylsilyl)oxy]-6-methyl-5-methylene-1,2,3,4,4a,5,5a,6-octahydro-7*H*-benzo[2,3]cyclobuta[1,2-*c*]isoquinolin-7-one (18a)

NaH (60% dispersion in mineral oil, 77.0 mg, 1.93 mmol, 1.57 equiv) was added to a solution of [2+2] photocycloaddition product **7a** (456 mg, 1.23 mmol, 1.00 equiv) in DMF (46 mL) and the resulting suspension was stirred for 45 min. MeI (278 µL, 631 mg, 4.44 mmol, 3.60 equiv) was added and the reaction mixture was stirred at r.t. for 18 h. Sat. aq NH_4Cl (30 mL), H_2O (10 mL), and Et_2O (50 mL) were added and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine (30 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 3.5 × 14 cm, P–EtOAc, 5:1) to afford the N-alkylated isoquinolone **18a** as a colorless solid; yield: 414 mg (1.08 mmol, 88%); mp 82 °C; R_f = 0.49 (P–EtOAc, 2:1) [UV/CAM].

IR (ATR): 2928 (vs), 2855 (s), 1651 (vs), 1089 (m), 835 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1 H, C8-H), 7.49 (virt. td, $^3J \cong$ 7.6 Hz, ^4J = 1.5 Hz, 1 H, C10-H), 7.31 (ddd, $^3J \cong$ 7.9 Hz, ^3J = 7.3, ^4J = 1.2 Hz, 1 H, C9-H), 7.23 (dd, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1 H, C11-H), 4.87–4.83 (m, 1 H, C5-C*H*H), 4.70–4.63 (m, 1 H, C5-CH*H*), 4.62 (d, ^4J = 2.4 Hz, 1 H, C5a-H), 3.82 (dd, ^3J = 10.9 Hz, ^3J = 5.9 Hz, 1 H, C1-H), 3.24 (s, 3 H, NCH_3), 2.86–2.75 (m, 1 H, C4a-H), 2.20–2.07 (m, 1 H, C4-*H*H), 2.00–1.89 (m, 1 H, C2-*H*H), 1.85–1.77 (m, 1 H, C3-*H*H), 1.50 (m, 1 H, C2-H*H*), 1.41–1.27 (m, 2 H, C3-H*H*, C4-H*H*), 0.68 [s, 9 H, $SiC(CH_3)_3$], –0.24 [s, 3 H, $Si(CH_3)(CH_3)$], –0.70 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.8 (s, C7), 152.8 (s, C5), 145.1 (s, C11a), 132.0 (d, C10), 127.7 (d, C8), 127.0 (d, C11), 126.8 (d, C9), 104.1 (t, C5=CH_2), 76.3 (d, C1), 59.7 (d, C5a), 51.0 (d, C4a), 46.3 (s, C11b), 35.4 (q, NCH_3), 32.1 (t, C2), 28.9 (t, C4), 25.6 [q, $SiC(CH_3)_3$], 22.5 (t, C3), 17.7 [s, $SiC(CH_3)_3$], –4.9 [q, $Si(CH_3)(CH_3)$], –5.8 [q, $Si(CH_3)(CH_3)$]; despite prolonged acquisition time, the signal for carbon atom C7a was not detected.

MS (ESI): *m*/*z* = 384 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{34}NO_2Si$: 384.2359; found: 384.2356.

1-[(*tert*-Butyldimethylsilyl)oxy]-6-methyl-2,3,4,4a,5a,6-hexahydro-1*H*-benzo[2,3]cyclobuta[1,2-*c*]isoquinoline-5,7-dione (19a)

A solution of the N-alkylated isoquinolone **18a** (296 mg, 772 µmol, 1.00 equiv) in CH_2Cl_2 (20 mL) was treated with NMO monohydrate (320 mg, 2.37 mmol, 3.08 equiv) and aq 4% OsO_4 (256 µL, 10.2 mg, 40.1 µmol, 0.05 equiv). The reaction mixture was stirred for 16 h at r.t. The reaction was quenched by the addition of sat. aq $Na_2S_2O_3$ (1 mL) and the resulting mixture was stirred for 1 h. The solvents were removed in vacuo and the remaining residue was washed with CH_2Cl_2 (75 mL). The CH_2Cl_2 solution of the crude product was dried (Na_2SO_4), filtered, and the solvent was removed in vacuo to furnish the respective crude diol. The crude diol was dissolved in acetone (48 mL) and treated with aq $NaIO_4$ (0.20 M, 522 mg, 2.44 mmol, 3.17 equiv). The reaction mixture was stirred for 2 h at r.t. and then filtered over a short pad of Celite. The solvent was removed in vacuo and the residue was partitioned between EtOAc (150 mL) and brine (40 mL). The layers were separated and the organic layer was washed with brine (40 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 3.5 × 15 cm, P–EtOAc, 4:1) to give the cyclobutanone **19a** as a colorless solid; yield: 192 mg (790 µmol, 65%); mp 127 °C; R_f = 0.96 (P–EtOAc, 1:1) [UV/CAM].

