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A New, Efficient and Stereoselective Synthesis of Tricyclic and Tetracyclic Compounds by Samarium Diiodide Induced Cyclisations of Naphthyl-Substituted Arylketones—An Easy Access to Steroid-Like Skeletons

Francesca Aulenta, Mathias Berndt, Irene Brüdgam, Hans Hartl, Sebastian Sörgel, and Hans-Ulrich Reißig*[a]

Dedicated to Professor Herbert Mayr on the occasion of his 60th birthday

Abstract: In this report, we present the application of samarium diiodide induced cyclisations of naphthyl-substituted ketones towards an easy and stereoselective access to tri- and tetracyclic-functionalised compounds. Typical naphthalene derivatives were studied to investigate the scope and limitations of this novel cyclisation process. The model substrates studied demonstrate that the samarium ketyl cyclisations are essentially restricted to the formation of six-membered rings. The diastereoselectivity of these reactions is strongly influenced by the connection of the alkyl side chain to the naphthalene core. γ-Naphth-1-yl-substituted ketones furnished cyclisation products, such as **17** or **22**–**26**, as single diastereomers, whereas γ-naphth-2-yl-substituted precursors gave mixtures of diastereomers—as demonstrated by the conversion of model compound **10** into tricyclic products **18a**/**18b**, or that of cyclohexanone derivative **33** into tetracyclic diastereomers **34a**/**34b**. Cyclic ketones as ketyl precursors furnished steroid-like tetracyclic skeletons; however, due to the *cis*/*cis* fusion of rings B/C and C/D these products have an "unnatural" bowl-like shape. Several of the cyclisation products have been identified by X-ray analyses, which not only proved the constitutions, but also the relative configurations and the preferred conformations. Steroid analogue **23** was subjected to subsequent transformations, which demonstrate that the styrene-like double bond of such compounds can be used for further structural diversification. First attempts to synthesise related azasteroids by incorporating nitrogen atoms into the ketone moiety are also reported. Thus, pyrrolidine derivatives **44** and **47** as well as piperidine derivatives **50** and **52** were subjected to samarium diiodide induced cyclisations. The expected tetracyclic products **48**, **49a**/**49b**, **51** and **53a**/**53b** were obtained in moderate to good yields. The stereoselectivities observed follow the rules already established for the all-carbon precursors. The resulting products, bearing a nitrogen atom in ring D, are interesting azasteroid analogues with "unnatural" configuration.

Keywords: electron transfer · ketyls · radical reactions · samarium diiodide · steroids

Introduction

It is well established that radical chemistry offers a wide array of useful transformations for the construction of complex molecular architectures.[1] Among all, the cyclisations of carbon-centred radicals onto unsaturated functional groups have been considered as one of the most useful synthetic tools for C–C bond formation and have been used as key steps in many natural product syntheses.[2] In the last 25 years, samarium diiodide has played a central role in radical chemistry as a unique electron-transfer reagent,[3] and this prominent position is witnessed by the ever-growing number of original publications and reviews.[4] This reagent is particularly effective to induce reductive couplings of carbonyl groups with carbon–carbon multiple bonds in high yield and good stereoselectivity. Along this line, Molander and coworkers[5] and other authors[6] have widely investigated the intramolecular ketyl–olefin coupling, which leads to interestingly functionalised cyclic compounds. In our group, samari-

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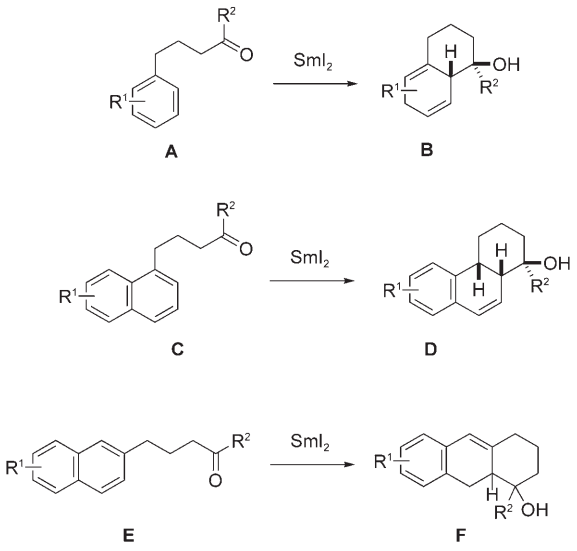
[+] Responsible for X-ray crystal structure analysis.

um diiodide was employed for new intramolecular couplings of ketyls with alkenyl, alkynyl, aryl and hetaryl substituents, yielding synthetically useful products, such as benzannulated cyclooctane and cyclooctene derivatives,[7] hexahydronaphthalenes[8] and indoles.[9] These reactions are promoted by the samarium diiodide–hexamethylphosphoramide (HMPA) complex,[10] whereupon an electron is transferred from this complex to the carbonyl group, thus generating a radical anion (samarium ketyl). Intramolecular attack of this samarium ketyl to the unsaturated functionality, followed by a second electron transfer, generates an organosamarium species, which, upon regioselective protonation, leads to the final cyclised products. The use of an excess of HMPA as an additive is in most of these cases a requirement to favour the forward reaction and to control the outcome in terms of product distribution and stereoselectivity.[11]

The samarium diiodide intramolecular couplings of γ-aryl ketones **A** established a novel stereoselective route to hexahydronaphthalene derivatives **B**.[8,12] With this method,[13] we delivered a new solution to the challenging goal of dearomatising benzene derivatives,[14] providing synthetically valuable functionalised intermediates of type **B** (Scheme 1).



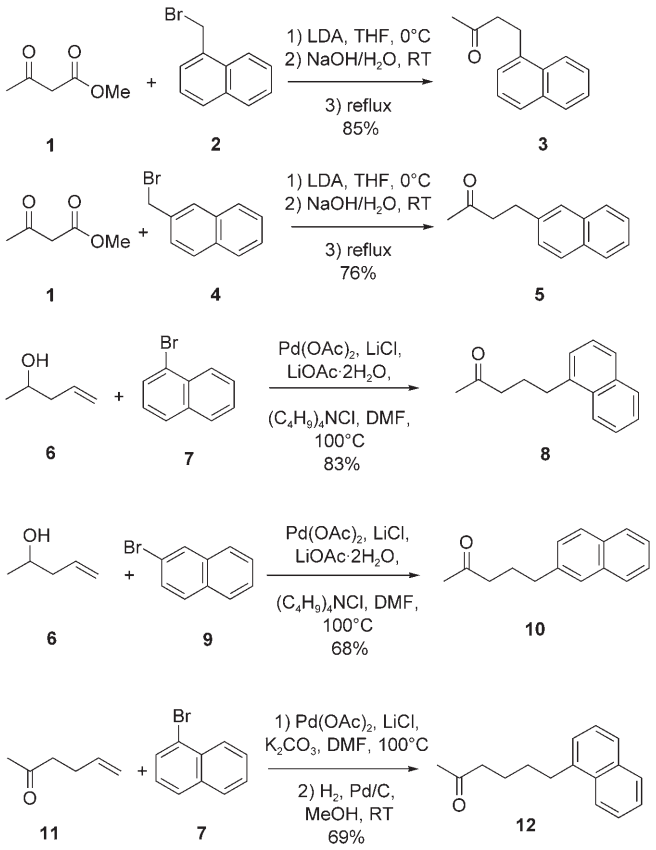
Scheme 1. Samarium diiodide promoted cyclisations of γ-aryl ketones **A** and γ-naphthyl ketones **C** or **E** leading to the cyclisation products **B**, **D** or **F**.

These results prompted us to investigate suitable naphthyl ketones **C** and **E**, which should lead to tricyclic compounds **D** or **F**. In general, naphthalene derivatives should be even more favourable substrates compared to benzene derivatives, due to the lower reduction potential of the fused 10π-electron systems[15] and the "decreased loss of aromaticity" during the cyclisation process. Furthermore, we expected that these transformations would also occur with high diastereoselectivity.

In a preliminary communication,[16] we demonstrated that application of this methodology indeed allows stereoselective syntheses of compounds **D** and also of related tetracyclic products which resemble steroids with unnatural *cis*/*cis* fusion of rings B/C/D. We also reported that precursors **E** underwent similar reductive cyclisations to products **F**, albeit with low diastereoselectivity. In this full account, we describe in detail our efforts aimed at synthesising these polycyclic compounds by means of the samarium diiodide promoted reductive cyclisations. We also present the first applications of this methodology to the couplings of naphthyl-substituted pyrrolidinone and piperidinone derivatives, ultimately leading to highly functionalised nitrogen-containing tetracyclic products, which may be regarded as azasteroids.

Results and Discussion

Tricyclic compounds: To investigate the applicability and substrate-dependence of the samarium diiodide induced cyclisations, we prepared a series of simple acyclic naphthyl-substituted ketones (Scheme 2) differing in the chain length (from β- to δ-substituted ketones) and in the position of the naphthyl ring, at which the aliphatic chain was connected (C-1 or C-2). Ketones **3**[17] and **5** were obtained by alkylation of methyl 3-oxobutanoate (**1**) with bromomethylnaphthalenes **2** or **4**, followed by saponification and decarboxylation.[18] Syntheses of ketones **8** and **10**[13b] were performed by means of Heck reactions of the corresponding bromonaph-



Scheme 2. Synthesis of the naphthyl-substituted ketones **3**, **5**, **8**, **10** and **12**.

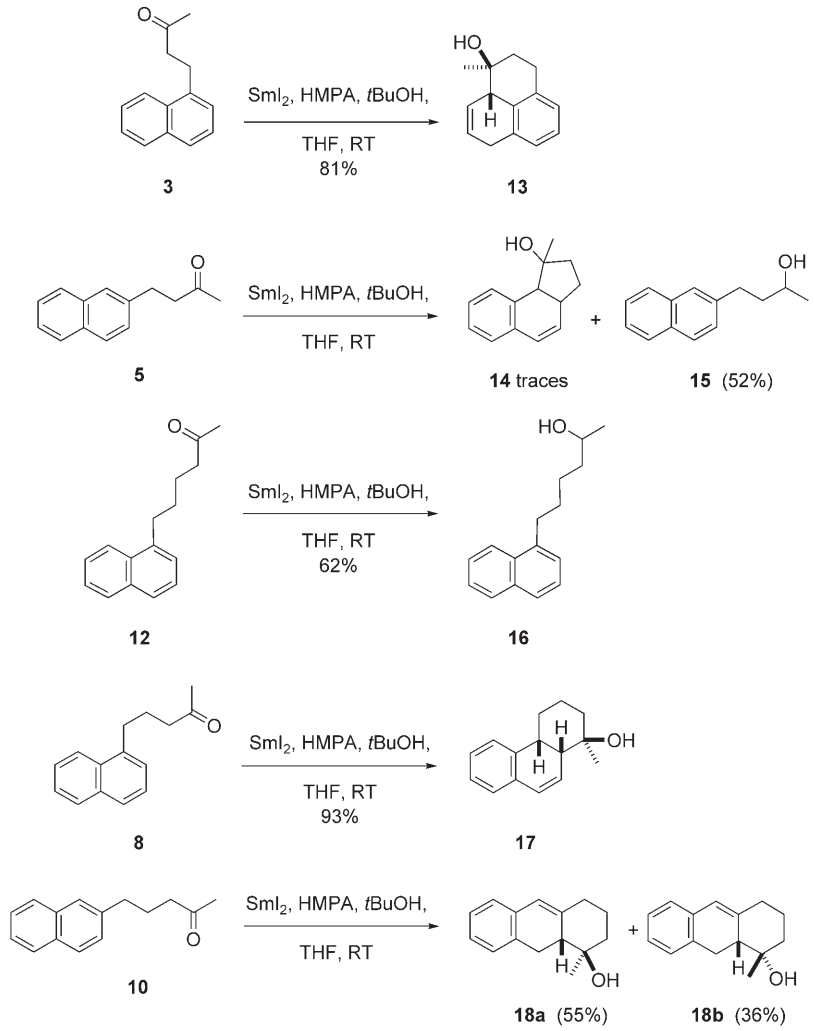
thalenes **7** or **9** with 4-penten-2-ol (**6**) and subsequent isomerisation according to a literature procedure.[19] A Heck coupling followed by hydrogenation was employed for the preparation of compound **12**.

It was anticipated that cyclisations of β-, γ-, and δ-naphthyl-substituted ketones **3**, **5**, **8**, **10**, and **12** would occur by means of 5-*exo*-trig, 6-*exo*-trig, and 7-*exo*-trig processes,[20] leading to tricyclic compounds containing new five-, six-, or seven-membered rings. However, rather surprisingly, the cyclisation of ketone **3** under standard conditions (2.2 equiv SmI_2, 18 equiv HMPA, 2.2 equiv of *t*BuOH, RT) proceeded via a 6-*exo*-trig pathway, affording tricyclic compound **13**[13b] in good yield and as a single diastereomer (Scheme 3).[21] The final protonation of the organosamarium species occurred regioselectively, affording product **13** with a deconjugated double bond and an intact aromatic ring.[22] In the case of **5**, in which a 6-*exo*-trig cyclisation is not feasible, the main reaction pathway was the reduction of the carbonyl group to deliver the corresponding alcohol **15**[23] in 52% yield; only traces of the cyclisation product **14** were identified. An analogous result was observed when the δ-naphthyl-substituted ketone **12** was subjected to the reductive coupling which provided only alcohol **16**[24] in 62% yield.

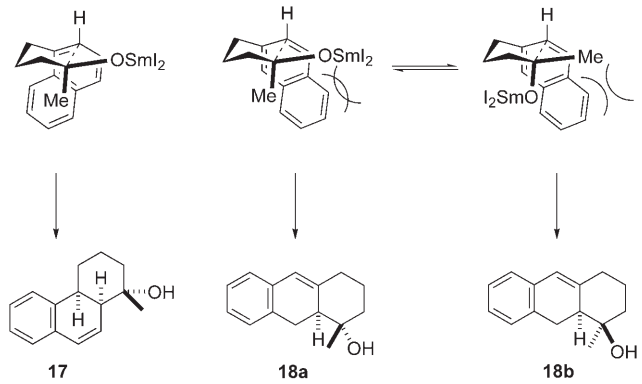
Very pleasingly, ketones **8** and **10** afforded the cyclised products **17**, **18a** and **18b** in excellent yields. These observations lead to the conclusion that the cyclisations are essentially confined to the formation of six-membered rings (Scheme 3). Similar results have been obtained for the related benzene derivatives.[4b] It is interesting to note that 1-substituted naphthalene derivative **8** afforded only one diastereomer with *cis*-annulated rings B and C as depicted. This relative configuration was assigned by ^{1}H NMR spectroscopy in which a coupling constant of $J = 5.4$ Hz between the two bridgehead protons clearly indicates their *cis* relationship. The configuration at the hydroxyl group bearing carbon was assigned in analogy to the related products **22**–**26** (see below).

While tricyclic compound **17** was formed as a single diastereomer, product **18** was isolated as a 60:40 mixture of two diastereomers in very good yield. The relative configurations of the two products were assigned by ^{1}H NMR spectroscopy; in this case, the chemical shift of the bridgehead proton is indicative for the *cis* or *trans* relationship to the hydroxyl group. In the *cis*-configured **18a**, the signal of this proton appeared at 3.24–3.44 ppm, whereas for the other isomer, the chemical shift was 2.47 ppm. A plausible explanation for the loss of diastereoselectivity might be found in the competing steric interaction between the naphthalene ring and the bulky $OSmI_2$ substituent (Scheme 4). For this reason the six-membered transition structures with an equatorially and axially arranged $OSmI_2$ group have similar stability and thus two diastereomers are formed. When these factors are absent, the samarium alcoholate for steric reasons generally seems to prefer an equatorial position, a model which also operates in the case of the highly stereoselective conversion of **8** into **17**.[25]

It should also be noted that the transformation of **10** into **18a/b** is a highly regioselective process. No products derived from attack of the samarium ketyl to C-1 of the naphthalene ring were isolated. The constitution of compounds **18a/b** is clearly shown by their NMR



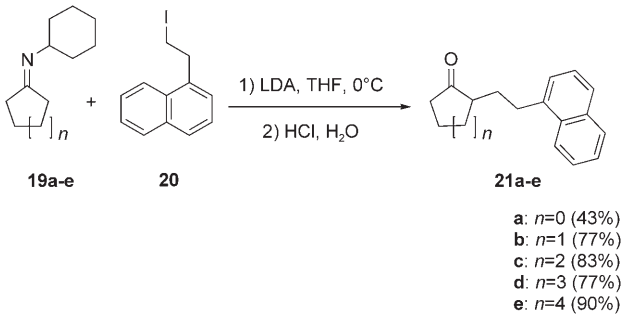
Scheme 3. SmI_2-induced cyclisation of ketones **3**, **5**, **12**, **8** and **10**.



Scheme 4. Proposed chair-like transition structures for the cyclisations of substrates **8** and **10**, leading to **17** and **18a/b** (for clarity of the illustration, we have depicted the enantiomers of the products drawn in Scheme 3; HMPA ligands at samarium are omitted for simplicity).

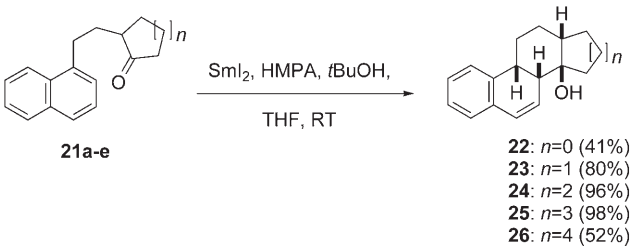
spectroscopic data and was strongly supported by the X-ray crystal structure analysis of the closely related product **34a** (see below). The regioselectivity observed is in contradiction to the result reported by Shono et al.[13] for the related electrochemical reductive cyclisation of compound **10**. We assume that the higher steric hindrance involved with a samarium ketyl causes this altered regioselectivity.

Tetracyclic compounds: The two acyclic γ-naphthyl-substituted ketones **8** and **10** afforded tricycles in very good yields with newly formed six-membered rings. We therefore expected that using cyclic γ-naphthyl ketones of type **21** as precursors of samarium diiodide induced cyclisations would lead to tetracyclic products with steroid-like skeletons. The synthesis of the precursor ketones **21a–e** was achieved by α-alkylation of Schiff-bases **19a–e** (derived from the corresponding ketones) with naphthyl-substituted alkyl iodide **20**,[26] followed by hydrolysis of the resulting imine under acidic conditions (Scheme 5).



Scheme 5. Synthesis of the precursor ketones **21a–e**.

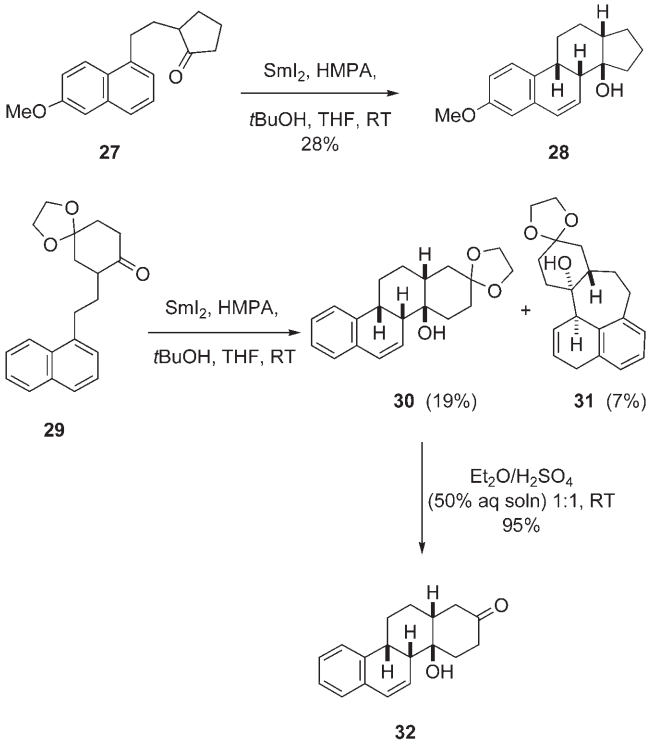
Most gratifyingly, tetracyclic products **22–26** were obtained in good to excellent yield as single diastereomers when ketones **21a–e** underwent standard reductive coupling conditions with samarium diiodide (Scheme 6). In the case of compounds **22** and **26**, incorporating four-membered and



Scheme 6. SmI_2-induced cyclisations of the cyclic γ-naphthyl-substituted ketones **21a–e**, leading to tetracyclic products **22–26**.

eight-membered rings, the yields are only moderate. However, these two experiments have only been performed in small scale and are not yet optimised. In all cases, the relative configurations of products were assigned by two-dimensional NMR spectroscopy (COSY, HMQC, NOESY), demonstrating the expected *cis*/*cis* fusion of rings B/C and C/D. This arrangement forces the molecules to adopt a bowl-like shape and therefore to display steroid-like skeletons with "unnatural" configuration and geometry.

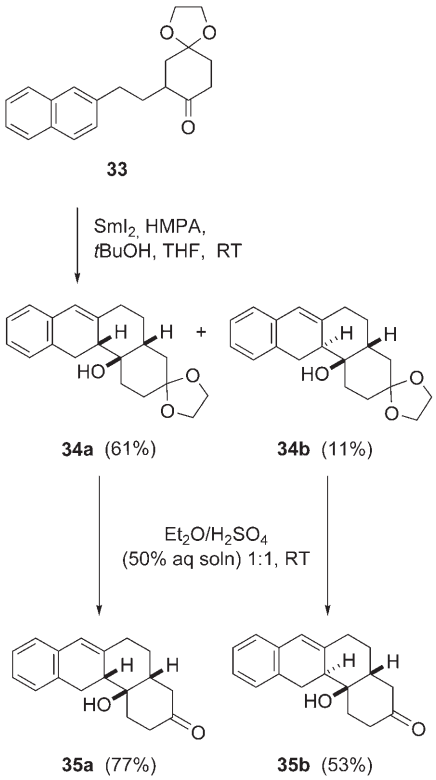
We also examined the cyclisation of selected γ-naphthyl-substituted ketones already containing a functional group that could provide a handle for subsequent modifications. The first example is represented by the introduction of a methoxy group in the 6-position of the naphthalene ring (Scheme 7). An oxygen functionality in this position is present in most naturally occurring steroids and it apparently plays a crucial role for the interaction of these molecules



Scheme 7. SmI_2-induced cyclisations of ketones **27** and **29**.

with the respective receptors.[27] However, rather unfortunately, the presence of an electron-releasing group at the naphthyl ring has a negative influence on the cyclisation efficacy and compound **27**[28] gave the expected tetracyclic product **28** in approximately 28% yield only. The reaction led in large extent to decomposition of the starting material and/or of the product, which made the purification of the cyclised product very tedious. Hence, only characterisation by ^{1}H NMR spectroscopy was possible. Oxygen substituents with lower electron-donating properties at the naphthyl group, such as acetoxy, may improve the cyclisation efficacy.

Introduction of a ketal group as a "masked" ketone, as in precursor **29**,[29] also resulted in impoverished yields of the expected tetracyclic product **30**, which was obtained in 19% yield (Scheme 7). Surprisingly, the regioselectivity was also reduced and a second product **31** was isolated in 7% yield. In this case, the cyclisation occurred onto the 8-position of the naphthalene ring, leading to the formation of a tetracyclic compound containing a seven-membered ring and a deconjugated double bond. Similar unexpected observations have been made with other cyclohexanone derivatives bearing additional substituents, in which compounds analogous to **31** were formed in up to 30% yield.[16] The constitution and relative configuration of **31** were assigned by X-ray crystal structure analysis (Figure 1). Cleavage of the ketal



Scheme 8. SmI_2-induced cyclisation of ketone **33**.

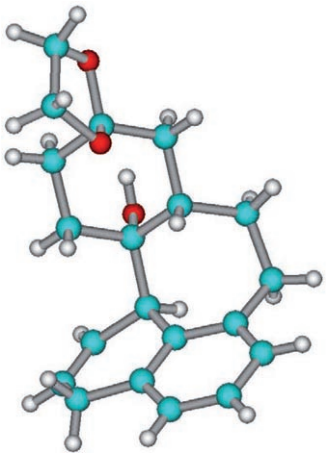


Figure 1. Structure of compound **31**.

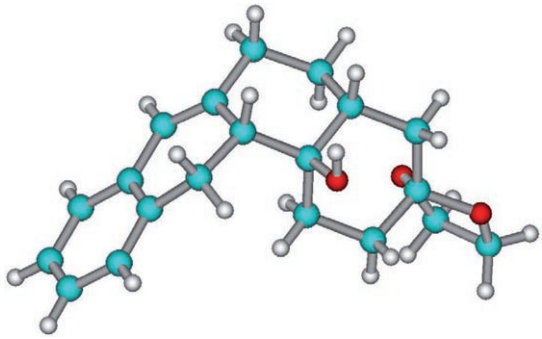


Figure 2. Structure of compound **34a**.

group in tetracycle **30** furnished the expected ketone **32** in an excellent 95% yield. This product is crystalline and hence again allowed relative configuration to be proved by X-ray analysis.

Like the result reported above for the cyclisation of **10**, the cyclisation of the 2-substituted naphthalene derivative **33**[29] also led to the formation of two diastereomers **34a** and **34b** (6:1) in a satisfactory overall yield (Scheme 8). Whereas the minor isomer **34b** is an oil, tetracycle **34a** formed suitable crystals and hence its relative configuration was unequivocally determined by X-ray crystal structure analysis (Figure 2). Both diastereomers **34a** and **34b** show the expected *cis* annulation of rings C/D, but they differ in the relative configuration of the bridgehead hydrogen sharing rings B and C.

Cleavage of the ketal groups of **34a** and **34b** afforded ketones **35a** in 77% yield and **35b** in moderate 53% yield. The hydroxyl group in **35b** is arranged *trans* to one of the bridgehead hydrogen atoms and therefore may have suffered water elimination under the acidic conditions employed, eventually leading to undesired decomposed material. Compound **35a** is crystalline and its structure was also unambiguously proved by X-ray analysis (Figure 3).

Subsequent transformations: The styrene-type double bond in tetracyclic products **22**–**26**, **28**, **30** and **32** provide an attractive handle for synthetic manipulations. Examples of

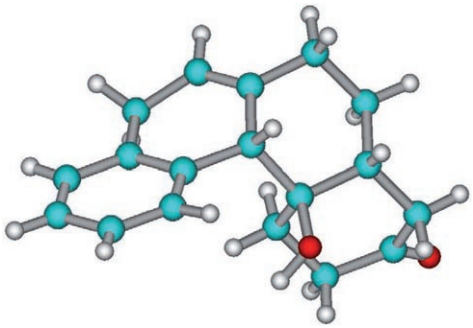
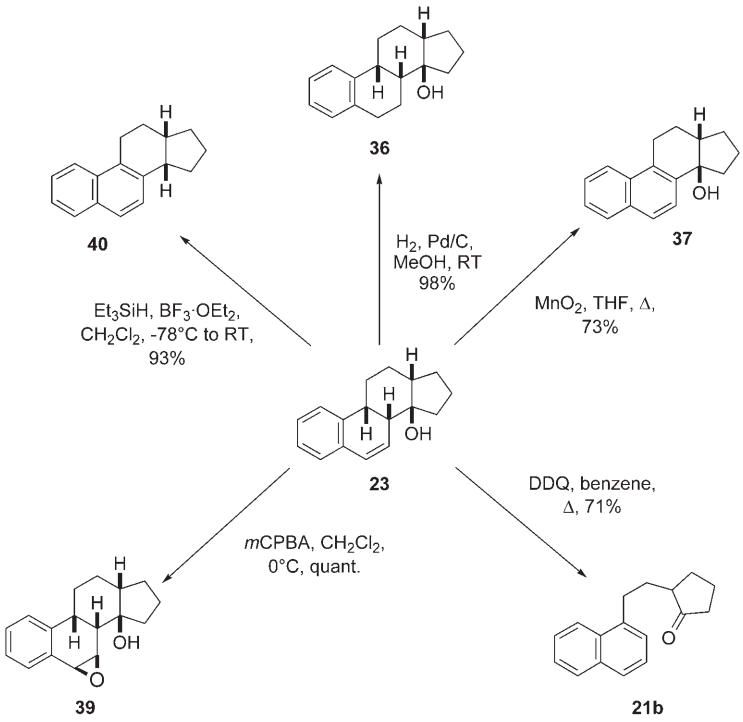


Figure 3. Structure of compound **35a**.

possible transformations of compounds employing steroid analogue **23** as a substrate are represented in Scheme 9. Reduction of the conjugated double bond of **23** by hydrogen in

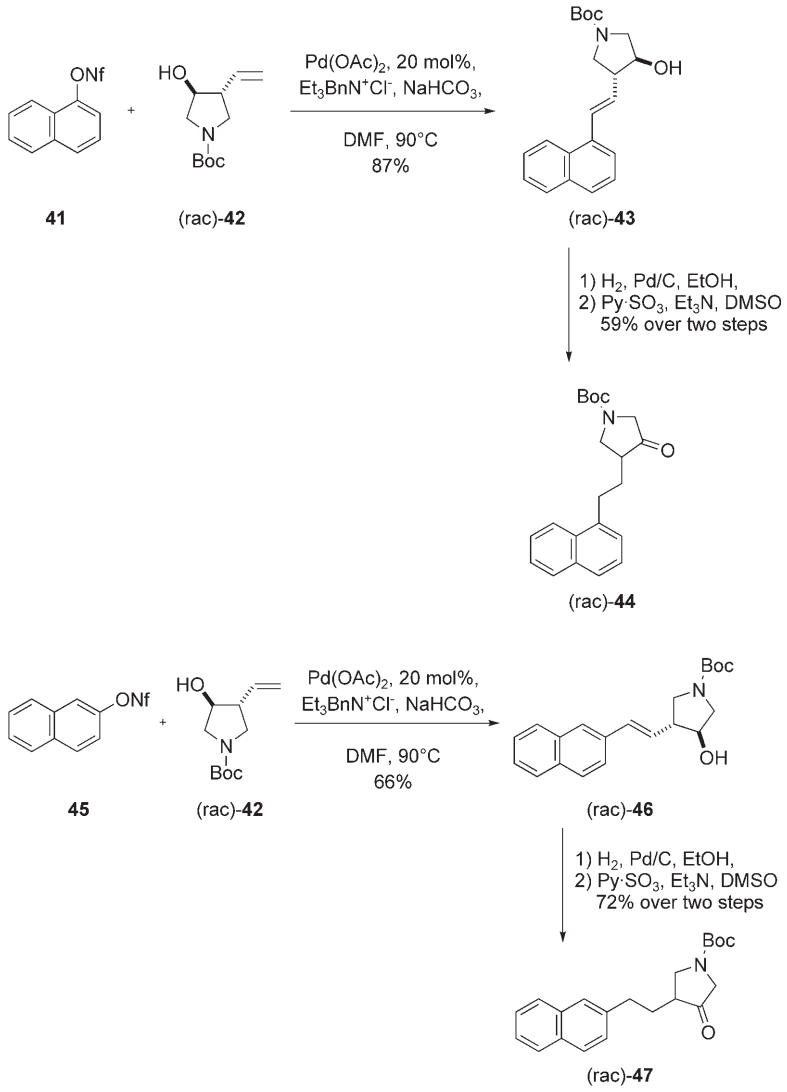


Scheme 9. Examples of chemical transformations of tetracyclic compound **23**.

the presence of Pd/C proceeded uneventfully and afforded compound **36** in almost quantitative yield. Oxidation of **23** with MnO_2 in THF furnished naphthalene derivative **37** in 73% yield.[30] Very surprisingly, oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) did not provide the expected product **37**, but instead afforded cyclisation precursor **21b** in 71% yield. The detailed mechanism of this unusual fragmentation is not clear; however, a related oxidative transformation was reported by Singh et al.[31] Smooth epoxidation of **23** was achieved under standard conditions with *m*-chloroperbenzoic acid (*m*CPBA) affording quantitatively pentacyclic compound **39**. The introduction of the oxygen atom occurred entirely stereoselectively from the less-hindered convex face of the molecule and *cis* to the bridgehead hydroxyl group. X-ray crystal structure analysis of **39** provided evidence of its relative configuration and hence also that of the precursor **23**.[32] Substitution of the tertiary hydroxyl group of **23** by hydride was attempted by treatment with triethylsilane and trifluoroboron-etherate.[33] However, under these conditions, elimination of water was observed instead, and by double-bond migration, naphthalene derivative **40** was isolated in very good yield. Whereas transformations, such as **23**→**21b** and **23**→**40**, deserve further investigations to clarify their generality, the epoxidation proceeded smoothly on several substrates of type **23**[34] and provides an excellent possibility for interesting structural diversifications of the steroid analogues.