IR (ATR): 2929 (s), 2856 (s), 1786 (vs), 1651 (vs), 1253 (m), 834 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1 H, C8-H), 7.54 (virt. td, $^3J \cong$ 7.8 Hz, ^4J = 1.4 Hz, 1 H, C10-H), 7.37 (virt. td, $^3J \cong$ 7.8 Hz, ^4J = 1.2 Hz, 1 H, C9-H), 7.29 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1 H, C11-H), 4.99 (d, ^4J = 2.3 Hz, 1 H, C5a-H), 4.09 (dd, ^3J = 10.7 Hz, ^3J = 5.7 Hz, 1 H, C1-H), 3.23 (s, 3 H, NCH_3), 3.13 (virt. td, $^3J \cong$ 9.9 Hz, ^4J = 2.3 Hz, 1 H, C4a-H), 2.14–2.07 (m, 1 H, C4-*H*H), 2.07–2.00 (m, 1 H, C2-*H*H), 1.96–1.91 (m, 1 H, C3-*H*H), 1.58–1.50 (m, 1 H, C2-H*H*), 1.50–1.43 (m, 2 H, C3-H*H*, C4-H*H*), 0.68 [s, 9 H, $SiC(CH_3)_3$], –0.20 [s, 3 H, $Si(CH_3)(CH_3)$], –0.68 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 204.8 (s, C5), 162.1 (s, C7), 142.6 (s, C11a), 132.7 (d, C10), 129.7 (s, C7a), 128.4 (d, C8), 127.8 (d, C11), 127.1 (d, C9), 75.9 (d, C1), 70.6 (d, C5a), 65.0 (d, C4a), 41.5 (s, C11b), 35.4 (q, NCH_3), 31.4 (t, C2), 25.6 [q, $SiC(CH_3)_3$], 23.4 (t, C4), 22.9 (t, C3), 17.7 [s, $SiC(CH_3)_3$], –4.9 [q, $Si(CH_3)(CH_3)$], –5.9 [q, $Si(CH_3)(CH_3)$].

MS (ESI): *m*/*z* = 386 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{22}H_{32}NO_3Si$: 386.2152; found: 386.2151.

1-[(*tert*-Butyldimethylsilyl)oxy]-7-methyl-2,3,4,4a,6a,7-hexahydroisoindolo[1,7a-*c*]isoquinoline-5,8(1*H*,6*H*)-dione (20a)

A solution of cyclobutanone **19a** (64.6 mg, 168 µmol, 1.00 equiv) in CH_2Cl_2 (2 mL) was treated with a solution of MSH[17] (54.1 mg, 251 µmol, 1.50 equiv) in CH_2Cl_2 (2 mL) at 0 °C (**CAUTION!** For precautions when working with MSH, see the general remarks section and the literature[17b]). The resulting mixture was stirred for 1 h at 0 °C whereupon the solvent was removed in vacuo at r.t. (!). The residue was redissolved in a mixture of benzene (2.4 mL) and MeOH (0.8 mL) and added to a suspension of activated basic Al_2O_3 (activity I, 500 mg) in MeOH (2 mL). The suspension was stirred for 19 h and then filtered through a pad of Celite. After removal of the solvents in vacuo, the crude product was purified by flash chromatography [SiO_2, 2 × 15 cm, EtOAc (1% Et_3N)] to provide the γ-lactam **20a** as a colorless resin; yield: 64.6 mg (161 µmol, 96%); R_f = 0.42 (EtOAc) [UV/CAM].

IR (ATR): 2926 (s), 2855 (m), 1714 (s), 1654 (vs), 1092 (m), 837 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (dd, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 1 H, C9-H) 7.54 (virt. td, $^3J \cong$ 7.9 Hz, ^4J = 1.5 Hz, 1 H, C11-H), 7.37 (virt. td, $^3J \cong$ 7.7 Hz, ^4J = 1.1 Hz, 1 H, C10-H), 7.33 (dd, ^3J = 7.9 Hz, ^4J = 1.1 Hz, 1 H, C12-H), 7.05 (s, 1 H, N6-H), 5.34 (s, 1 H, C6a-H), 3.80 (dd, ^3J = 11.2 Hz, ^3J = 4.6 Hz, 1 H, C1-H), 3.20 (s, 3 H, N7-CH_3), 2.87 (dd, ^3J = 12.0 Hz, ^3J = 6.5 Hz, 1 H, C4a-H), 2.22–2.15 (m, 1 H, C4-*H*H), 1.96–1.89 (m, 2 H, C2-*H*H, C3-*H*H), 1.63–1.44 (m, 2 H, C2-H*H*, C3-H*H*), 1.39–1.30 (m, 1 H, C4-H*H*), 0.67 [s, 9 H, $SiC(CH_3)_3$], –0.27 [s, 3 H, $Si(CH_3)(CH_3)$], –0.75 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 175.7 (s, C5), 162.7 (s, C8), 141.5 (s, C12a), 132.9 (d, C11), 129.4 (s, C8a), 128.2 (d, C9), 127.8 (d, C10), 126.2 (d, C12), 77.9 (d, C1), 71.0 (d, C6a), 51.0 (d, C4a), 50.8 (s, C12b), 35.4 (q, N7-CH_3), 32.1 (t, C2), 27.1 (t, C4), 25.7 [q, $SiC(CH_3)_3$], 22.7 (t, C3), 17.7 [s, $SiC(CH_3)_3$], –5.4 (q, $SiCH_3$), –5.9 [q, $Si(CH_3)(CH_3)$].

MS (ESI): *m*/*z* = 401 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{22}H_{32}N_2O_3Si$: 401.2260; found: 401.2257.