Nitrogen-containing tetracycles—synthesis of azasteroid derivatives: Considering the growing importance of unnatural azasteroid derivatives in pharmaceutical chemistry,[35] we have also focused our efforts towards the synthesis of nitrogen-containing tetracycles by using samarium diiodide induced cyclisations of naphthyl-substituted pyrrolidinone and piperidinone derivatives **44**, **47**, **50** and **52**.[36] Syntheses of precursors **44** and **47** were carried out by a three-step procedure involving an initial Heck reaction[37] between the naphthyl nonaflates **41** or **45** and homoallylic alcohol **42**.[38] The coupling products **43** and **46** were obtained in good yield and without formation of conceivable double-bond isomers. Hydrogenation of the double bonds and oxidation of the alcohols by the pyridine·SO_3 complex in DMSO furnished the required ketones **44** and **47** (Scheme 10).[39] The NMR spectra of these compounds recorded at room temperature showed the presence of two distinct amide rotamers—a phenomenon well documented for amides and carbamate groups and attributable to the presence of the Boc group.[40]

Gratifyingly, samarium diiodide induced couplings of ketones **44**, **47**, **50** and **52** afforded the desired tetracyclic compounds **48**, **49a/b**, **51** and **53a/b** in moderate to good yields. In accordance with the above-mentioned results, 1-substituted naphthalene derivatives **44** and **50** led to the formation of **48** and **51** as single diastereomers with the expected *cis*-junctions of rings B/C/D, whilst the 2-substituted naphthalene derivatives **47** and **52** afforded mixtures of diastereomers **49a/b** (dr: 1.2:1) and **53a/b** (dr: 2:1). It is also interesting to note that the reactions of substrates **44** and **47** were less efficient—when compared to **50** and **52**—leading to the cyclised compounds **48** and **49** only in moderate yields (Scheme 11).[41] Compounds **51** and **53a/b** were rather unstable due to the presence of a tertiary amine moiety which causes rapid oxidation by the air. Purification of the minor isomer **53b** was not completely successful, and the identification of this product was carried out in the mixture of the two isomers by ^{1}H NMR spectroscopy.



Scheme 10. Synthesis of the pyrrolidinone derivatives **44** and **47**.

Conclusion

We have demonstrated that γ-naphthyl-substituted ketones are very good substrates for samarium diiodide promoted reductive couplings. These reactions afforded tri- and tetracyclic compounds in moderate to excellent yields and often with high diastereoselectivity. Several of these tetracycles present steroid-like skeletons but with "unnatural" configuration. Our new approach nicely complements alternative strategies for the de novo synthesis of steroidal compounds.[42] The presence of a styrene-type double bond allows many chemical transformations and the introduction of additional functional groups, thus leading to structurally highly diversified compounds. Using this methodology, it was also possible to synthesise nitrogen-containing tetracycles, some of which also display steroid-type skeletons. The methods described here not only contribute to the evaluation of scope and limitations of the samarium–ketyl-arene cyclisations, but they also lead to synthetically interesting products. The biological activity of the steroid analogues is currently being investigated and will be reported in due course.[43]

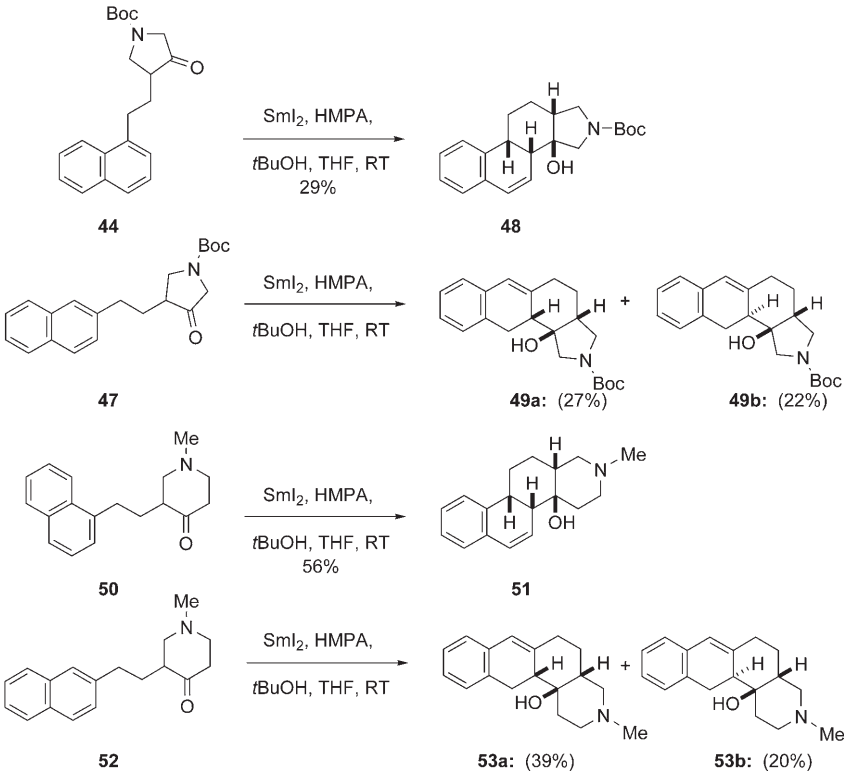
Experimental Section

General information: Reactions were performed under argon in flame-dried flasks, and solvents and reagents were added by syringes. 1,2-Diiodoethane was purified by sublimation under vacuum (0.2 mbar, 50 °C). THF and diethyl ether were freshly distilled from sodium/benzophenone under argon. Hexamethylphosphoramide and *tert*-butanol were distilled from calcium hydride (HMPA: 130 °C, 12 mbar; *t*BuOH: 55 °C, 1013 mbar) and stored over molecular sieves (4 Å) under argon. Argon was purged through the solution to eliminate residual oxygen prior to use. **Warning**: *HMPA has been identified as a carcinogenic reagent. Use of gloves is required during handling. Reactions and chromatography should be performed in well-ventilated hoods.* Triethylamine and diisopropylamine were distilled from potassium hydroxide and stored over KOH under argon. Dichloromethane was distilled over calcium hydride and stored over molecular sieves (4 Å) under argon. Ethanol was distilled from magnesium oxide and stored over molecular sieves (4 Å) under argon. Dry DMF and dry dimethylsulfoxide were purchased from Aldrich and used as obtained under an atmosphere of argon.

Methyl acetylacetate (**1**), 1-(bromomethyl)naphthalene (**2**), 2-(bromomethyl)naphthalene (**4**), 1-bromonaphthalene (**7**), 2-bromonaphthalene (**9**), 4-penten-2-ol (**6**) and 5-hexen-2-one (**11**) were purchased from Fluka, Aldrich, Acros, or Merck and used as received. *N*-Cyclohexyl-*N*-cycloalkylidenamines (**19a–e**)[44] and 1-(2-iodoeth-1-yl)naphthalene (**20**)[45] were synthesised according to literature procedures.

Products were purified by flash chromatography on silica gel (230–400 mesh, Merck) or neutral alumina (activity III, Fluka). Preparative HPLC was carried out on a nucleosil 50–5 column (diameter 16 mm, length 244 mm) and a Knauer variable UV detector ($\lambda = 255$ nm) and a Knauer refractometer were used. Unless otherwise stated, yields refer to analytically pure samples.

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 250 (250 MHz), Bruker AC 270 (270 MHz), AC 500 (500 MHz) and Joel Eclipse 500 (500 MHz) spectrometers. Integrals are in accordance with assignments; coupling constants are given in Hz. IR spectra were measured with an FTIRD spectrometer Nicolet 5 SXC. MS and HRMS analyses were performed on Finnigan MAT 711 (EI, 80 eV, 8 kV), MAT CH7A (EI, 80 eV, 3 kV) instruments. Elemental analyses were recorded with an "Elemental-Analyzer" (Perkin–Elmer). Melting points were measured with a Reichert apparatus and are uncorrected. Single-crystal X-ray data were collected on a Bruker SMART CCD diffractometer ($Mo_{K\alpha}$ radiation, $l =$



Scheme 11. Synthesis of the nitrogen-containing tetracyclic products **48**, **49**, **51** and **53**.

0.71073 Å, graphite monochromator), empirical absorption correction by using symmetry-equivalent reflections (SADABS),[46] structure solution and refinement by SHELXS-97[47] and SHELXL-97[48] in the WINGX System.[49] The hydrogen atoms were located by difference Fourier syntheses. CCDC-606010, -606011 and -606013 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses of cyclisation precursors

Typical procedure for the synthesis of ketones 3 and 5: Methyl acetylacetate (**1**, 10.0 mmol) was added to a solution of lithium diisopropylamide (20.0 mmol) in THF (50 mL) at 0 °C. The solution was stirred at 0 °C for 20 min then a solution of 1-(bromomethyl)naphthalene (**2**) or 2-(bromomethyl)naphthalene (**4**) (10.0 mmol) in THF (20 mL) was added dropwise. The mixture was stirred for an additional 20 min at 0 °C, then quenched by addition of 10% aq HCl (35 mL) and the product was extracted with Et_2O. The organic phase was washed with water until a neutral pH was reached and then dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product and sodium hydroxide (15.0 mmol) were suspended in distilled water (12 mL) and stirred at RT for 10 h, then at reflux for 4 h. The mixture was then cooled down and the product extracted in Et_2O. The combined organic layers were dried with $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel.

4-(1-Naphthyl)-2-butanone (3): Compound **1** (1.16 g, 10.0 mmol) and **2** (2.21 g, 10.0 mmol) afforded 2.78 g of crude alkylation product which was treated with sodium hydroxide (0.60 g, 15.0 mmol). Purification by column chromatography on silica gel (hexane/ethyl acetate 9:1) furnished **3** as a pale-yellow oil (1.69 g, 85%). The analytical data is in agreement with those reported in the literature.[50]

4-(2-Naphthyl)-2-butanone (5): Compound **1** (1.16 g, 10.0 mmol) and **4** (2.21 g, 10.0 mmol) afforded 2.94 g of crude alkylation product, which was subsequently treated with sodium hydroxide (0.60 g, 15.0 mmol). Purification by column chromatography on silica gel (hexane/ethyl acetate 9:1) provided **5** as a pale-yellow oil (1.52 g, 76%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 7.84–7.74 (m, 3H; Ar), 7.61 (br s, 1H; Ar), 7.50–7.41 (m, 2H; Ar), 7.31 (d, J = 8.8 Hz, 1H; Ar), 3.04 (t, J = 7.6 Hz, 2H; CH_2), 2.78 (t, J = 7.6 Hz, 2H; CH_2), 2.11 ppm (s, 3H; CH_3); ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 207.8 (s; CO), 138.5, 133.5, 132.0 (3s; Ar), 128.0, 127.6, 127.4, 127.0, 126.3, 126.0, 125.3 (7d; Ar), 44.8 (t; CH_2), 30.0 (q; CH_3), 29.9 ppm (t; CH_2); IR (film): $\tilde{\nu}$ = 3050–2900 (=C–H, C–H), 1700 (C=O), 1605 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{14}H_{14}O$ (198.3): C 84.81, H 7.12; found: C 84.52, H 6.70.

5-(1-Naphthyl)-2-pentanone (8): 1-Bromonaphthalene (**7**) (2.07 g, 10.0 mmol), 4-penten-2-ol (**6**) (1.29 g, 15.0 mmol), palladium(II) acetate (1.00 g, 4.50 mmol), tetra-*n*-butylammonium chloride (5.56 g, 20.0 mmol), LiCl (0.424 g, 10.0 mmol) and lithium acetate-dihydrate (2.60 g, 25.0 mmol) were suspended in DMF (20 mL) and the mixture was stirred for 72 h at 100 °C. After cooling, the reaction was quenched with brine (50 mL) and the product was extracted with Et_2O (3× 50 mL). The combined organic layers were dried with Na_2SO_4, filtered, and the solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography on silica gel (hexane/ethyl acetate 4:1) to yield **8** as a colourless oil (1.75 g, 83%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 8.06 (d, J = 8.1 Hz, 1H; Ar), 7.84 (d, J = 7.4 Hz, 1H; Ar), 7.71 (d, J = 8.1 Hz, 1H; Ar), 7.55–7.42 (m, 2H; Ar), 7.38 (t, J = 8.1 Hz, 1H; Ar), 7.29 (d, J = 7.4 Hz, 1H; Ar), 3.07 (t, J = 7.4 Hz, 2H; CH_2), 2.51 (t, J = 7.4 Hz, 2H; CH_2), 2.12 (s, 3H; CH_3), 2.03 ppm (quint., $J \approx$ 7.4 Hz, 2H; CH_2); ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 207.0 (s; CO), 137.7, 137.6, 133.9 (3s; Ar), 128.7, 126.7, 126.1, 125.8, 125.5, 125.4, 123.8 (7d; Ar), 43.1, 32.2 (2t; CH_2), 30.0 (q; CH_3), 24.5 ppm (t; CH_2); IR (film): $\tilde{\nu}$ = 3100–2850 (=C–H, C–H), 1715 (C=O), 1595 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{15}H_{16}O$ (212.3): C 84.87, H 7.60; found: C 84.76, H 7.36.

6-(1-Naphthyl)-2-hexanone (12): 1-Bromonaphthalene (**7**) (4.14 g, 20.0 mmol), 5-hexen-2-one (**11**) (2.95 g, 30.0 mmol), LiCl (1.27 g, 29.9 mmol), K_2CO_3 (10.4 g, 75.0 mmol) and palladium(II) acetate (0.673 g, 3.00 mmol) were suspended in DMF (20 mL) and stirred at 100 °C for 4 h. After cooling, the reaction was quenched with brine (50 mL) and the product was extracted with Et_2O (3×50 mL). The combined organic layers were dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure to leave the crude product, which was filtered over silica gel (hexane/ethyl acetate 4:1). The crude product was dissolved in MeOH (50 mL) and added to a suspension of Pd/C (10%, 1.00 g) in MeOH (100 mL) under an atmosphere of H_2. The mixture was stirred at RT for 24 h, then filtered over a pad of Celite and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 9:1 to 4:1) to afford **12** as a colourless oil (3.14 g, 69%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 7.97 (br d, J = 7.8 Hz, 1H; Ar), 7.81 (br d, J = 7.8 Hz, 1H; Ar), 7.67 (d, J = 8.3 Hz, 1H; Ar), 7.50–7.25 (m, 4H; Ar), 3.04 (t, J = 7.2 Hz, 2H; CH_2), 2.43 (t, J = 7.2 Hz, 2H; CH_2), 2.08 (s, 3H; CH_3), 1.74–1.64 ppm (m, 4H; CH_2); ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 208.8 (s; CO), 138.2, 133.8, 131.7 (3s; Ar), 128.7, 126.5, 125.8, 125.6, 125.4, 125.3, 123.7 (7d; Ar), 43.4, 32.8, 30.1 (3t; CH_2), 29.8 (q; CH_3), 23.8 ppm (t; CH_2); IR (film): $\tilde{\nu}$ = 3050–

2800 (=C–H, C–H), 1720 (C=O), 1600 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{16}H_{18}O$ (226.3): C 84.91, H 8.02; found: C 84.55, H 7.81.

Typical procedure for the synthesis of ketones 21: *n*-Butyllithium (1.8 equiv) was added to a solution of diisopropylamine (1.6 equiv) in THF (2 mL $mmol^{-1}$) at 0 °C. The solution was stirred for 20 min at 0 °C and then a solution of the imine **19** (1.5 equiv) in THF (0.5 mL $mmol^{-1}$) was added and the mixture was stirred for a further 30 min at this temperature. A solution of 1-(2-iodoeth-1-yl)naphthalene (**20**) (1 equiv) in THF (0.5 mL $mmol^{-1}$) was finally added and the mixture was stirred for 30 min at 0 °C. After this time, a HCl (2 N) solution was added and the product was extracted with ethyl acetate. The combined organic phases were washed with brine, dried with Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure and the residue purified by column chromatography on silica gel.

2-(1-Naphthylethyl)-1-cyclobutanone (21a): N-Cyclohexyl-N-cyclobutylidenamine (**19a**) (0.800 g, 5.30 mmol), diisopropylamine (0.8 mL, 5.60 mmol), *n*-butyllithium (2.5 mL, 6.25 mmol; 2.5 M in hexane) and **20** (0.987 g, 3.50 mmol) afforded, after purification by column chromatography (hexane/ethyl acetate 9.5:0.5), **21a** as a colourless oil (0.340 g, 43 %). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 8.15 (d, J = 8.3 Hz, 1H; Ar), 7.87 (d, J = 8.3 Hz, 1H; Ar), 7.75 (d, J = 8.3 Hz, 1H; Ar), 7.65–7.29 (m, 4H; Ar), 3.36–2.89 (m, 5H; CH, CH_2), 2.22–2.05 (m, 2H; CH_2), 2.00–1.84 (m, 1H; CH_2), 1.62 ppm (quint., $J \approx 9.5$ Hz, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 211.9 (s; CO), 137.4, 133.8, 131.7 (3s; Ar), 128.8, 126.7, 126.1, 125.8, 125.5, 125.4, 123.1 (7d; Ar), 59.9 (d; CH), 44.4, 30.6, 30.3, 16.9 ppm (4t; CH_2); IR (film): $\tilde{\nu}$ = 3050–2850 (=C–H, C–H), 1750 (C=O), 1600 cm^{-1} (C=C); MS (EI, 80 eV): *m/z* (%): 224 (28) $[M]^+$, 141 (100) $[M-C_5H_7O]^+$; HRMS (80 eV): calcd for $C_{16}H_{16}O$: 224.1201; found: 224.1224; elemental analysis calcd (%) for $C_{16}H_{16}O$ (224.3): C 85.68, H 7.19; found: C 85.11, H 7.03.