1-[(*tert*-Butyldimethylsilyl)oxy]-6,7-dimethyl-2,3,4,4a,6a,7-hexahydroisoindolo[1,7a-*c*]isoquinoline-5,8(1*H*,6*H*)-dione (21a)

By Methylation of γ-Lactam 20a

NaH (60% dispersion in mineral oil, 9.5 mg, 239 µmol, 1.64 equiv) was added to a solution of γ-lactam **20a** (58.5 mg, 146 µmol, 1.00 equiv) in DMF (6 mL) and the resulting suspension was stirred for 45 min. MeI (40.0 µL, 90.8 mg, 640 µmol, 4.38 equiv) was added and the reaction mixture was stirred at r.t. for 19 h. Sat. aq NH_4Cl (10 mL), H_2O (5 mL), and Et_2O (20 mL) were added, and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (40 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 2 × 15 cm, EtOAc) to give the N-alkylated γ-lactam **21a** as a colorless resin; yield: 48.8 mg (118 µmol, 81%).

By the Photochemical Beckmann Rearrangement of Cyclobutanone 19a via Oxaziridine 23

A solution of cyclobutanone **19a** (30.0 mg, 77.8 µmol, 1.00 equiv) in CH_2Cl_2 (5 mL) over activated molecular sieves (3Å, 300 mg) was treated with $MeNH_2$ (2.0 M in THF, 470 µL, 29.0 mg, 934 µmol, 12.0 equiv).

The resulting mixture was stirred for 23 h at 40 °C. Upon cooling to r.t., the reaction mixture was filtered over a short pad of Celite under argon atmosphere. The solvents were removed in vacuo. The residue was redissolved in CH_2Cl_2 (3 mL) and cooled to –40 °C. A suspension of *m*-CPBA (70%, 20.1 mg, 81.7 mg, 1.05 equiv) and $MgSO_4$ (60 mg) in CH_2Cl_2 (2 mL) was filtered via a syringe filter to remove the solid components. The obtained solution of the dried peracid was also cooled down to –40 °C. Under exclusion of light (!), the $MeNH_2$ solution was added dropwise to the solution of the peracid in CH_2Cl_2. After the addition was complete, the reaction mixture was stirred for 20 h at –40 °C under exclusion of light (!). Under an argon atmosphere, the mixture was quickly transferred into a photo tube and irradiated (λ = 300 nm) at r.t. for 8 h. After removal of the solvent in vacuo, the crude product was purified by flash chromatography (SiO_2, 2 × 13 cm, P–EtOAc, 2:1 → 1:1 → 0:1) to give the γ-lactam **21a** as a colorless resin; yield: 17.1 mg (41.2 µmol, 53%); R_f = 0.46 (EtOAc) [UV/CAM].

IR (ATR): 2948 (s), 2929 (s), 2857 (m), 1699 (s), 1654 (vs), 1091 (m), 836 cm^{-1} (m).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.11 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1 H, C9-H), 7.53 (virt. td, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1 H, C11-H), 7.39–7.32 (m, 2 H, C10-H, C12-H), 5.21 (s, 1 H, C6a-H), 3.84 (dd, ^3J = 11.1 Hz, ^3J = 4.7 Hz, 1 H, C1-H), 3.34 (s, 3 H, N7-CH_3), 2.97–2.91 (m, 1 H, C4a-H), 2.76 (s, 3 H, N6-CH_3), 2.23–2.14 (m, 1 H, C4-*H*H), 1.99–1.88 (m, 2 H, C2-*H*H, C3-*H*H), 1.70–1.45 (m, 2 H, C2-H*H*, C3-H*H*), 1.29–1.18 (m, 1 H, C4-H*H*), 0.69 [s, 9 H, SiC(CH_3)$_3$], –0.28 [s, 3 H, Si(*C*H_3)(CH_3)], –0.70 [s, 3 H, Si(CH_3)(*C*H_3)].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 173.4 (s, C5), 163.3 (s, C8), 141.8 (s, C12a), 132.9 (d, C11), 129.6 (s, C8a), 128.1 (d, C9), 127.7 (d, C10), 125.8 (d, C12), 77.8 (d, C1), 75.7 (d, C6a), 50.5 (d, C4a), 49.3 (s, C12b), 37.0 (q, N7-CH_3), 32.3 (t, C2), 26.7 (t, C4), 26.5 (q, N6-CH_3), 25.8 [q, SiC(*C*H_3)$_3$], 22.8 (t, C3), 17.8 [s, SiC(CH_3)$_3$], –5.6 [q, Si(*C*H_3)(CH_3)], –5.7 [q, Si(CH_3)(*C*H_3)].

MS (ESI): *m*/*z* = 415 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{35}N_2O_3Si$: 415.2417; found: 415.2418.

Methyl 6-[(*tert*-Butyldimethylsilyl)oxy]-6-(2-methyl-1-oxo-1,2-dihydroisoquinolin-4-yl)hexanoate (24) and 1-[(*tert*-Butyldimethylsilyl)oxy]-5-methoxy-7-methyl-1,2,3,4,4a,5,6a,7-octahydro-8*H*-isobenzofuro[1,7a-*c*]isoquinolin-8-one (25)

A solution of cyclobutanone **19a** (32.6 mg, 84.6 µmol) in anhydrous MeOH (16 mL) was purged with argon in an ultrasound bath for 15 min. After irradiation (λ = 300 nm) at r.t. for 4 h, the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 2 × 14 cm, P–EtOAc, 3:1) to provide the methyl ester **24** and acetal **25** as colorless resins.

Methyl Ester 24

Yield: 18.1 mg (43.3 µmol, 52%); R_f = 0.46 (EtOAc) [UV/CAM].

IR (ATR): 2950 (s), 2928 (s), 2855 (m), 1737 (s), 1653 (vs), 1631 (s), 1604 (m), 1253 (m), 1094 (m), 1074 (m), 835 (s), 773 (s), 700 cm^{-1} (m).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.48 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1 H, C8-H), 7.77 (d, ^3J = 8.3 Hz, 1 H, C5-H), 7.64 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.5 Hz, 1 H, C6-H), 7.48 (ddd, ^3J = 8.0 Hz, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1 H, C7-H), 7.10 (s, 1 H, C3-H), 4.89 (t, ^3J = 6.1 Hz, 1 H, C1′-H), 3.63 (s, 3 H, CO_2CH_3), 3.60 (s, 3 H, NCH_3), 2.29 (t, ^3J = 7.4 Hz, 2 H, C5′-H_2), 1.80 (virt. td, $^3J_1 \cong$ 8.1 Hz, $^3J_2$ = 6.1 Hz, 2 H, C2′-H_2), 1.70–1.55 (m, 2 H, C4′-H_2), 1.48–1.34 (m, 2 H, C3′-H_2), 0.89 [s, 9 H, SiC(CH_3)$_3$], 0.07 [s, 3 H, Si(*C*H_3)(CH_3)], –0.11 [s, 3 H, Si(CH_3)(*C*H_3)].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.2 (s, *C*O_2CH_3), 162.4 (s, C1), 135.1 (s, C4a), 131.9 (d, C6), 130.0 (d, C7), 128.5 (d, C5), 126.7 (d, C8), 126.1 (s, C8a), 122.9 (d, C3), 119.3 (s, C4), 71.1 (d, C1′), 51.6 (q, CO_2CH_3), 38.7 (t, C2′), 37.3 (q, NCH_3), 34.1 (t, C5′), 25.9 [q, SiC(*C*H_3)$_3$], 25.4 (t, C3′), 24.9 (t, C4′), 18.3 [s, SiC(CH_3)$_3$], –4.5 [q, Si(*C*H_3)(CH_3)], –4.9 (q, Si(CH_3)(*C*H_3)].

MS (ESI): *m*/*z* = 418 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{36}NO_4Si$: 418.2414; found: 418.2407.

Acetal 25

Acetal **25** was contaminated with unseparable traces of lactone **22a** and starting material **19a**; yield: 4.31 mg (10.3 µmol, 12%); R_f = 0.77 (P–EtOAc, 1:1) [UV/CAM].

IR (ATR): 2929 (s), 2856 (s), 1786 (vs), 1651 (vs), 1253 (m), 834 cm^{-1} (w).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.15 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1 H, C9-H), 7.51 (virt. td, $^3J \cong$ 7.6 Hz, ^4J = 1.5 Hz, 1 H, C11-H), 7.34–7.27 (m, 2 H, C10-H, C12-H), 5.53 (s, 1 H, C6a-H), 4.53 (s, 1 H, C5-H), 3.91 (dd, ^3J = 11.1 Hz, ^3J = 4.7 Hz, 1 H, C1-H), 3.28 (s, 3 H, NCH_3), 2.88 (s, 3 H, OCH_3), 2.72 (dd, ^3J = 12.5 Hz, ^3J = 6.3 Hz, 1 H, C4a-H), 1.96–1.90 (m, 1 H, C4-*H*H), 1.89–1.84 (m, 2 H, C2-*H*H, C3-*H*H), 1.52–1.41 (m, 1 H, C2-H*H*, C3-H*H*), 1.31–1.20 (m, 1 H, C4-H*H*), 0.65 [s, 9 H, SiC(CH_3)$_3$], –0.25 [s, 3 H, Si(*C*H_3)(CH_3)], –0.80 [s, 3 H, Si(CH_3)(*C*H_3)].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.9 (s, C8), 144.5 (s, C12a), 132.1 (d, C11), 128.4 (s, C8a), 127.6 (d, C9), 126.4 (d, C10), 125.5 (d, C12), 107.7 (d, C5), 91.7 (d, C6a), 78.7 (d, C1), 54.0 (q, OCH_3), 53.5 (d, C4a), 50.0 (s, 12b), 34.9 (NCH_3), 31.5 (t, C2), 26.9 (t, C4), 25.6 [s, SiC(*C*H_3)$_3$], 22.4 (t, C3), 17.6 [s, SiC(CH_3)$_3$], –5.1 [q, Si(*C*H_3)(CH_3)], –6.1 [q, Si(CH_3)(*C*H_3)].

MS (ESI): *m*/*z* = 418 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{36}NO_4Si$: 418.2414; found: 418.2411.