2-(1-Naphthylethyl)-1-cyclopentanone (21b): N-Cyclohexyl-N-cyclopentylidenamine (**19b**) (12.4 g, 75.0 mmol), diisopropylamine (11.2 mL, 80.0 mmol), *n*-butyllithium (34.9 mL, 87.3 mmol; 2.5 M in hexane) and **20** (14.1 g, 50.0 mmol) afforded, after purification by column chromatography (hexane/ethyl acetate 9:1), **21b** as a colourless oil (9.16 g, 77 %). The analytical data are in agreement with those reported in the literature.[51]

2-(1-Naphthylethyl)-1-cyclohexanone (21c): N-Cyclohexyl-N-cyclohexylidenamine (**19c**) (0.902 g, 5.00 mmol), diisopropylamine (0.8 mL, 5.60 mmol), *n*-butyllithium (2.5 mL, 6.25 mmol; 2.5 M in hexane) and **20** (0.987 g, 3.50 mmol) afforded, after purification by column chromatography (hexane/ethyl acetate 19:1), **21c** as a colourless oil (0.731 g, 83 %). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 8.05 (d, J = 8.1 Hz, 1H; Ar), 7.84 (d, J = 8.1 Hz, 1H; Ar), 7.70 (d, J = 7.8 Hz, 1H; Ar), 7.56–7.30 (m, 4H; Ar), 3.15 (t, J = 8.0 Hz, 2H; CH_2), 2.39–1.53 ppm (m, 11H; CH, CH_2); ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 213.6 (s; CO), 134.0, 132.8, 128.6 (3s; Ar), 128.8, 126.7, 125.9, 125.8, 125.6, 125.5, 123.7 (7d; Ar), 58.7 (d; CH), 38.2, 30.8, 30.7, 29.8, 20.7, 16.1 ppm (6t; CH_2); IR (film): $\tilde{\nu}$ = 3050–2850 (=C–H, C–H), 1715 (C=O), 1600 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{18}H_{20}O$ (252.4): C 85.67, H 7.99; found: C 85.12, H 7.63.

2-(1-Naphthylethyl)-1-cycloheptanone (21d): N-Cyclohexyl-N-cycloheptylidenamine (**19d**) (5.79 g, 30.0 mmol), diisopropylamine (4.5 mL, 32.1 mmol), *n*-butyllithium (14.1 mL, 35.3 mmol; 2.5 M in hexane) and **20** (5.63 g, 20.0 mmol) afforded, after purification by column chromatography (hexane/ethyl acetate 19:1), **21d** as a colourless oil (4.10 g, 77 %). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 8.05 (d, J = 8.3 Hz, 1H; Ar), 7.85 (d, J = 8.3 Hz, 1H; Ar), 7.72 (d, J = 7.8 Hz, 1H; Ar), 7.57–7.29 (m, 4H; Ar), 3.13–2.82 (m, 2H; CH, CH_2), 2.69–2.31 (m, 2H; CH_2), 2.22–2.03 (m, 1H; CH_2), 1.95–1.12 (m, 8H; CH_2), 0.98–0.79 ppm (m, 2H; CH_2); ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 215.8 (s; CO), 133.8, 128.5 (2s; Ar), 128.9, 127.7, 126.5, 126.4, 125.7, 125.5, 123.7 (7d; Ar), 51.6 (d; CH), 43.0, 33.4, 31.7, 30.6, 29.3, 28.6, 24.2 ppm (7t; CH_2). IR (film): $\tilde{\nu}$ = 3045–2850 (=C–H, C–H), 1700 (C=O), 1595 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{19}H_{22}O$ (266.4): C 85.67, H 8.32; found: C 85.55, H 8.25.

2-(1-Naphthylethyl)-1-cyclooctanone (21e): N-Cyclohexyl-N-cyclooctylidenamine (**19e**) (6.22 g, 30.0 mmol), diisopropylamine (4.5 mL, 32.1 mmol), *n*-butyllithium (14.1 mL, 35.3 mmol; 2.5 M in hexane) and **20** (5.63 g, 20.0 mmol) afforded, after purification by column chromatography (hexane/ethyl acetate 9:1 to 7:3), **21e** as a pale-yellow oil (5.05 g, 90 %). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 8.02 (d, J = 8.3 Hz, 1H; Ar), 7.81 (d, J = 8.3 Hz, 1H; Ar), 7.68 (d, J = 7.5 Hz, 1H; Ar), 7.55–7.23 (m, 4H; Ar), 3.09–2.81 (m, 2H; CH_2), 2.77–0.81 ppm (m, 15H; CH, CH_2); ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 219.8 (s; CO), 138.0, 133.8, 131.7 (3s; Ar), 128.6, 126.6, 125.9, 125.8, 125.5, 125.4, 123.7 (7d; Ar), 50.3 (d; CH), 42.3, 33.7, 33.1, 31.0, 27.4, 25.5, 25.3, 24.7 ppm (8t; CH_2); IR (film): $\tilde{\nu}$ = 3050–2800 (=C–H, C–H), 1710 (C=O), 1605 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{20}H_{24}O$ (280.4): C 85.67, H 8.63; found: C 84.81, H 8.66.

General procedure for the synthesis of ketones 29, 33, 50 and 52:[52] *n*-Butyllithium (1.0–1.5 equiv) was added to a solution of diisopropylamine (2.0–3.2 equiv) in THF (3 mL $mmol^{-1}$) at −78 °C and the solution was stirred for 30 min. A solution of the corresponding SAMP hydrazone (1.0–1.3 equiv) in THF (1.6 mL $mmol^{-1}$) was then slowly added at −78 °C and the mixture was stirred for 4 h and allowed to warm to 0 °C. The reaction vessel was again cooled to −78 °C and a solution of 1-(2-bromoethyl)naphthalene or 2-(2-bromoethyl)naphthalene[53] (1.0 equiv) in THF (1.6 mL $mmol^{-1}$) was added. The solution was stirred overnight whilst allowing the temperature to rise to RT. The mixture was then quenched by careful addition of a saturated aqueous solution of ammonium chloride and the product was repeatedly extracted with Et_2O. The combined organic layers were dried with $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was dissolved in Et_2O and stirred vigorously with a saturated aqueous solution of oxalic acid (3 mL) at 0 °C for 4 h. The aqueous layer was separated, the product extracted with Et_2O, and the combined organic layers were dried with $MgSO_4$. The mixture was then filtered and the solvent removed under reduced pressure to leave the crude product, which was purified by column chromatography.

7-[2-(1-Naphthyl)ethyl]-1,4-dioxaspiro[4.5]decan-8-one (29): According to the sequence described above, (2*S*)-2-(methoxymethyl)-*N*-[1,4-dioxaspiro[4.5]dec-8-ylidene]pyrrolidin-1-amine (1.10 g, 4.08 mmol), diisopropylamine (1.47 mL, 10.5 mmol), *n*-butyllithium (1.98 mL, 4.95 mmol; 2.5 M in hexane) and 1-(2-bromoethyl)naphthalene (0.764 g, 3.25 mmol) afforded after column chromatography on neutral alumina (hexane/ethyl acetate 3:1) **29** as a colourless oil (0.925 g, 92 %). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 8.18 (d, J = 8.5 Hz, 1H; Ar), 7.82 (d, J = 8.0 Hz, 1H; Ar), 7.69 (d, J = 7.3 Hz, 1H; Ar), 7.54–7.25 (m, 4H; Ar), 4.02–3.95 (m, 4H; OCH_2), 3.15, 2.98 (2ddd, J = 13.3, 11.1, 5.3 Hz, 1H each; CH_2), 2.78, 2.67 (2m, 1H each; CH, CH_2), 2.39 (ddd, J = 14.7, 4.3, 3.7 Hz, 1H; CH_2), 2.28–1.90 (m, 4H; CH_2), 1.81 (t, J = 13.1 Hz, 1H; CH_2), 1.60 ppm (m, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 211.4 (s; CO), 138.6, 134.0, 132.1 (3s; Ar), 128.8, 126.8, 126.1, 125.9, 125.7, 125.6, 124.2 (7d; Ar), 107.5 (s; C-5), 64.8, 64.7 (2t; C-2, C-3), 46.4 (d; C-7), 41.1, 38.5, 35.9, 30.9, 30.8 ppm (5t; CH_2); IR (film): $\tilde{\nu}$ = 3060–2880 (=C–H, C–H), 1710 (C=O), 1600 cm^{-1} (C=C); MS (EI, 80 eV): *m/z* (%): 310 (17) $[M]^+$, 155 (100) $[C_8H_{11}O_3+C_{12}H_{11}]^+$, 141 (21) $[C_{11}H_9]^+$; HRMS (EI, 80 eV): calcd for $C_{20}H_{22}O_3$: 310.1568; found: 310.1557.

7-[2-(2-Naphthyl)ethyl]-1,4-dioxaspiro[4.5]decan-8-one (33): According to the sequence described above, (2*S*)-2-(methoxymethyl)-*N*-[1,4-dioxaspiro[4,5]dec-8-ylidene]pyrrolidin-1-amine (1.33 g, 4.95 mmol), diisopropylamine (1.79 mL, 12.7 mmol), *n*-butyllithium (2.40 mL, 6.00 mmol; 2.5 M in hexane) and 2-(2-bromoethyl)naphthalene (0.927 g, 3.94 mmol) afforded, after column chromatography on silica gel (hexane/ethyl acetate 4:1), **33** as a colourless oil (0.976 g, 80 %). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.76–7.73 (m, 2H; Ar), 7.72 (d, J = 8.4 Hz, 1H; Ar), 7.59 (s, 1H; Ar), 7.42–7.36 (m, 2H; Ar), 7.30 (dd, J = 8.4, 1.6 Hz, 1H; Ar), 3.93–3.92 (m, 4H; OCH_2), 2.80–2.70 (m, 2H; CH_2), 2.65 (sept, J = 6.6 Hz, 1H; CH), 2.58 (dd, J = 14.1, 6.6 Hz, 1H; CH_2), 2.34 (ddd, J = 14.1, 5.0, 3.4 Hz, 1H; CH_2), 2.20–2.16 (m, 1H; CH_2), 2.13 (ddd, J = 13.2, 5.8, 3.4 Hz, 1H; CH_2), 1.99–1.92 (m, 2H; CH_2), 1.74 (t, J = 13.2 Hz, 1H; CH_2), 1.60–1.52 ppm (m, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 211.3 (s; CO), 139.6, 133.8, 132.1 (3s; Ar), 127.9, 127.6, 127.5, 127.4, 126.4, 125.9, 125.1 (7d; Ar), 107.4 (s, C-5), 64.7, 64.6 (2t; C-2, C-3), 45.8 (d; C-7), 40.7, 34.7, 33.9, 33.3, 30.8 ppm (5t; CH_2); IR (film): $\tilde{\nu}$ = 3050–2885 (=C–H, C–H), 1715 (C=O), 1600 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{20}H_{22}O_3$ (310.4): C 77.39, H 7.14; found: C 76.79, H 6.74.

1-Methyl-3-[2-(1-naphthyl)ethyl]piperidin-4-one (50): According to the sequence described above, (2*S*)-2-(methoxymethyl)-*N*-(1-methylpiperidin-4-ylidene)pyrrolidin-1-amine (0.475 g, 2.10 mmol), diisopropylamine (0.60 mL, 4.27 mmol), *n*-butyllithium (0.84 mL, 2.10 mmol; 2.5 M in hexane) and 1-(2-bromoethyl)naphthalene (0.51 g, 2.17 mmol) afforded, after column chromatography on neutral alumina (hexane/ethyl acetate 3:1), the alkylation product as a colourless oil (0.559 g, 70%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.04 (d, J = 8.4 Hz, 1H; Ar), 7.83 (dd, J = 8.0, 1.0 Hz, 1H; Ar), 7.69 (dd, J = 6.7, 2.6 Hz, 1H; Ar), 7.51–7.43 (m, 2H; Ar), 7.38–7.37 (m, 2H; Ar), 3.44 (m, 1H; CH), 3.37 (m, 1H; CH_2), 3.25 (s, 3H; OCH_3), 3.23–3.19 (m, 1H; CH), 3.12–3.09 (m, 2H; CH_2), 3.04–3.00 (m, 3H; CH_2), 2.93 (dd, J = 11.5, 2.0 Hz, 1H; CH_2), 2.73 (dt, J = 13.3, 5.5 Hz, 1H; CH_2), 2.48 (d, J = 8.8 Hz, 1H; CH_2), 2.25 (s, 3H; NCH_3), 2.24–2.14 (m, 2H; CH_2), 2.08–2.00 (m, 3H; CH_2), 1.99 (dd, J = 10.9, 2.9 Hz, 1H; CH_2), 1.85–1.79 (m, 2H; CH_2), 1.64–1.57 ppm (m, 1H; CH_2).

The alkylation product (0.080 g, 0.21 mmol) was dissolved in Et_2O (1 mL) and stirred vigorously with a saturated aqueous solution of oxalic acid (1 mL) at 0 °C for 4 h. The aqueous layer was separated, the product was extracted with Et_2O (3×2 mL), and the combined organic layers were dried with $MgSO_4$. The mixture was then filtered and the solvent removed under reduced pressure to afford **50** as a colourless oil (0.052 g, 93%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.13 (m, 1H; Ar), 7.83 (dt, J = 8.0, 0.7 Hz, 1H; Ar), 7.69 (d, J = 8.3 Hz, 1H; Ar), 7.51 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H; Ar), 7.45 (ddd, J = 8.0, 6.9, 1.4 Hz, 1H; Ar), 7.37 (dd, J = 8.0, 6.9 Hz, 1H; Ar), 7.30 (m, 1H; Ar), 3.17 (ddd, J = 13.9, 10.3, 5.7 Hz, 1H; CH_2), 3.07 (ddd, J = 11.2, 5.7, 2.5 Hz, 1H; CH_2), 3.01 (ddd, J = 13.9, 10.3, 6.6 Hz, 2H; CH_2), 2.70–2.60 (m, 2H; CH_2), 2.42 (dd, J = 11.2, 3.6 Hz, 1H; CH_2), 2.39 (dd, J = 4.7, 3.6 Hz, 1H; CH_2), 2.36 (s, 3H; NCH_3), 2.28–2.21 (m, 1H; CH_2), 2.18 (t, J = 11.2 Hz, 1H; CH_2), 1.57 ppm (ddt, J = 13.9, 10.3, 5.7 Hz, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 210.4 (s; CO), 138.2, 134.0, 131.9 (3s; Ar), 128.2, 126.8, 126.1, 126.0, 125.6, 125.5, 124.0 (7d; Ar), 61.7, 56.3 (2t; CH_2), 49.3 (d, CH), 45.4 (q; CH_3), 41.3, 30.8, 28.7 ppm (3t; CH_2); IR (film): $\tilde{\nu}$ = 3060–2785 (=CH, C–H), 1715 (C=O), 1595 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{18}H_{21}NO$ (267.4): C 80.86, H 7.92, N 5.24; found: C 80.99, H 8.03, N 5.09.

1-Methyl-3-[2-(2-naphthyl)ethyl]piperidin-4-one (52): According to the sequence described above, (2*S*)-2-(methoxymethyl)-*N*-(1-methylpiperidin-4-ylidene)pyrrolidin-1-amine (0.823 g, 3.66 mmol), diisopropylamine (1.32 mL, 9.39 mmol), *n*-butyllithium (1.77 mL, 4.43 mmol; 2.5 M in hexane), and 2-(2-bromoethyl)naphthalene (0.685 g, 2.91 mmol) afforded, after column chromatography on aluminium oxide (hexane/ethyl acetate 3:1), the alkylation product as a colourless oil (0.806 g, 73%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.79–7.73 (m, 3H; Ar), 7.63 (s, 1H; Ar), 7.44–7.37 (m, 2H; Ar), 7.34 (dd, J = 8.4, 1.7 Hz, 1H; Ar), 3.48–3.46 (m, 1H; CH_2), 3.36 (s, 3H; OCH_3), 3.30–3.25 (m, 3H; CH_2), 3.09–3.03 (m, 1H; CH_2), 2.83–2.77 (m, 2H; CH_2), 2.67–2.59 (m, 2H; CH_2), 2.49–2.42 (m, 4H; CH_2, CH), 2.25 (s, 3H; CH_3), 2.22–2.17 (m, 1H; CH_2), 2.16–2.14 (m, 1H; CH_2), 2.04–2.00 (m, 1H; NCH_2), 1.93–1.90 (m, 1H; CH_2), 1.85–1.80 (m, 2H; CH_2), 1.70–1.67 ppm (m, 1H; CH_2).