1-[(*tert*-Butyldimethylsilyl)oxy]-7-methyl-2,3,4,4a,6a,7-hexahydro-8*H*-isobenzofuro[1,7a-*c*]isoquinoline-5,8(1*H*)-dione (22a)

A solution of cyclobutanone **19a** (30.0 mg, 77.8 µmol, 1.00 equiv) in CH_2Cl_2 (2 mL) was treated with $NaHCO_3$ (13.1 mg, 156 µmol, 2.00 equiv). The mixture was cooled to 0 °C and *m*-CPBA (70%, 38.4 mg, 156 µmol, 2.00 equiv) was added in one portion. The reaction mixture was stirred for 2 h at 0 °C. Sat. aq $NaHCO_3$ (10 mL) and EtOAc (30 mL) were added and the layers were separated. The organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 2 × 7 cm, P–EtOAc, 1:1) to give the lactone **22a** as a colorless solid; yield: 30.3 mg (75.5 µmol, 97%); mp 181 °C; R_f = 0.20 (P–EtOAc, 4:1) [UV/CAM].

IR (ATR): 2949 (vs), 2930 (s), 2857 (m), 1773 (vs), 1664 (vs), 1095 (w), 836 cm^{-1} (w).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.18 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1 H, C9-H), 7.59 (virt. td, $^3J \cong$ 7.7 Hz, ^4J = 1.5 Hz, 1 H, C11-H), 7.42 (virt. td, $^3J \cong$ 7.8 Hz, ^4J = 1.1 Hz, 1 H, C10-H), 7.32 (dd, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1 H, C12-H), 5.96 (s, 1 H, C6a-H), 3.85 (dd, ^3J = 11.1 Hz, ^3J = 4.8 Hz, 1 H, C1-H), 3.31 (s, 3 H, NCH_3), 3.17–3.11 (m, 1 H, C4a-H), 2.34–2.16 (m, 1 H, C4-*H*H), 2.09–1.91 (m, 2 H, C2-*H*H, C3-*H*H), 1.69–1.48 (m, 3 H, C2-H*H*, C3-H*H*, C4-H*H*), 0.68 [s, 9 H, SiC(CH_3)$_3$], –0.24 [s, 3 H, Si(*C*H_3)(CH_3)], –0.75 [s, 3 H, Si(CH_3)(*C*H_3)].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.4 (s, C5), 162.7 (s, C8), 139.8 (s, C12a), 133.2 (d, C11), 129.1 (s, C8a), 128.5 (d, C9), 128.3 (d, C10), 125.9 (d, C12), 91.5 (d, C6a), 77.3 (d, C1), 50.2 (d, C4a), 50.0 (s, C12b), 35.4 (q, NCH_3), 31.8 (t, C2), 26.0 (t, C4), 25.6 [q, $SiC(CH_3)_3$], 22.8 (t, C3), 17.6 [s, $SiC(CH_3)_3$], –5.3 [q, $Si(CH_3)(CH_3)$], –6.0 [q, $Si(CH_3)(CH_3)$].

MS (ESI): *m*/*z* = 402 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{22}H_{32}NO_4Si$: 402.2100; found: 402.2097.

X-ray Crystal Data[31]

Formula: $C_{22}H_{31}NO_4Si$; M_r = 401.57; crystal color and shape: yellow fragment, crystal dimensions = 0.43 × 0.59 × 0.70 mm; crystal system: monoclinic; space group *P* $2_1/n$ (no. 14); *a* = 11.3546(5), *b* = 15.6564(6), *c* = 12.5518(5) Å, *β* = 99.562(2)°; *V* = 2200.36(16) Å^3; $\mu(Mo_{K\alpha})$ = 0.133 mm^{-1}; ρ_{calcd}=1.212 g cm^{-3}; *θ*-range = 2.10–25.40°; data collected: 46842; independent data [$I_o>2\sigma(I_o)$/all data/R_{int}]: 3576/4038/0.0311; data/restraints/parameters: 4038/0/259; *R*1 [$I_o>2\sigma(I_o)$/all data]: 0.0402/0.0474; *wR*2 [$I_o>2\sigma(I_o)$/all data]: 0.1005/0.1060; GOF = 1.049; $\Delta\rho_{max/min}$: 0.72/–0.22 e Å^{-3}.

1-[(*tert*-Butyldimethylsilyl)oxy]-6-methyl-5-methylene-1,2,3,4,4a,5,5a,6-octahydro-7*H*-benzo[2,3]cyclobuta[1,2-*c*][1,3]dioxolo[4,5-*g*]isoquinolin-7-one (18b)

NaH (60% dispersion in mineral oil, 11.6 mg, 290 µmol, 1.20 equiv) was added to a solution of [2+2] photocycloaddition product **7b** ((100 mg, 242 µmol, 1.00 equiv) in DMF (9 mL) and the resulting suspension was stirred for 45 min. MeI (53.7 µL, 122 mg, 208.12 µmol, 3.60 equiv) was added and the reaction mixture was stirred at r.t. for 19 h. Sat. aq NH_4Cl (10 mL), H_2O (5 mL) and Et_2O (20 mL) were added and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 3.5 × 12 cm, P–EtOAc, 5:1) to give the N-alkylated isoquinolone **18b** as a colorless resin; yield: 43.0 mg (101 µmol, 42%); R_f = 0.39 (P–EtOAc, 5:1) [UV/CAM].