Acid treatment of the alkylation product (0.100 g, 0.26 mmol) afforded **52** as a colourless oil (0.067 g, 96%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.79–7.75 (m, 3H; Ar), 7.60 (s, 1H; Ar), 7.46–7.39 (m, 2H; Ar), 7.32 (dd, J = 8.4, 1.6 Hz, 1H; Ar), 3.10 (ddd, J = 11.3, 5.6, 2.2 Hz, 1H; CH_2), 3.04–2.99 (m, 1H; CH_2), 2.84–2.74 (m, 2H; CH_2), 2.66–2.59 (m, 2H; CH, CH_2), 2.46 (dt, J = 11.3, 3.6 Hz, 1H; CH_2), 2.39 (s, 3H; NCH_3), 2.38–2.35 (m, 1H; CH_2), 2.29–2.20 (m, 2H; CH_2), 1.57 ppm (m, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 209.7 (s; CO), 139.1, 133.6, 132.0 (3s; Ar), 127.9, 127.5, 127.4, 127.1, 126.3, 125.8, 125.1 (7d; Ar), 61.2, 56.0 (2t; CH_2), 48.5 (d; CH), 45.2 (q; CH_3), 40.8, 33.3, 28.7 ppm (3t; CH_2); IR (film): $\tilde{\nu}$ = 3050–2785 (=CH, C–H), 1715 (C=O), 1600 cm^{-1} (C=C); MS (EI, 80 eV): m/z (%): 267 (27) $[M]^+$, 141 (22) $[C_{11}H_9]^+$, 126 (100) $[M-C_{11}H_9]^+$; HRMS (80 eV): calcd for $C_{18}H_{21}NO$: 267.16232; found: 267.16366.

***tert*-Butyl 3-hydroxy-4-[(*E*)-2-(1-naphthyl)vinyl]pyrrolidine-1-carboxylate (43)**: A high-pressure tube was loaded with sodium hydrogencarbonate (0.335 g, 4.00 mmol), triethylbenzylammonium chloride (0.340 g, 1.50 mmol), 1-naphthyl nonaflate **41** (0.426 g, 1.00 mmol), palladium(II) acetate (45 mg, 0.20 mmol) and DMF (4 mL). The suspension was stirred at RT under argon for 10 min, then a solution of **42** (0.700 g, 3.29 mmol) in DMF (2 mL) was added. The vessel was sealed and heated to 90 °C for 48 h. After cooling to RT, the mixture was quenched with distilled water. The product was extracted with ethyl acetate (3×10 mL), the combined organic layers were washed with brine (2×10 mL), dried with $MgSO_4$ and the solvent was removed under reduced pressure to give the crude product, which was further purified by column chromatography on silica gel (hexane/ethyl acetate 6:1) and preparative HPLC (hexane/*iso*-propanol 95:5) to afford **43** as a colourless oil (0.294 g, 87%).[54] ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.06, 7.83 (2d, J = 7.7 Hz, 1H each; Ar), 7.76 (d, J = 8.1 Hz, 1H; Ar), 7.53 (d, J = 7.1 Hz, 1H; Ar), 7.49–7.47 (m, 2H; Ar), 7.42–7.40 (m, 1H; Ar), 7.25 (d, J = 15.5 Hz, 1H; =CH), 6.05 (dd, J = 15.5, 8.1 Hz, 1H; =CH), 4.18 (m, 1H; CH), 3.81–3.67 (m, 2H; CH_2), 3.41 (dd, J = 11.0, 6.9 Hz, 0.5H; CH_2), 3.33 (m, 1H; CH_2), 3.27 (dd, J = 11.3, 5.4 Hz, 1H; CH_2), 2.95 (m, 2H; CH, OH), 1.48 ppm (s, 9H; *t*Bu); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 154.6 (s; CO), 134.6, 133.6, 131.2 (3s; Ar), 131.0, 129.6 (2d; CH=CH), 128.6, 128.1, 126.2, 125.9, 125.7, 123.9, 123.7 (7d; Ar), 79.6 (s; *t*Bu), 75.2, 74.5 (2d; CH), 52.4, 52.2 (2t; CH_2), 50.3 (d; CH), 49.7, 49.4 (2t; CH_2), 28.5 ppm (q; *t*Bu); IR (film): $\tilde{\nu}$ = 3400 (OH), 3060–2885 (=CH, C–H), 1670 (C=O), 1600 cm^{-1} (C=C); MS (EI, 80 eV): m/z (%): 340 (6) $[M+H]^+$, 339 (23) $[M]^+$, 283 (39) $[M-C_4H_9]^+$, 57 (100) $[C_4H_9]^+$; HRMS (80 eV): calcd for $C_{21}H_{25}NO_3$: 339.18344; found: 339.18288.

***tert*-Butyl 3-[2-(1-naphthyl)ethyl]-4-oxopyrrolidine-1-carboxylate (44)**: Hydrogen was bubbled through a suspension of Pd/C (10%, 44 mg) in EtOH (5 mL) for 2 h, then a solution of **43** (220 mg, 0.65 mmol) in EtOH (1 mL) was added and the mixture was stirred at RT under an atmosphere of hydrogen for 3 h. The solid residue was filtered through a pad of silica and thoroughly washed with EtOH. The organic solvent was removed under reduced pressure to afford the reduction product as a colourless oil (0.168 g, 76%).[54] ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.98 (d, J = 8.2 Hz, 1H; Ar), 7.84, 7.70 (2m, 1H each; Ar), 7.51–7.46 (m, 2H; Ar), 7.38 (m, 1H; Ar), 7.30 (d, J = 6.0 Hz, 1H; Ar), 4.01 (brs, 1H; CH), 3.64–3.56 (m, 2H; CH_2), 3.24–3.14 (m, 1H; CH_2), 3.11–3.08 (m, 3H; CH_2), 2.70, 2.66 (2s, 1H; OH), 2.20–2.08 (m, 1H; CH), 1.96–1.91 (m, 1H; CH_2), 1.65–1.62 (m, 1H; CH_2), 1.46 ppm (s, 9H; *t*Bu); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 154.7 (s; CO), 137.6, 133.8, 131.6 (3s; Ar), 128.8, 126.7, 125.9, 125.8, 125.5, 125.4, 123.3 (7d; Ar), 79.4 (s; *t*Bu), 75.3, 74.5 (2d; CH), 52.7, 52.4, 49.4, 48.9 (4t; CH_2), 46.1, 45.5 (2d; CH), 32.5, 31.1 (2t; CH_2), 28.4 ppm (q; *t*Bu); IR (film): $\tilde{\nu}$ = 3420 (OH), 3060–2880 (=CH, C–H), 1670 (C=O), 1595 cm^{-1} (C=C); MS (EI, 80 eV): m/z (%): 341 (7) $[M]^+$, 285 (42) $[M-C_4H_9]^+$, 240 (10) $[M-C_5H_9O_2]^+$, 154 (9) $[C_{12}H_{11}]^+$, 141 (27) $[C_{11}H_9]^+$, 85 (27) $[C_5H_9O]^+$, 57 (100) $[C_4H_9]^+$; HRMS (80 eV): calcd for $C_{21}H_{27}NO_3$: 341.19910; found: 341.19866.

A solution of this reduction product (0.168 g, 0.49 mmol) and triethylamine (0.129 mL, 0.93 mmol) in DMSO (4 mL) was cooled to 0 °C and Py·SO_3 complex (0.131 g, 0.84 mmol) was added. The mixture was stirred for 10 min at this temperature and then allowed to warm to RT and stirred for a further 2 h. Distilled water was added and the product was extracted with CH_2Cl_2 (3×5 mL). The combined organic phases were washed with brine (3×5 mL), dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 5:1) to afford **44** as colourless oil (0.128 g, 77%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.04 (d, J = 8.4 Hz, 1H; Ar), 7.88 (d, J = 7.4 Hz, 1H; Ar), 7.75 (d, J = 8.4 Hz, 1H; Ar), 7.55–7.50 (m, 2H; Ar), 7.41 (t, J = 7.4 Hz, 1H; Ar), 7.34 (d, J = 6.6 Hz, 1H; Ar), 4.20–4.00 (m, 1H; CH_2), 3.89, 3.71 (2brd, J = 19.2 Hz, 1H each; NCH_2), 3.38–3.27 (m, 1H; CH_2), 3.18 (brs, 2H; CH_2), 2.61 (brs, 1H; CH), 2.30–2.26 (m, 1H; CH_2), 1.86 (m, 1H; CH_2), 1.52 ppm (s, 9H; *t*Bu); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 212.6 (s; CO), 154.4 (s; CO), 137.0, 134.1, 131.8 (3s; Ar), 129.0, 127.2, 126.3, 126.2, 125.8, 125.6, 123.7 (7d; Ar), 80.2 (s; *t*Bu), 52.9, 52.5 (2t; CH_2), 48.5, 48.2 (2d; CH), 47.1, 46.8, 30.2, 29.6 (4t; CH_2), 28.3 ppm (q; *t*Bu); IR (film): $\tilde{\nu}$ = 3060–2875 (=CH, C–H), 1755–1670 (C=O), 1595 cm^{-1} (C=C); MS (EI, 80 eV): m/z (%): 339 (14) $[M]^+$, 283 (31) $[M-C_4H_9]^+$, 239 (5) $[M-C_5H_9O_2]^+$, 141 (30) $[C_{11}H_9]^+$, 57 (100) $[C_4H_9]^+$; HRMS (80 eV): calcd for $C_{21}H_{25}NO_3$: 339.18344; found: 339.18266.

***tert*-Butyl 3-hydroxy-4-[(*E*)-2-(2-naphthyl)vinyl]pyrrolidine-1-carboxylate (46)**: According to the procedure described above, 2-naphthyl nonaflate **45** (0.374 g, 0.88 mmol), sodium hydrogencarbonate (0.294 g, 3.51 mmol), triethylbenzylammonium chloride (0.298 g, 1.32 mmol), palladium(II) acetate (39 mg, 0.17 mmol) and **42** (0.560 g, 2.63 mmol) afforded after purification by column chromatography on silica gel (hexane/ethyl acetate 5:1) **46** as a colourless solid (0.195 g, 66%).[54] M.p. 152–154°C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.81–7.76 (m, 3H; Ar), 7.68 (s, 1H; Ar), 7.55 (dd, J = 8.6, 1.4 Hz, 1H; Ar), 7.47–7.43 (m, 2H; Ar), 6.67 (d, J = 15.9, 1H; CH=CH), 6.17 (dd, J = 15.9, 8.3 Hz, 1H; CH=CH), 4.19 (dd, J = 11.8, 5.9 Hz, 1H; CH), 3.78 (dd, J = 10.6, 5.5 Hz, 1H; CH_2), 3.72 (dd, J = 10.4, 7.4 Hz, 1H; CH_2), 3.37 (dd, J = 10.4, 7.4 Hz, 1H; CH_2), 3.26 (dd, J = 10.6, 5.5 Hz, 1H; CH_2), 2.89 (m, 1H; CH), 2.36 (br s, 1H; OH), 1.48 ppm (s, 9H; *t*Bu); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 154.6 (s; CO), 134.1, 133.5 (2s; Ar), 132.9 (d; =CH), 132.5 (s; Ar), 128.2 (d; Ar), 128.0 (d; =CH), 127.9, 127.6, 126.3, 126.1, 125.9, 123.3 (6d; Ar), 79.6 (s; *t*Bu), 76.0, 74.5 (2d; CH), 52.3, 52.0 (2t; CH_2), 50.1, 49.5 (2d; CH), 49.3, 48.7 (2t; CH_2), 28.5 ppm (q; *t*Bu); IR (KBr): $\tilde{\nu}$ = 3475–3440 (OH), 2975–2870 (=CH, CH), 1690 (C=O), 1595 cm^{-1} (C=C); MS (EI, 80 eV): *m*/*z* (%): 339 (28) $[M]^+$, 283 (49) $[M-C_4H_8]^+$, 57 (100) $[C_4H_9]^+$; HRMS (80 eV): calcd for $C_{21}H_{25}NO_3$: 339.18344; found: 339.18358.

***tert*-Butyl 3-[2-(2-naphthyl)ethyl]-4-oxopyrrolidine-1-carboxylate (47)**: According to the procedure described above, **46** (0.170 g, 0.50 mmol) and Pd/C (10%, 34 mg) afforded the reduction product as a colourless oil (0.168 g, 98%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.77 (m, 3H; Ar), 7.60 (s, 1H; Ar), 7.43 (m, 2H; Ar), 7.30 (d, J = 8.2 Hz, 1H; Ar), 4.00 (m, 1H; CH), 3.60–3.57 (m, 2H; CH_2), 3.19–3.16 (m, 1H; CH_2), 3.06 (dd, J = 10.5, 6.0 Hz, 1H; CH_2), 2.83–2.78 (m, 2H; CH_2), 2.70 (br s, 1H; OH), 2.10–1.93 (m, 1H; CH), 1.90 (m, 1H; CH_2), 1.60 (dtd, J = 13.6, 9.1, 5.8 Hz, 1H; CH_2), 1.42 ppm (s, 9H; *t*Bu); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 154.7 (s; CO), 139.0, 133.5, 131.8 (3s; Ar), 128.0, 127.5, 127.3, 127.0, 126.3, 125.9, 125.2 (7d; Ar), 79.4 (s; *t*Bu), 75.3, 74.5 (2d; CH), 52.7, 52.4, 49.4, 48.8 (4t; CH_2), 45.7, 45.0 (2d; CH), 34.0, 33.0 (2t; CH_2), 28.4 ppm (q; *t*Bu); IR (film): $\tilde{\nu}$ = 3485 (OH), 3045–2900 (=CH, C−H), 1680 (C=O), 1600 cm^{-1} (C=C); MS (EI, 80 eV): *m*/*z* (%): 341 (2) $[M]^+$, 285 (9) $[M-C_4H_8]^+$, 154 (8) $[C_{12}H_{11}]^+$, 141 (22) $[C_{11}H_9]^+$, 57 (100) $[C_4H_9]^+$; HRMS (80 eV): calcd for $C_{21}H_{27}NO_3$: 341.19910; found: 341.19869.

According to the procedure described above, the reduction product (0.150 g, 0.44 mmol), triethylamine (0.115 mL, 0.83 mmol) and the Py·SO_3 complex (0.117 g, 0.75 mmol) afforded, after column chromatography on silica gel (hexane/ethyl acetate 5:1), **47** as a colourless solid (0.109 g, 73%). M.p. 77–79°C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.81–7.77 (m, 3H; Ar), 7.62 (s, 1H; Ar), 7.44 (m, 2H; Ar), 7.31 (dd, J = 8.3, 1.6 Hz, 1H; Ar), 4.13–4.10 (m, 1H; CH_2), 3.87–3.81 (m, 1H; CH_2), 3.69–3.65 (m, 1H; CH_2), 3.31 (m, 1H; CH_2), 2.90–2.79 (m, 2H; CH_2), 2.53 (br s, 1H; CH), 2.27–2.22 (m, 1H; CH_2), 1.79–1.75 (m, 1H; CH_2), 1.48 ppm (s, 9H; *t*Bu); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 212.9 (s; CO), 154.4 (s; CO), 138.2, 133.6, 132.3 (3s; Ar), 128.3, 127.7, 127.5, 127.2, 126.7, 126.2, 125.5 (7d; Ar), 80.4 (s; *t*Bu), 53.1, 52.9 (2t; CH_2), 49.0, 48.3 (2d; CH), 47.0, 46.6, 33.4, 30.3 (4t; CH_2), 28.5 ppm (q; *t*Bu); IR (KBr): $\tilde{\nu}$ = 3050–2870 (=CH, C−H), 1750–1680 (C=O), 1595 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{21}H_{25}NO_3$ (339.4): C 74.31, H 7.42, N 4.13; found: C 73.97, H 7.50, N 3.93.

Cyclisation experiments

General experimental procedure for the samarium diiodide induced cyclisations: Samarium (2.4–2.9 equiv) and 1,2-diiodoethane (2.2–2.5 equiv) were suspended in THF (25 mL/2.4 mmol SmI_2) under an atmosphere of argon and stirred at RT until the colour of the solution turned into dark blue (approximately 2 h). The flask was then gently evacuated, purged with argon and HMPA (18 equiv) was added. The corresponding ketone (1.0 equiv) and *t*BuOH (2.0 equiv) were dissolved in THF (15 mL mmol^{-1} of ketone), argon was purged through for 10 min and the solution was then added to the deep violet solution of SmI_2 in THF/HMPA. The mixture was stirred for 16 h at RT and then quenched by addition of saturated aqueous sodium hydrogencarbonate solution (15 mL). The aqueous phase was extracted with Et_2O (3×20 mL) and the combined organic layers were washed once with distilled water and twice with brine, then dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure to give the crude cyclisation product.