IR (ATR): 2929 (vs), 2856 (s), 1648 (vs), 1473 (vs), 1268 (m), 1247 (m), 836 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (s, 1 H, C8-H), 6.62 (s, 1 H, C12-H), 6.01 (d, ^2J = 1.5 Hz, 1 H, OC*H*HO), 5.98 (d, ^2J = 1.5 Hz, 1 H, OCH*H*O), 4.88–4.83 (m, 1 H, C5-C*H*H), 4.70 (dd, ^2J = 1.2 Hz, ^4J = 2.4 Hz, 1 H, C5-CH*H*), 4.56 (d, ^4J = 2.4 Hz, 1 H, C5a-H), 3.73 (dd, ^3J = 10.9 Hz, ^3J = 5.9 Hz, 1 H, C1-H), 3.20 (s, 3 H, NCH_3), 2.82–2.69 (m, 1 H, C4a-H), 2.15–2.06 (m, 1 H, C4-*H*H), 1.97–1.88 (m, 1 H, C2-*H*H), 1.82–1.74 (m, 1 H, C3-*H*H), 1.52–1.40 (m, 1 H, C2-H*H*), 1.37–1.20 (m, 2 H, C3-H*H*, C4-H*H*), 0.69 [s, 9 H, $SiC(CH_3)_3$], –0.20 [s, 3 H, $Si(CH_3)(CH_3)$], –0.60 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.4 (s, C7), 152.7 (s, C11a), 150.8 (s, C5), 146.8 (s, C8a), 140.2 (s, C12a), 124.6 (s, C7a), 107.4 (d, C8), 106.3 (d, C12), 104.1 (t, C5=*C*H$_2$), 101.6 (t, O*C*H$_2$O), 75.8 (d, C1), 59.5 (d, C5a), 50.9 (d, C4a), 46.5 (s, C12b), 35.4 (q, NCH_3), 32.0 (t, C2), 28.9 (t, C4), 25.6 [q, $SiC(CH_3)_3$], 22.4 (t, C3), 17.7 [s, $SiC(CH_3)_3$], –4.9 [q, $Si(CH_3)(CH_3)$], –5.6 [q, $Si(CH_3)(CH_3)$].

MS (ESI): *m*/*z* = 428 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{24}H_{34}NO_4Si$: 428.2257; found: 428.2257.

1-[(*tert*-Butyldimethylsilyl)oxy]-6-methyl-2,3,4,4a,5a,6-hexahydro-1*H*-benzo[2,3]cyclobuta[1,2-*c*][1,3]dioxolo[4,5-*g*]isoquinoline-5,7-dione (19b) and 1-[(*tert*-Butyldimethylsilyl)oxy]-7-methyl-2,3,4,4a,6a,7-hexahydro-8*H*-[1,3]dioxolo[4,5-*g*]isobenzofuro[1,7a-*c*]isoquinoline-5,8(1*H*)-dione (22b)

A solution of the N-alkylated isoquinolone **19a** (43.0 mg, 101 µmol, 1.00 equiv) in CH_2Cl_2 (2 mL) was treated with NMO monohydrate (40.7 mg, 301 mmol, 2.98 equiv) and aq 4% OsO_4 (32 µL, 1.29 mg, 5.07 µmol, 0.05 equiv). The reaction mixture was stirred for 20 h at r.t. The reaction was quenched by the addition of sat. aq $Na_2S_2O_3$ (1 mL) and the resulting mixture was stirred for 1 h. The solvents were removed in vacuo and the remaining residue was washed with CH_2Cl_2 (50 mL) and the CH_2Cl_2 solution was dried (Na_2SO_4). Filtration and removal of the solvent in vacuo furnished the respective crude diol. The crude diol was dissolved in acetone (6 mL) and treated with aq $NaIO_4$ (210 mM, 67.3 mg, 315 µmol, 3.12 equiv). The reaction mixture was stirred for 45 min at r.t. and then filtered over a short pad of Celite. The solvent was removed in vacuo and the residue was partitioned between EtOAc (30 mL) and brine (20 mL). The layers were separated and the organic layer was washed with brine (20 mL), dried (Na_2SO_4), and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 2 × 15 cm, P–EtOAc, 4:1) to give the cyclobutanone **19b** and the lactone **22b** as colorless resins.

Cyclobutanone 19b

Yield: 20.4 mg (52.2 µmol, 52%); R_f = 0.84 (CH_2Cl_2–MeOH, 95:5) [UV/CAM].

IR (ATR): 2929 (s), 2857 (s), 1786 (vs), 1650 (vs), 1474 (vs), 1268 (s), 1249 (m), 1088 (m), 1038 (m), 839 (m), 775 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (s, 1 H, C8-H), 6.66 (s, 1 H, C12-H), 6.02 (d, ^2J = 1.3 Hz, 1 H, OC*H*HO), 5.99 (d, ^2J = 1.3 Hz, 1 H, OCH*H*O), 4.92 (d, ^4J = 2.3 Hz, 1 H, C5a-H), 4.04 (dd, ^3J = 10.8 Hz, ^3J = 5.8 Hz, 1 H, C1-H), 3.18 (s, 3 H, NCH_3), 3.07 (virt. td, $^3J \cong$ 10.1 Hz, ^4J = 2.3 Hz, 1 H, C4a-H), 2.12–2.05 (m, 1 H, C4-*H*H), 2.05–1.99 (m, 1 H, C2-*H*H), 1.94–1.88 (m, 1 H, C3-*H*H), 1.58–1.48 (m, 1 H, C2-H*H*), 1.45–1.38 (m, 2 H, C3-H*H*, C4-H*H*), 0.71 [s, 9 H, $SiC(CH_3)_3$], –0.15 [s, 3 H, $Si(CH_3)(CH_3)$], –0.53 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 205.0 (s, C5), 161.8 (s, C7), 151.4 (s, C11a), 147.6 (s, C8a), 137.7 (s, 12a), 124.5 (s, C7a), 107.8 (d, C8), 106.1 (d, C12), 101.9 (t, O*C*H$_2$O), 75.4 (d, C1), 70.4 (d, C5a), 65.0 (d, C4a), 41.8 (s, 12b), 35.3 (q, NCH_3), 31.4 (t, C2), 25.6 [q, $SiC(CH_3)_3$], 23.4 (t, C4), 22.8 (t, C3), 17.7 [s, $SiC(CH_3)_3$], –4.9 [q, $Si(CH_3)(CH_3)$], –5.6 [q, $Si(CH_3)(CH_3)$].