***rac*-(1*R*,9a*R*)-1-Methyl-2,3,7,9a-tetrahydro-1*H*-phenalen-1-ol (13)**: According to the general procedure, samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.23 g, 18.0 mmol), **3** (0.198 g, 1.00 mmol) and *t*BuOH (0.148 g, 2.00 mmol) afforded after purification by column chromatography on silica gel (hexane/ethyl acetate 9:1 to 8:2) **13** as a colourless solid (0.161 g, 81%). The analytical data are in agreement with those reported in the literature.[13b]

***rac*-(1*S*,4a*S*,10a*S*)-1-Methyl-1,2,3,4,5a,10a-hexahydrophenanthren-1-ol (17)**: According to the general procedure, samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.23 g, 18.0 mmol), **8** (0.212 g, 1.00 mmol) and *t*BuOH (0.148 g, 2.00 mmol) afforded after purification by column chromatography on silica gel (hexane/ethyl acetate/triethylamine 9.4:0.5:0.1) **17** as a colourless oil (0.198 g, 93%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.16–7.09 (m, 3H; Ar), 7.06–7.01 (m, 1H; Ar), 6.46 (dd, J = 9.7, 3.2 Hz, 1H; =CH), 5.68 (br d, J = 9.7 Hz, 1H; =CH), 3.11 (td, J = 12.1, 5.4 Hz, 1H; CH), 2.57 (m, 1H; CH), 1.75–1.44 (m, 6H; CH_2, OH), 1.34 (s, 3H; CH_3), 1.38–1.31 ppm (m, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 140.6, 132.7 (2s; Ar), 128.8, 128.7, 128.3, 128.2, 127.6, 126.3 (6d; Ar, =CH), 71.5 (s; C-1), 46.4, 36.7 (2d; CH), 35.0 (t; CH_2), 28.7 (q; CH_3), 27.3, 20.0 ppm (2t; CH_2); IR (film): $\tilde{\nu}$ = 3420 (OH), 3100–2900 (=C−H, C−H), 1600 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{15}H_{18}O$ (214.3): C 84.07, H 8.47; found: C 84.22, H 8.33.

***rac*-(1*S*,9a*S*)- and *rac*-(1*R*,9a*S*)-1-Methyl-1,2,3,4,9,9a-hexahydroanthracen-1-ol (18a) and (18b)**: According to the general procedure, samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.23 g, 18.0 mmol), **10** (0.212 g, 1.00 mmol) and *t*BuOH (0.148 g, 2.00 mmol) afforded after purification by column chromatography on silica gel (hexane/ethyl acetate/triethylamine 9.4:0.5:0.1) **18a** (0.117 g, 55%) and **18b** (0.078 g, 36%) as colourless oils.

*Compound **18a***: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39 (d, J = 7.3 Hz, 1H; Ar), 7.20–7.12 (m, 3H; Ar), 5.63 (s, 1H, 5-H), 3.44–3.24 (m, 3H; CH_2, CH), 2.33–2.28 (m, 1H; CH_2), 2.07–1.98 (m, 1H; CH_2), 1.93–1.74 (m, 4H; CH_2, OH), 1.52–1.41 (m, 1H; CH_2), 0.84 ppm (s, 3H; CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 137.8, 135.0, 133.7 (3s; C-4a, Ar), 129.4, 128.3, 126.2, 125.5 (4d; Ar), 117.9 (d; C-5), 76.5 (s; C-1), 53.0 (d; C-9a), 41.0, 35.4, 30.3, 25.6 (4t; CH_2), 20.9 ppm (q; CH_3); IR (film): $\tilde{\nu}$ = 3450 (OH), 3100–2850 (=C−H, C−H), 1600 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{15}H_{18}O$ (214.3): C 84.07, H 8.47; found: C 84.34, H 8.47.

*Compound **18b***: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.09–7.04 (m, 3H; Ar), 6.91 (d, J = 6.5 Hz, 1H; Ar), 6.17 (s, 1H, 5-H), 3.19 (dd, J = 17.3, 3.5 Hz, 1H; CH_2), 3.08 (dd, J = 17.3, 10.4 Hz, 1H; CH_2), 2.47 (dd, J = 10.4, 3.5 Hz, 1H; CH), 2.39–2.34 (m, 1H; CH_2), 2.15 (dt, J = 13.2, 5.0 Hz, 1H; CH_2), 1.86–1.75 (m, 3H; CH_2, OH), 1.61 (dt, J = 13.2, 5.2 Hz, 1H; CH_2), 1.45 (qt, J = 13.2, 4.4 Hz, 1H; CH_2), 1.01 ppm (s, 3H; CH_3); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 140.8, 133.37, 133.35 (3s; C-4a, Ar), 127.2, 126.5, 126.0, 125.5 (4d; Ar), 121.7 (d; C-5), 75.2 (s; C-1), 48.3 (d; C-9a), 42.8, 35.0, 26.2, 25.0 (4t; CH_2), 20.6 ppm (q; CH_3); IR (film): $\tilde{\nu}$ = 3450 (OH), 3100–2850 (=C−H, C−H), 1600 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{15}H_{18}O$ (214.3): C 84.07, H 8.47; found: C 84.08, H 8.25.

***rac*-(2a*R*,2b*R*,8b*R*,10a*R*)-1,2b,8b,9,10,10a-Hexahydrocyclobuta[*a*]phenanthren-2a(2*H*)-ol (22)**: According to the general procedure, samarium (0.161 g, 1.07 mmol), 1,2-diiodoethane (0.277 g, 0.981 mmol), HMPA (1.44 g, 8.03 mmol), **21a** (0.100 g, 0.446 mmol) and *t*BuOH (0.066 g, 0.89 mmol) afforded after purification by column chromatography on silica gel (hexane/ethyl acetate 19:1) product **22** (0.041 g, 41%) as a colourless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.17–7.13 (m, 3H; Ar), 7.03 (d, J = 7.5 Hz, 1H; Ar), 6.47 (dd, J = 9.6, 2.5 Hz, 1H; =CH), 6.18 (dd, J = 9.6, 4.9 Hz, 1H; =CH), 3.02 (m, 1H; CH), 2.67 (m, 1H; CH), 2.26 (m, 1H; CH), 2.14–2.06 (m, 2H; CH_2), 1.91–1.78 (m, 2H; CH_2), 1.74–1.67 (m, 1H; CH_2), 1.63 (br s, 1H; OH), 1.52–1.45 (m, 1H; CH_2), 1.39 (m, 1H; CH_2), 1.27–1.20 ppm (m, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 139.0, 133.4 (2s; Ar), 128.4, 128.0 (2d; =CH), 127.5, 126.4, 126.3, 126.2 (4d; Ar), 75.2 (s; C-2a), 43.5, 43.3, 36.3 (3d; CH), 33.2, 24.5, 23.0, 18.9 ppm (4t; CH_2); IR (film): $\tilde{\nu}$ = 3380 (OH), 3035–2830 (=C−H, C−H), 1630 cm^{-1} (C=C); MS (EI, 80 eV): *m*/*z* (%): 226 (20) $[M]^+$, 196 (100) $[M-CH_2O]^+$, 181 (16) $[M-C_2H_5O]^+$; HRMS (80 eV): calcd for $C_{16}H_{18}O$:

226.13577; found: 226.13655; elemental analysis calcd (%) for $C_{16}H_{18}O$ (226.3): C 84.91, H 8.02; found: C 84.71, H 7.97.

***rac*-(3a*R*,3b*R*,9b*R*,11a*S*)-1,2,3,3b,9b,10,11,11a-Octahydro-3a*H*-cyclopenta[*a*]phenanthren-3a-ol (23)**: According to the general procedure, samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.23 g, 18.0 mmol), **21b** (0.238 g, 1.00 mmol) and *t*BuOH (0.148 g, 2.00 mmol) afforded after purification by column chromatography on silica gel (hexane/ethyl acetate 19:1 to 9:1) **23** (0.193 g, 80%) as a colourless solid. M.p. = 114–116 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.22–7.09 (m, 3H; Ar), 7.02 (d, J = 7.7 Hz, 1H; Ar), 6.52 (d, J = 9.5 Hz, 1H; =CH), 6.18 (dd, J = 9.5, 5.2 Hz, 1H; =CH), 3.30–3.22 (m, 1H; CH), 2.65 (dd, J = 7.0, 5.2 Hz, 1H; CH), 2.42–2.28 (m, 1H; CH_2), 2.04–1.89 (m, 1H; CH_2), 1.80–1.70 (m, 1H; CH), 1.65–1.60 (m, 1H; CH_2), 1.60–1.55 (m, 2H; CH_2), 1.55–1.20 ppm (m, 5H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 137.2, 134.4 (2s; Ar), 129.9, 128.5 (2d; =CH), 127.4, 126.2, 126.0, 124.1 (4d; Ar), 84.1 (s; C-3a), 47.6, 44.2, 36.5 (3d; CH), 33.2, 29.1, 28.0, 24.4, 19.8 ppm (5t; CH_2); IR (KBr): $\tilde{\nu}$ = 3380 (OH), 3050–2800 cm^{-1} (=C–H, C–H); MS (EI, 80 eV): m/z (%): 240 (52) $[M]^+$, 223 (3) $[M-H_2O]^+$, 154 (49), 129 (62), 128 (100) $[C_{10}H_8]^+$; HRMS (80 eV): calcd for $C_{17}H_{20}O$: 240.1514; found: 240.1537. elemental analysis calcd (%) for $C_{17}H_{20}O$ (240.4): C 84.96, H 8.39; found: 84.67, H 8.25.

***rac*-(4a*R*,4b*R*,10b*R*,12a*S*)-1,3,4,4b,10b,11,12,12a-Octahydrobenzo[*a*]phenanthren-4a(2*H*)-ol (24)**: According to the general procedure, samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.23 g, 18.0 mmol), **21c** (0.252 g, 1.00 mmol) and *t*BuOH (0.148 g, 2.00 mmol) afforded, after purification by column chromatography on silica gel (hexane/ethyl acetate from 19:1 to 9:1), product **24** (0.245 g, 96%) as a colourless solid. M.p. 106–108 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.20–7.10 (m, 3H; Ar), 7.01 (d, J = 7.5 Hz, 1H; Ar), 6.51 (d, J = 9.8 Hz, 1H; =CH), 6.18 (dd, J = 9.8, 5.7 Hz, 1H; =CH), 3.25 (m, 1H; CH), 2.63 (dd, J = 7.0, 5.7 Hz, 1H; CH), 2.37–2.30 (m, 1H; CH_2), 2.00–1.90 (m, 1H; CH_2), 1.79–1.72 (m, 1H; CH), 1.68–1.54 (m, 5H; CH_2, OH), 1.46–1.20 ppm (m, 6H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 137.2, 134.4 (2s; Ar), 129.9, 128.4 (2d; =CH), 127.3, 126.2, 125.9, 124.1 (4d; Ar), 84.0 (s; C-4a), 47.5, 44.1, 36.5 (3d; CH), 33.2, 29.0, 26.4, 24.4, 19.8, 19.7 ppm (6t; CH_2); IR (KBr): $\tilde{\nu}$ = 3365 (OH), 3000–2800 cm^{-1} (= C–H, C–H); elemental analysis calcd (%) for $C_{18}H_{22}O$ (254.4): C 84.99, H 8.72; found: C 84.90, H 8.58.

***rac*-(4b*R*,6a*S*,11a*R*,11b*R*)-4b,5,6,6a,7,8,9,10,11,11b-Decahydro-11a*H*-cyclohepta[*a*]phenanthren-11a-ol (25)**: According to the general procedure, samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.23 g, 18.0 mmol), **21d** (0.266 g, 1.00 mmol) and *t*BuOH (0.148 g, 2.00 mmol) afforded, after purification by column chromatography on silica gel (hexane/ethyl acetate 19:1 to 9:1), **25** (0.263 g, 98%) as a colourless solid. M.p. 109–111 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.16–7.08 (m, 3H; Ar), 7.03–6.98 (m, 1H; Ar), 6.45 (dd, J = 9.9, 2.7 Hz, 1H; =CH), 6.06 (dd, J = 9.9, 3.3 Hz, 1H; =CH), 3.17 (m, 1H; CH), 2.53 (m, 1H; CH), 1.97–1.15 ppm (m, 16H; CH, CH_2, OH); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 139.9, 133.1 (2s; Ar), 129.0, 127.8, 127.4, 126.2*, 125.9 (5d; Ar, =CH), 76.5 (s; C-11a), 46.5, 44.6, 37.3 (3d; CH), 33.3, 29.8, 29.5, 29.1, 24.4, 20.8, 19.7 ppm (7t; CH_2), * = signal with higher intensity; IR (KBr): $\tilde{\nu}$ = 3435 (OH), 3060–2800 cm^{-1} (=C–H, C–H); elemental analysis calcd (%) for $C_{19}H_{24}O$ (268.4): C 85.03, H 9.01; found: C 84.90, H 8.58.

***rac*-(4b*R*,6a*S*,11a*R*,12b*R*)-4b,6,6a,7,8,9,10,11,12,12b-Decahydrocyclooct[*a*]phenanthren-12(5*H*)-ol (26)**: According to the general procedure, samarium (0.180 g, 1.20 mmol), 1,2-diiodoethane (0.310 g, 1.10 mmol), HMPA (1.61 g, 9.00 mmol), **21e** (0.140 g, 0.50 mmol) and *t*BuOH (0.074 g, 1.00 mmol) afforded after purification by column chromatography on silica gel (hexane/ethyl acetate 9:1 to 7:3) and preparative HPLC (hexane/ethyl acetate 17:3) **26** (0.073 g, 52%, purity ≈90%) as a colourless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.26 (br d, J ≈ 7.5 Hz, 1H; Ar), 7.16 (td, J = 7.5, 1.3 Hz, 1H; Ar), 7.09, 6.99 (2tt, J = 7.3, 1.3 Hz, 1H each; Ar), 6.56 (d, J = 9.8 Hz, 1H; =CH), 6.12 (dd, J = 9.8, 6.0 Hz, 1H; =CH), 3.19 (m, 1H; CH), 2.56–2.50 (m, 2H; CH_2), 2.38 (m, 1H; CH), 1.85–0.86 ppm (m, 16H; CH, CH_2, OH); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 138.9, 135.4 (2s; Ar), 131.2, 129.8, 127.5, 125.9, 125.5, 122.9 (6d; Ar, = CH), 63.1 (s; C-12), 42.8, 42.0, 35.6 (3d; CH), 32.3, 30.0, 29.6, 28.4, 26.6, 26.2, 26.0, 23.1 ppm (8t; CH_2); IR (film): $\tilde{\nu}$ = 3435 (OH), 3025–2850 cm^{-1} (=C–H, C–H); MS (EI, 80 eV): m/z (%): 264 (6) $[M-H_2O]^+$, 207 (100), 128 (70) $[C_{10}H_8]^+$.

***rac*-(3a*R*,3b*R*,9b*R*,11a*S*)-7-Methoxy-1,2,3,3b,9b,10,11,11a-octahydro-3a*H*-cyclopenta[*a*]phenanthren-3a-ol (28)**: According to the general procedure, samarium (0.180 g, 1.20 mmol), 1,2-diiodoethane (0.310 g, 1.10 mmol), HMPA (1.61 g, 9.00 mmol), **27** (0.134 g, 0.50 mmol) and *t*BuOH (0.074 g, 1.00 mmol) afforded, after purification by column chromatography on silica gel (hexane/ethyl acetate 19:1 to 9:1), **28** as a pale-yellow oil (0.038 g, ≈28%, purity 80–90%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 7.19–7.05 (m, 3H; Ar), 6.44 (dd, J ≈ 9.5, 2.7 Hz, 1H; =CH), 6.20 (br d, J ≈ 9.5 Hz, 1H; =CH), 3.20–3.00 (m, 1H; CH), 3.75 (s, 3H; OCH_3), 2.49 (m, 1H; CH), 2.37–1.01 ppm (m, 12H; CH, CH_2, OH).

***rac*-(4a*R*,10b*R*,12a*R*)-1,3,4,4b,10b,11,12,12a-Octahydro-4a*H*-spiro[chrysene-2,2′-[1,3]dioxolan-4a-ol (30) and *rac*-(8a*R*,12a*S*,12b*S*)-3,7,8,8a,9,11,12,12b-octahydro-12a*H*-spiro[benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene-10,2′-[1,3]dioxolan]-12a-ol (31)**: According to the general procedure, samarium (1.13 g, 7.52 mmol), 1,2-diiodoethane (1.79 g, 6.37 mmol), HMPA (8.93 g, 49.9 mmol), **29** (0.860 g, 2.77 mmol) and *t*BuOH (0.406 g, 5.48 mmol) afforded, after column chromatography on silica gel (hexane/ethyl acetate 3.5:1 to 3:1) and preparative HPLC (hexane/ethyl acetate 7:3), **30** (0.166 g, 19%) and **31** (0.060 g, 7%), both as a colourless solid.