MS (ESI): *m*/*z* = 430 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{32}NO_5Si$: 430.2050; found: 430.2048.

Lactone 22b

Yield: 13.3 mg (29.8 µmol, 30%); R_f = 0.77 (CH_2Cl_2–MeOH, 95:5) [UV/CAM].

IR (ATR): 2929 (s), 2857 (s), 1774 (s), 1660 (s), 1479 (vs), 1286 (m), 1256 (s), 1088 (m), 1038 (m), 837 (m), 776 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (s, 1 H, C9-H), 6.70 (s, 1 H, C13-H), 6.04 (d, ^2J = 1.3 Hz, 1 H, OC*H*HO), 6.02 (d, *J* = 1.3 Hz, 1 H, OCH*H*O), 5.91 (s, 1 H, C6a-H), 3.80 (dd, ^3J = 11.1 Hz, ^3J = 4.8 Hz, 1 H, C1-H), 3.27 (s, 3 H, NCH_3), 3.02 (dd, ^3J = 11.6 Hz, ^3J = 6.9 Hz, 1 H, C4a-H), 2.27–2.17 (m, 1 H, C4-*H*H), 2.03–1.92 (m, 1 H, C2-*H*H), 1.64–1.59 (m, 1 H, C3-*H*H), 1.55–1.45 (m, 1 H, C2-H*H*), 1.38–1.17 (m, 2 H, C3-H*H*, C4-H*H*), 0.70 [s, 9 H, $SiC(CH_3)_3$], –0.19 [s, 3 H, $Si(CH_3)(CH_3)$], –0.61 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.4 (s, C5), 162.2 (s, C8), 151.9 (s, C12a), 147.9 (s, C9a), 135.0 (s, C13a), 124.0 (s, C8a), 107.9 (d, C9), 105.3 (d, C13), 102.1 (t, OCH_2O), 91.7 (d, C6a), 76.7 (d, C1), 50.5 (s, C13b), 50.2 (d, C4a), 35.3 (q, NCH_3), 31.8 (t, C2), 26.1 (t, C4), 25.6 [q, $SiC(CH_3)_3$], 22.7 (t, C3), 17.6 [s, $SiC(CH_3)_3$], –5.2 [q, $Si(CH_3)(CH_3)$], –5.7 [q, $Si(CH_3)(CH_3)$].

MS (ESI): *m*/*z* = 446 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{32}NO_6Si$: 446.1999; found: 446.1996.

1-[(*tert*-Butyldimethylsilyl)oxy]-7-methyl-2,3,4,4a,6a,7-hexahydro-[1,3]dioxolo[4,5-*g*]isoindolo[1,7a-*c*]isoquinoline-5,8(1*H*,6*H*)-dione (20b)

A solution of cyclobutanone **19b** (16.7 mg, 38.9 µmol, 1.00 equiv) in CH_2Cl_2 (1 mL) was treated with a solution of MSH[17] (13.4 mg, 62.2 µmol, 1.60 equiv) in CH_2Cl_2 (1 mL) at 0 °C (**CAUTION!** For precautions when working with MSH, see the general remarks section and the literature[17b]). The resulting mixture was stirred for 1 h at 0 °C whereupon the solvent was removed in vacuo at r.t. (!). The residue was redissolved in a mixture of benzene (750 µL) and MeOH (0.25 µL) and added to a suspension of activated basic Al_2O_3 (activity I, 500 mg) in MeOH (1 mL). The suspension was stirred for 20 h and then filtered through a pad of Celite. After removal of the solvents in vacuo, the crude product was purified by flash chromatography (SiO_2, 2 × 7 cm, P–EtOAc, 1:1) to give the γ-lactam **20b** as a colorless resin; yield: 13.4 mg (30.1 µmol, 77%); R_f = 0.12 [P–EtOAc, 1:1 (1% Et_3N)] [UV/CAM].