*Compound **30***: M.p. 123–125 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.25 (d, J = 7.4 Hz, 1H; Ar), 7.20 (dt, J = 7.4, 1.3 Hz, 1H; Ar), 7.14 (m, 1H; Ar), 7.02 (dd, J = 7.4, 1.0 Hz, 1H; Ar), 6.63 (d, J = 9.7 Hz, 1H; CH=CH), 6.16 (dd, J = 9.7, 5.9 Hz, 1H; CH=CH), 3.90–3.78 (m, 4H; OCH_2), 3.27 (m, 1H; CH_2), 2.48 (m, 2H; CH_2, CH), 2.16 (dd, J = 13.8, 5.7 Hz, 1H; CH_2), 1.99 (qd, J = 13.8, 2.6 Hz, 1H; CH_2), 1.77–1.68 (m, 3H; CH_2, CH), 1.52 (ddd, J = 13.8, 6.7, 3.4 Hz, 1H; CH_2), 1.45 (dt, J = 13.8, 2.6 Hz, 1H; CH_2), 1.42–1.38 (m, 1H; CH_2), 1.35–1.30 (m, 2H; CH_2), 1.19 ppm (td, J = 13.8, 4.1 Hz, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 137.6, 134.7 (2s; Ar), 130.3, 128.8 (2d; =CH), 127.8, 126.3, 125.9, 123.6 (4d; Ar), 108.6 (s, O–C–O), 74.0 (s; C-4a), 64.3, 63.6 (2t; OCH_2), 47.7, 44.7, 37.0 (3d; CH), 35.7, 30.3, 26.4, 26.0, 25.6 ppm (5t; CH_2); IR (KBr): $\tilde{\nu}$ = 3460 (OH), 3030–2870 (=CH, CH), 1595 cm^{-1} (C=C); MS (EI, 80 eV): m/z (%): 312 (49) $[M]^+$, 294 (25) $[M-H_2O]^+$, 99 (100); HRMS (80 eV): calcd for $C_{20}H_{24}O_3$: 312.17255; found: 312.17355.

*Compound **31***: M.p. 143–148 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.09 (t, J = 7.5 Hz, 1H; Ar), 6.97 (m, 2H; Ar), 6.11 (dddd, J = 10.0, 4.9, 2.2, 0.7 Hz, 1H; CH_2), 6.06 (dddd, J = 10.0, 4.9, 3.0, 0.5 Hz, 1H; CH_2), 3.86–3.76 (m, 4H; OCH_2), 3.73–3.71 (m, 1H; CH), 3.33 (m, 1H; CH_2), 3.28 (m, 1H; CH_2), 3.06 (ddd, J = 14.9, 11.0, 7.3 Hz, 1H; CH_2), 2.75 (ddd, J = 14.9, 11.0, 1.9 Hz, 1H; CH_2), 1.85–1.84 (m, 1H; CH_2), 1.82–1.75 (m, 3H; CH_2), 1.65 (br s, 1H; OH), 1.57–1.52 (m, 1H; CH_2), 1.50–1.41 (m, 2H; CH_2, CH), 1.29 (dt, J = 13.1, 3.1 Hz, 1H; CH_2), 1.17 ppm (td, J = 13.9, 4.5 Hz, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 139.1, 134.2, 133.8 (3s; Ar), 127.3 (d; =CH), 126.8, 126.6, 126.5 (3d; Ar), 126.3 (d; =CH), 108.9 (s; O–C–O), 64.3, 64.2 (2t; OCH_2), 48.3, 38.9 (2d; CH), 37.7, 31.4, 31.0, 30.5, 30.4, 25.5 ppm (6t; CH_2). IR (KBr): $\tilde{\nu}$ = 3540–3470 (O–H), 3030–2820 (=CH, C–H), 1590 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{20}H_{24}O_3$ (312.4): C 76.89, H 7.74; found C 76.55, H 7.45.

***rac*-(4a′*R*,12a′*R*,12b′*R*) (34a) and *rac*-(4a′*R*,12a′*S*,12b′*R*)-1′,2′,4′,4a′,5′,6′,12′,12a′-Octahydro-12b′*H*-spiro[1,3-dioxolane-2,3′-tetraphen]-12b′-ol (34b)**: According to the general procedure, samarium (1.01 g, 6.72 mmol), 1,2-diiodoethane (1.75 g, 6.20 mmol), HMPA (8.00 g, 44.6 mmol), **33** (0.771 g, 2.48 mmol) and *t*BuOH (0.363 g, 4.89 mmol) afforded **34a** as a colourless solid (0.473 g, 61%) and **34b** as a colourless oil (0.087 g, 11%), after column chromatography on silica gel (hexane/ethyl acetate 3:1). Compound **34a** was further purified by repeated washing of the solid with cold Et_2O. Compound **34b** was purified by preparative HPLC (hexane/ethyl acetate 4:1).

*Compound **34a***: M.p. 151–153 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.04–7.03 (m, 3H; Ar), 6.90 (dd, J = 6.4, 1.3 Hz, 1H; Ar), 6.16 (s, 1H; =CH), 3.90–3.81 (m, 4H; OCH_2), 3.20 (dd, J = 17.3, 2.1 Hz, 1H; CH_2), 3.10 (dd, J = 17.3, 10.4 Hz, 1H; CH_2), 2.43 (d, J = 10.4 Hz, 1H; CH), 2.37 (ddd, J = 12.2, 4.3, 2.2 Hz, 1H; CH_2), 2.22 (dd, J = 14.1, 5.9 Hz, 1H; CH_2), 2.16 (dd, J = 13.1, 5.0 Hz, 1H; CH_2), 2.03 (dd, J = 13.1, 4.3 Hz, 1H; CH_2), 1.80–1.74

(m, 2H; CH_2, CH), 1.70–1.60 (m, 2H; CH_2), 1.45–1.41 (m, 2H; CH_2), 1.38 (brs, 1H; OH), 1.35 ppm (dq, $J=14.1$, 2.2 Hz, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): $\delta=140.3$ (s; *C*=CH), 133.5, 133.3 (2s; Ar), 127.1, 126.6, 126.1, 125.6 (4d; Ar), 121.3 (d; =CH), 108.5 (s; O–C–O), 75.8 (s; C-12b′), 64.3, 63.4 (2t; OCH_2), 48.9, 45.3 (2d; CH), 35.5, 35.4, 31.4, 29.5, 26.2, 23.7 ppm (6t; CH_2); IR (KBr): $\tilde{\nu}=3430$ (OH), 3075–2840 (=CH, C–H), 1595 cm^{-1} (C=C); MS (EI, 80 eV): *m*/*z* (%): 312 (14) $[M]^+$, 294 (7) $[M-H_2O]^+$, 156 (100); HRMS (80 eV): calcd for $C_{20}H_{24}O_3$: 312.17255; found: 312.17325; elemental analysis calcd (%) for $C_{20}H_{24}O_3$ (312.4): C 76.89, H 7.74; found: C 76.17, H 7.56.

Compound ***34b***: ^1H NMR ($CDCl_3$, 500 MHz): $\delta=7.38$ (m, 1H; Ar), 7.20–7.15 (m, 3H; Ar), 5.68–5.67 (m, 1H; =CH), 4.00–3.82 (m, 4H; OCH_2), 3.44–3.27 (m, 3H; CH_2, CH), 2.36–2.33 (m, 1H; CH_2), 2.28 (dd, $J=13.6$, 5.2 Hz, 1H; CH_2), 2.13–2.04 (m, 3H; CH_2, CH), 1.86 (dt, $J=14.0$, 3.8 Hz, 1H; CH_2), 1.77 (dd, $J=13.1$, 4.2 Hz, 1H; CH_2), 1.74–1.71 (m, 1H; CH_2), 1.64 (brs, 1H; OH), 1.48–1.42 (m, 2H; CH_2), 0.81 ppm (m, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): $\delta=137.7$ (s; *C*=CH), 135.8, 133.7 (2s; Ar), 129.1, 128.6, 126.5, 125.9 (4d; Ar), 117.8 (d; =CH), 108.9 (s; O–C–O), 77.0 (s; C-12b′), 64.4, 63.6 (2t; OCH_2), 53.4, 43.7 (2d; CH), 35.6, 35.5, 31.9, 30.7, 29.8, 24.8 ppm (6t; CH_2); IR (film): $\tilde{\nu}=3465$ (OH), 3055–2875 (=CH, CH), 1600 cm^{-1} (C=C); MS (EI, 80 eV): *m*/*z* (%): 313 (3) $[M+H]^+$, 312 (13) $[M]^+$, 294 (8) $[M-H_2O]^+$, 156 (100); HRMS (80 eV): calcd for $C_{20}H_{24}O_3$: 312.17255; found: 312.17366.

***tert*-Butyl *rac*-(3a*S*,3b*R*,9b*R*,11a*R*)-3a-hydroxy-1,3,3a,3b,9b,10,11,11a-octahydro-2*H*-naphtho[2,1-*e*]isoindole-2-carboxylate (48)**: According to the general procedure, samarium (0.159 g, 1.06 mmol), 1,2-diiodoethane (0.250 g, 0.90 mmol), HMPA (1.16 g, 6.46 mmol), **44** (0.122 g, 0.36 mmol) and *t*BuOH (0.055 g, 0.74 mmol) afforded, after column chromatography on silica gel (hexane/ethyl acetate 3:1 to 1:1) and preparative HPLC (hexane/isopropanol 95:5), **48** as a colourless solid (0.035 g, 29%).[54] M.p. = 157–160 °C; ^1H NMR (CD_3CN, 500 MHz): $\delta=7.29$–7.24 (m, 1H; Ar), 7.23–7.16 (m, 2H; Ar), 7.08 (td, $J=7.0$, 1.3 Hz, 1H; Ar), 6.57 (dd, $J=9.9$, 3.6 Hz, 1H; =CH), 6.20–6.11 (m, 1H; =CH), 3.46 (dd, $J=10.5$, 6.3 Hz, 1H; CH_2), 3.27 (m, 1H; CH), 3.01 (m, 2H; OH, CH_2), 2.93 (d, $J=12.0$ Hz, 1H; CH_2), 2.78 (m, 1H; CH_2), 2.68–2.65 (m, 1H; CH), 2.45–2.36 (m, 1H; CH_2), 2.05–1.95 (m, 1H; CH), 1.70–1.67 (m, 2H; CH_2), 1.35, 1.27 (2s, ≈4.5H each; *t*Bu), 1.23–1.20 ppm (m, 1H; CH_2); ^{13}C NMR (CD_3CN, 126 MHz): $\delta=155.5$, 155.4 (2s; CO), 135.2, 130.4 (2s; Ar), 130.2, 129.4 (2d; =CH), 128.8, 127.4, 127.3, 125.5 (4d; Ar), 80.1 (s; C-3a), 79.3 (s; *t*Bu), 54.8, 54.1, 51.7, 51.1 (4t; NCH_2), 46.7, 46.0, 44.0, 43.9, 37.2, 37.1 (6d; CH), 28.6, 28.5 (2q; *t*Bu), 25.9, 25.5 (2d; CH), 24.8, 24.4 ppm (2t; CH_2); IR (KBr): $\tilde{\nu}=3360$ (OH), 3055–2850 (=CH, C–H), 1670–1660 cm^{-1} (C=O); MS (EI, 80 eV): *m*/*z* (%): 341 (6) $[M]^+$, 57 (100) $[C_4H_9]^+$; HRMS (80 eV): calcd for $C_{21}H_{27}NO_3$: 341.19910; found: 341.19879.

***tert*-Butyl *rac*-(3a*R*,11a*R*,11b*S*)- and *rac*-(3a*R*,11a*S*,11b*S*)-11b-hydroxy-1,3,3a,4,5,11,11a,11b-octahydro-2*H*-naphtho[2,3-*e*]isoindole-2-carboxylate (49a) and (49b)**: According to the general procedure, samarium (0.113 g, 0.75 mmol), 1,2-diiodoethane (0.203 g, 0.72 mmol), HMPA (0.93 g, 5.20 mmol), **47** (0.098 g, 0.29 mmol) and *t*BuOH (0.041 g, 0.56 mmol) afforded after purification by column chromatography on silica gel (hexane/ethyl acetate 3:1 to 1:1) **49a** (0.027 g, 27%) and **49b** as colourless solids (0.022 g, 22%).

Compound ***49a***: M.p. 185–188 °C; ^1H NMR (CD_3OD, 500 MHz): $\delta=$ 7.06–7.04 (m, 3H; Ar), 6.93 (m, 1H; Ar), 6.27 (s, 1H; =CH), 3.61 (td, $J=$ 9.9, 5.6 Hz, 1H; NCH_2), 3.15–2.92 (m, 5H; CH_2), 2.73–2.67 (m, 1H; CH), 2.41 (dt, $J=13.3$, 3.1 Hz, 1H; CH_2), 2.24 (td, $J=13.3$, 4.4 Hz, 1H; CH_2), 2.05 (m, 1H; CH), 1.94 (m, 1H; CH_2), 1.41, 1.35 (2s, ≈4.5H each; *t*Bu), 1.23–1.12 ppm (m, 1H; CH_2); ^{13}C NMR (CD_3OD, 126 MHz): $\delta=155.8$ (s, CO), 139.7, 139.6, 134.5, 134.4, 133.6, 133.5 (6s; *C*=CH, Ar), 128.1, 128.0, 127.6, 127.5, 127.2, 127.1, 126.4, 126.3 (8d; Ar), 123.4, 123.3 (2d; =CH), 83.3, 82.6 (2s; *t*Bu), 80.5, 80.4 (2s; C-11b), 52.3, 51.8, 51.2 (3t; NCH_2), 47.7, 46.9, 45.4, 45.3 (4d; CH), 34.0, 33.9, 32.0, 31.8 (4t; CH_2), 28.4, 28.3 (2q; *t*Bu), 28.2, 28.0 ppm (2t; CH_2); IR (KBr): $\tilde{\nu}=3400$ (OH), 3095–2885 (=CH, C–H), 1690–1670 (C=O), 1600 cm^{-1} (C=C); MS (EI, 80 eV): *m*/*z* (%): 341 (6) $[M]^+$, 285 (23) $[M-C_4H_8]^+$, 240 (10) $[M-C_5H_9O_2]^+$, 57 (100) $[C_4H_9]^+$; HRMS (80 eV): calcd for $C_{21}H_{27}NO_3$: 341.19910; found: 341.19877.

Compound ***49b***: M.p. 187–190 °C; ^1H NMR (CD_3OD, 500 MHz): $\delta=7.62$ (d, $J=7.7$ Hz, 1H; Ar), 7.17–7.10 (m, 3H; Ar), 5.77 (m, 1H; =CH), 3.64 (td, $J=10.3$, 5.7 Hz, 1H; NCH_2), 3.60–3.57 (m, 1H; CH_2), 3.50–3.35 (m, 2H; CH_2, CH), 3.16 (dd, $J=12.5$, 11.7 Hz, 1H; CH_2), 3.12 (dd, $J=10.3$, 7.1 Hz, 1H; CH_2), 2.65 (d, $J=11.7$ Hz, 1H; CH_2), 2.35 (ddd, $J=12.5$, 3.9, 2.8 Hz, 1H; CH_2), 2.20 (quint., $J\approx6$ Hz, 1H; CH), 2.14 (m, 1H; CH_2), 2.02–1.97 (m, 1H; CH_2), 1.40, 1.35 (2s, ≈4.5H each; *t*Bu), 1.20 ppm (dt, $J=12.9$, 3.9 Hz, 1H; CH_2); ^{13}C NMR (CD_3OD, 126 MHz): $\delta=155.8$ (s; CO), 136.6, 133.6, 133.5, 133.1, 133.0 (5s; *C*=CH, Ar), 130.3, 130.2, 127.9, 127.8, 126.2, 126.1, 125.2, 125.1, 119.1, 119.0 (10 d; =CH, Ar), 83.9, 83.2 (2s; *t*Bu), 79.5, 79.4 (2s; C–O), 51.5, 50.9, 47.7 (3t; CH_2), 46.7 (d; CH), 34.3, 32.2, 32.1 (3t; CH_2), 29.8 (d; CH), 27.4, 27.3 ppm (2q; *t*Bu); IR (KBr): $\tilde{\nu}=3435$ (OH), 3065–2860 (=CH, C–H), 1700–1695 (C=O), 1615 cm^{-1} (C=C); MS (EI, 80 eV): *m*/*z* (%): 341 (3) $[M]^+$, 285 (17) $[M-C_4H_8]^+$, 57 (100) $[C_4H_9]^+$; HRMS (80 eV): calcd for $C_{21}H_{27}NO_3$: 341.19910; found: 341.19855.