IR (ATR): 3226 (w), 2927 (vs), 2856 (s), 1708 (s), 1651 (s), 1479 (s), 1251 (m), 1089 (w), 1038 (w), 836 (w), 776 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (s, 1 H, C9-H), 6.73 (s, 1 H, C13-H), 6.03 (d, ^2J = 1.3 Hz, 1 H, OC*H*HO), 6.00 (d, ^2J = 1.3 Hz, 1 H, OCH*H*O), 5.32 (s, 1 H, C6a-H), 3.76 (dd, ^3J = 11.3 Hz, ^3J = 4.8 Hz, 1 H, C1-H), 3.19 (s, 3 H, N7-CH_3), 2.77 (dd, ^3J = 11.9 Hz, ^3J = 6.5 Hz, 1 H, C4a-H), 2.24–2.17 (m, 1 H, C4-*H*H), 1.95–1.88 (m, 2 H, C2-*H*H, C3-*H*H), 1.62–1.53 (m, 1 H, C2-H*H*), 1.49–1.42 (m, 1 H, C3-H*H*), 1.38–1.22 (m, 1 H, C4-H*H*), 0.70 [s, 9 H, $SiC(CH_3)_3$], –0.21 [s, 3 H, $Si(CH_3)(CH_3)$], –0.60 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.6 (s, C5), 162.2 (s, C8), 151.6 (s, C12a), 147.5 (s, C9a), 136.8 (s, C13a), 124.2 (s, C8a), 107.7 (d, C9), 105.7 (d, C12), 102.0 (t, OCH_2O), 77.4 (d, C1), 71.2 (d, C6a), 51.4 (d, C4a), 50.9 (s, C13b), 35.2 (q, N7-CH_3), 32.1 (t, C2), 27.2 (t, C4), 25.7 [q, $SiC(CH_3)_3$], 22.6 (t, C3), 17.7 [s, $SiC(CH_3)_3$], –5.3 [q, $Si(CH_3)(CH_3)$], –5.6 [q, $Si(CH_3)(CH_3)$].

MS (ESI): *m*/*z* = 445 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{33}N_2O_5Si$: 445.2159; found: 445.2155.

1-[(*tert*-Butyldimethylsilyl)oxy]-6,7-dimethyl-2,3,4,4a,6a,7-hexahydro[1,3]dioxolo[4,5-*g*]isoindolo[1,7a-*c*]isoquinoline-5,8(1*H*,6*H*)-dione (21b)

NaH (60% dispersion in mineral oil, 3.2 mg, 80.0 µmol, 2.85 equiv) was added to a solution of γ-lactam **20b** (12.5 mg, 28.1 µmol, 1.00 equiv) in DMF (1.5 mL) and the resulting suspension was stirred for 45 min. MeI (10.0 µL, 22.7 mg, 160 µmol, 5.69 equiv) was added and the reaction mixture was stirred at r.t. for 21 h. Sat. aq NH_4Cl (5 mL), H_2O (10 mL), and Et_2O (20 mL) were added and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (40 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO_2, 2 × 10 cm, EtOAc) to give the N-alkylated γ-lactam **21b** as a colorless resin; yield: 8.0 mg (17.4 µmol, 62%); R_f = 0.37 (P–EtOAc, 1:1) [UV/CAM].

IR (ATR): 2929 (s), 2857 (s), 1698 (s), 1651 (vs), 1479 (vs), 1286 (m), 1252 (s), 1088 (m), 1038 (m), 836 (m), 776 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (s, 1 H, C9-H), 6.74 (s, 1 H, C13-H), 6.02 (d, ^2J = 1.4 Hz, 1 H, OC*H*HO), 5.98 (d, ^2J = 1.4 Hz, 1 H, OCH*H*O), 5.17 (s, 1 H, C6a-H), 3.78 (dd, ^3J = 11.2 Hz, ^3J = 4.8 Hz, 1 H, C1-H), 3.30 (s, 3 H, N7-CH_3), 2.81 (dd, ^3J = 12.2 Hz, ^3J = 6.4 Hz, 1 H, C4a-H), 2.75 (s, 3 H, N6-CH_3), 2.23–2.13 (m, 1 H, C4-*H*H), 2.00–1.87 (m, 2 H, C2-*H*H, C3-*H*H), 1.69–1.52 (m, 1 H, C2-H*H*), 1.52–1.40 (m, 1 H, C3-H*H*), 1.33–1.12 (m, 2 H, C4-H*H*), 0.72 [s, 9 H, $SiC(CH_3)_3$], –0.22 [s, 3 H, $Si(CH_3)(CH_3)$], –0.57 [s, 3 H, $Si(CH_3)(CH_3)$].

^{13}C NMR (126 MHz, $CDCl_3$): δ = 173.3 (s, C5), 162.8 (s, C8), 151.6 (s, C12a), 147.4 (s, C9a), 137.2 (s, C13a), 124.4 (s, C8a), 107.8 (d, C9), 105.6 (d, C12), 101.9 (t, OCH_2O), 77.2 (d, C1), 75.7 (d, C6a), 50.8 (d, C4a), 49.6 (C13b), 36.9 (q, N7-CH_3), 32.3 (t, C2), 26.7 (t, C4), 26.4 (q, N6-CH_3), 25.8 [q, $SiC(CH_3)_3$], 22.7 (t, C2), 17.8 [s, $SiC(CH_3)_3$], –5.4 [q, $Si(CH_3)(CH_3)$], –5.5 [q, $Si(CH_3)(CH_3)$].

MS (ESI): *m*/*z* = 459 [(M + H)$^+$].

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{35}N_2O_5Si$: 459.2315; found: 459.2310.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380756. Included are additional procedures and crystallographic data, emission spectrum of 350 nm light source, and NMR spectra.

Primary Data

Primary data for this article are available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000084 and can be cited using the following DOI: 10.4125/pd0067th.

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