***rac*-(4a*S*,4b*R*,10b*R*,12a*R*)-2-Methyl-1,3,4,4b,10b,11,12,12a-octahydronaphtho[2,1-*f*]isoquinolin-4a(1*H*)ol (51)**: According to the general procedure, samarium (0.537 g, 3.57 mmol), 1,2-diiodoethane (0.919 g, 3.28 mmol), HMPA (4.22 g, 23.6 mmol), **50** (0.350 g, 1.31 mmol) and *t*BuOH (0.200 g, 2.69 mmol) afforded, after column chromatography on neutral alumina (hexane/ethyl acetate 3:1), **51** as a colourless solid. The product was further purified by repeated washing with cold Et_2O (0.199 g, 56%). M.p. 124–128 °C; ^1H NMR (CD_3OD, 500 MHz): $\delta=7.28$ (d, $J=7.5$ Hz, 1H; Ar), 7.17 (td, $J=7.5$, 1.2 Hz, 1H; Ar), 7.10 (t, $J\approx7.3$ Hz, 1H; Ar), 7.01 (brd, $J=7.3$ Hz, 1H; Ar), 6.63 (d, $J=9.7$ Hz, 1H; =CH), 6.16 (dd, $J=9.7$, 6.1 Hz, 1H; =CH), 3.25 (m, 1H; CH), 2.60–2.54 (m, 1H; CH_2), 2.54 (dd, $J=11.4$, 3.5 Hz, 1H; CH_2), 2.45 (t, $J\approx6.5$ Hz, 1H; CH), 2.37 (m, 1H; CH_2), 2.27–2.23 (m, 1H; CH_2), 2.12–2.07 (m, 1H; CH_2), 2.05 (s, 3H; NCH_3), 2.02–1.95 (m, 1H; CH_2), 1.82–1.75 (m, 1H; CH_2), 1.55 (m, 2H; CH, CH_2), 1.32 (m, 1H; CH_2), 1.19 ppm (dt, $J=13.4$, 3.9 Hz, 1H; CH_2); ^{13}C NMR (CD_3OD, 126 MHz): $\delta=134.8$, 132.7 (2s; Ar), 127.4, 126.8 (2d; =CH), 125.1, 123.8, 123.5, 121.0 (4d; Ar), 69.0 (s; COH), 54.4, 49.2 (2t; CH_2), 44.7 (d; CH), 43.1 (q; NCH_3), 42.1, 34.7 (2d; CH), 25.6, 22.8, 22.7 ppm (3t; CH_2); IR (KBr): $\tilde{\nu}=3390$ (OH), 3030–2800 (=CH, C–H), 1595 cm^{-1} (C=C); MS (EI, 80 eV): *m*/*z* (%): 269 (17) $[M]^+$, 268 (8) $[M-H]^+$, 28 (100); HRMS (80 eV): calcd for $C_{18}H_{23}NO$: 269.17798; found: 269.17844.

***rac*-(4a*R*,12a*R*,12b*S*)- and *rac*-(4a*R*,12a*S*,12b*S*)-3-Methyl-2,3,4,4a,5,6,12,12a-octahydronaphtho[2,3-f]isoquinolin-12b(1*H*)ol (53a) and (53b)**: According to the general procedure, samarium (0.316 g, 2.10 mmol), 1,2-diiodoethane (0.544 g, 1.93 mmol), HMPA (2.48 g, 13.9 mmol), **52** (0.205 g, 0.77 mmol) and *t*BuOH (0.109 g, 1.47 mmol) afforded, after column chromatography on neutral alumina (hexane/ethyl acetate from 3:1 to 2:1), **53a** as a colourless solid, which was further purified by repeated washing with cold Et_2O (0.080 g, 39%) and **53b** as a colourless oil (0.041 g, 20%).

Compound ***53a***: M.p. 160–165 °C; ^1H NMR ($CDCl_3$, 500 MHz): $\delta=7.26$–7.02 (m, 3H; Ar), 6.90 (m, 1H; Ar), 6.19 (s, 1H; =CH), 3.19 (dd, $J=17.4$, 2.3 Hz, 1H; CH_2), 3.07 (dd, $J=17.4$, 10.5 Hz, 1H; CH_2), 2.48–2.37 (m, 5H; CH_2, CH), 2.22 (dd, $J=13.3$, 5.0 Hz, 1H; CH_2), 2.16 (s, 3H; NCH_3), 2.08–1.94 (m, 2H; CH_2), 1.80–1.71 (m, 2H; CH_2), 1.69 (brs, 1H; OH), 1.57 (m, 1H; CH), 1.23 ppm (dd, $J=14.2$, 2.3 Hz, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): $\delta=140.3$, 133.4, 133.3 (3s, *C*=CH; Ar), 127.0, 126.5, 126.1, 125.5 (4d; Ar), 121.5 (d; =CH), 73.8 (d; C-12b), 57.0, 51.5 (2t; CH_2), 48.6 (d; CH), 46.5 (q; NCH_3), 45.1 (d; CH), 34.9, 30.4, 26.7, 25.8 ppm (4t; CH_2); IR (KBr): $\tilde{\nu}=3310$ (OH), 2930–2800 (=CH, C–H), 1600 cm^{-1} (C=C); MS (EI, 80 eV): *m*/*z* (%): 269 (53) $[M]^+$, 268 (10) $[M-H]^+$, 58 (100); HRMS (80 eV): calcd for $C_{18}H_{23}NO$: 269.17798; found: 269.17758.

Compound ***53b***: ^1H NMR ($CDCl_3$, 250 MHz): $\delta=7.19$–7.13 (m, 1H; Ar), 7.05–7.00 (m, 3H; Ar), 5.68 (s, 1H; =CH), 3.22–3.15 (m, 1H; CH_2), 3.07 (dd, $J=17.4$, 10.5 Hz, 1H; CH_2), 2.57–2.34 (m, 5H; CH_2, CH), 2.37–2.22 (m, 1H; CH_2), 2.20 (s, 3H; NCH_3), 2.09–1.88 (m, 2H; CH_2), 1.86–1.67 (m, 3H; OH, CH_2), 1.23 (d, $J=14.0$ Hz, 1H; CH_2), 0.67 ppm (brd, $J\approx12.0$ Hz, 1H; CH).

Subsequent reactions of cyclisation products

General procedure for the ketal cleavage: To a solution of the corresponding ketal (**30**, **34a**, **34b**) in Et_2O (10 mL mmol^{-1}) was added a 50% aq solution of H_2SO_4 (10 mL mmol^{-1}). The mixture was vigorously stirred for 2 h at RT and then neutralized with a saturated solution of sodium hydrogencarbonate. The product was then repeatedly extracted with ethyl acetate and the combined organic layers were dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure.

***rac*-(4a*R*,4b*R*,10b*R*,12a*R*)-4a-Hydroxy-3,4,4a,4b,10b,11,12,12a-octahydrochrysen-2(1*H*)one (32)**: According to the general procedure above, **30** (0.166 g, 0.531 mmol) afforded, after column chromatography on silica gel (hexane/ethyl acetate 3:1), **32** as a colourless solid (0.136 g, 95%). M.p. 178–180°C; ^{1}H NMR (CD_3CN, 500 MHz): δ = 7.25 (d, J = 7.3 Hz, 1H; Ar), 7.20 (td, $J \approx 7.3$, J = 1.3 Hz, 1H; Ar), 7.15 (td, $J \approx 7.3$, J = 1.0 Hz, 1H; Ar), 7.06 (m, 1H; Ar), 6.67 (d, J = 9.8 Hz, 1H; =CH), 6.25 (dd, J = 9.8, 6.0 Hz, 1H; =CH), 3.31 (br t, $J \approx 6.3$ Hz, 1H; CH), 2.99 (dd, J = 14.0, 6.4 Hz, 1H; CH_2), 2.83 (s, 1H; OH), 2.57 (m, 1H; CH), 2.54–2.52 (m, 1H; CH_2), 2.48 (m, 1H; CH_2), 2.00–1.95 (m, 1H; CH), 1.84 (dt, J = 14.0, 2.2 Hz, 1H; CH_2), 1.83–1.81 (m, 1H; CH_2), 1.70–1.68 (m, 2H; CH_2), 1.61 (m, 1H; CH_2), 1.34–1.26 (m, 1H; CH_2), 1.23 ppm (dd, J = 14.2, 5.2 Hz, 1H; CH_2); ^{13}C NMR (CD_3CN, 126 MHz): δ = 212.3 (s; CO), 138.2, 135.8 (2s; Ar), 130.8, 130.4, 128.6, 127.2, 127.0, 124.1 (6d; =CH, Ar), 73.7 (s; C-4a), 48.1, 47.6 (2d; CH), 44.1 (t; CH_2), 37.5 (d; CH), 37.3, 28.7, 27.7, 25.6 ppm (4t; CH_2); IR (KBr): $\tilde{\nu}$ = 3510 (OH), 3070–2835 (=CH, C–H), 1690 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{18}H_{20}O_2$ (268.4): C 80.56, H 7.51; found: C 80.23, H 7.15.

***rac*-(4a*R*,12a*R*,12b*R*)-12b-Hydroxy-1,4,4a,5,6,12,12a,12b-octahydrotetraphen-3(2*H*)one (35a)**: According to the general procedure above, **34a** (0.400 g, 1.28 mmol) afforded, after column chromatography on silica gel (hexane/ethyl acetate 4:1), **35a** as a colourless solid (0.264 g, 77%). M.p. 144–146°C; ^{1}H NMR (CD_3CN, 500 MHz): δ = 7.10–7.02 (m, 3H; Ar), 6.90 (m, 1H; Ar), 6.19 (s, 1H; =CH), 3.25 (dd, J = 17.5, 2.5 Hz, 1H; CH_2), 3.15 (dd, J = 17.5, 10.5 Hz, 1H; CH_2), 3.08 (dd, J = 14.2, 6.1 Hz, 1H; CH_2), 2.60–2.52 (m, 2H; CH_2, CH), 2.40 (ddd, J = 13.0, 4.5, 2.2 Hz, 1H; CH_2), 2.23 (dt, J = 13.0, 4.9 Hz, 1H; CH_2), 2.14–2.10 (m, 1H; CH), 2.04–2.02 (m, 1H; CH_2), 2.00 (dt, J = 14.2, 2.0 Hz, 1H; CH_2), 1.91 (s, 1H; OH), 1.90–1.80 (m, 2H; CH_2), 1.71 (ddt, J = 14.6, 7.1, 2.0 Hz, 1H; CH_2), 1.28 ppm (dq, J = 13.3, $J \approx 4.5$ Hz, 1H; CH_2); ^{13}C NMR (CD_3CN, 126 MHz): δ = 211.8 (s; CO), 139.0, 133.1, 132.7 (3s; *C*=CH, Ar), 127.1, 126.9, 126.3, 125.8 (4d; Ar), 122.2 (d; =CH), 74.2 (s; C-12b), 48.4, 48.0 (2d; CH), 43.5, 36.2, 34.8, 31.8, 26.2, 26.0 ppm (6t; CH_2); IR (KBr): $\tilde{\nu}$ = 3425–3385 (OH), 3060–2845 (=CH, CH), 1690 (C=O), 1600 cm^{-1} (C=C); MS (EI, 80 eV): m/z (%): 268 (28) $[M]^+$, 250 (2) $[M-H_2O]^+$, 156 (100); HRMS (80 eV): calcd for $C_{18}H_{20}O_2$: 268.14633; found: 268.14533.

***rac*-(4a*R*,12a*S*,12b*R*)-12b-Hydroxy-1,4,4a,5,6,12,12a,12b-octahydrotetraphen-3(2*H*)one (35b)**: According to the general procedure above, **34b** (0.087 g, 0.28 mmol) afforded, after column chromatography on silica gel (hexane/ethyl acetate 4:1), **35b** as a colourless solid (0.040 g, 53%). M.p. = 122–124°C; ^{1}H NMR (CD_3CN, 500 MHz): δ = 7.52–7.48 (m, 1H; Ar), 7.20 (m, 1H; Ar), 7.18 (m, 1H; Ar), 7.15–7.12 (m, 1H; Ar), 5.70 (m, 1H; =CH), 3.44 (m, 1H; CH), 3.33 (m, 2H; CH_2), 3.12 (d, J = 0.8 Hz, 1H; OH), 3.09 (dd, J = 14.1, 6.5 Hz, 1H; CH_2), 2.46 (m, 1H; CH_2), 2.36–2.21 (m, 2H; CH, CH_2), 2.19–2.15 (m, 1H; CH_2), 2.01–1.96 (m, 1H; CH_2), 1.89–1.85 (m, 2H; CH_2), 1.83–1.75 (m, 1H; CH_2), 1.26 (dq, J = 13.3, 4.5 Hz, 1H; CH_2), 1.12 ppm (ddt, J = 14.3, 7.0, 2.1 Hz, 1H; CH_2); ^{13}C NMR (CD_3CN, 126 MHz): δ = 212.1 (s; CO), 138.2, 136.0, 134.6 (3s; *C*=CH; Ar), 131.5, 128.9, 127.2, 126.3 (4d; Ar), 119.6 (d; =CH), 77.0 (s; C-12b), 53.5, 48.0 (2d; CH), 44.3, 36.9, 35.9, 33.2, 30.9, 27.5 ppm (6t; CH_2); IR (KBr): $\tilde{\nu}$ = 3470 (OH), 3060–2850 (=CH, CH), 1700 (C=O), 1600 cm^{-1} (C=C); MS (EI, 80 eV): m/z (%): 268 (65) $[M]^+$, 250 (4) $[M-H_2O]^+$, 156 (100); HRMS (80 eV): calcd for $C_{18}H_{20}O_2$: 268.14633; found: 268.14596; elemental analysis calcd for $C_{18}H_{20}O_2$ (268.4): C 80.56, H 7.51; found: C 79.87, H 7.35.

***rac*-(3a*R*,3b*R*,9b*R*,11a*S*)-1,2,3,3b,4,5,9b,10,11,11a-Decahydro-3a*H*-cyclopenta[*a*]phenanthren-3a-ol (36)**: Compound **23** (0.240 g, 1.00 mmol) and Pd/C (10%, 0.100 g) in MeOH (12 mL) were stirred at RT for 24 h under a hydrogen atmosphere. Filtration through Celite and evaporation afforded **36** as a colourless solid (0.238 g, 98%). M.p. 108–111°C; ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 7.24–7.09 (m, 4H; Ar), 3.14 (m, 1H; CH), 2.96–2.74 (m, 3H; CH, CH_2), 2.19–1.48 ppm (m, 14H; CH, CH_2, OH); ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 141.2, 137.1 (2s; Ar), 128.4, 127.7, 125.8, 125.6 (4d; Ar), 82.6 (s; C-3a), 46.1, 44.2, 37.2 (3d; CH), 36.8, 30.0, 28.3, 26.7, 25.2, 22.0, 20.5 ppm (7t; CH_2); IR (KBr): $\tilde{\nu}$ = 3380 (OH), 3050–2800 cm^{-1} (=C–H, C–H); MS (EI, 80 eV): m/z (%): 242 (45) $[M]^+$, 224 (100) $[M-H_2O]^+$, 200 (26) $[M-C_2H_2O]^+$; HRMS (80 eV): calcd for $C_{17}H_{22}O$: 242.1670; found: 242.1666.

***rac*-(3a*R*,11a*S*)-1,2,3,10,11,11a-Hexahydro-3a*H*-cyclopenta[*a*]phenanthren-3a-ol (37)**: A mixture of **23** (0.100 g, 0.417 mmol) and MnO_2 (0.869 g, 10.0 mmol) in THF (25 mL) was stirred and heated under reflux. After 2 h, a second portion of MnO_2 (0.869 g, 10.0 mmol) was added, and the suspension heated further for 2 h. After cooling to RT, the mixture was filtered through Celite, evaporated and the residue dissolved in CH_2Cl_2. The solution was washed with HCl (1N) and distilled water, dried with $MgSO_4$, filtered and the solvent was evaporated. The crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate 9:1) to afford **37** as a colourless solid (0.073 g, 73%). M.p. 93–95°C; ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 7.97, 7.79 (2d, J = 8.1, 1H each; Ar), 7.73–7.63 (m, 2H; Ar), 7.54–7.42 (m, 2H; Ar), 3.72 (m, 1H; CH), 3.31 (dt, J = 16.7, 4.6 Hz, 1H; CH_2), 2.97 (ddd, J = 16.7, 10.7, 5.5 Hz, 1H; CH_2), 2.35–1.22 ppm (m, 9H; CH_2, OH); ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 138.7, 132.4, 131.5, 131.2 (4s; Ar), 128.3, 126.7, 126.0, 125.4*, 123.7 (5d; Ar), 82.2 (s; C-3a), 47.9 (d; CH), 40.5, 30.3, 28.4, 24.8, 22.1 ppm (5t; CH_2), *=signal with higher intensity; IR (KBr): $\tilde{\nu}$ = 3380 (OH), 3050–2800 cm^{-1} (=C–H, C–H); MS (EI, 80 eV): m/z (%): 238 (100) $[M]^+$, 209 (99) $[M-C_2H_5]^+$, 196 (90) $[M-C_2H_2O]^+$; elemental analysis calcd for $C_{17}H_{18}O$ (238.3): C 85.67, H 7.61; found: C 85.15, H 7.47.

DDQ oxidation of 23: Compound **23** (0.100 g, 0.417 mmol) and DDQ (0.191 g, 0.841 mmol) were dissolved in benzene (3 mL) and stirred at reflux for 2 h. The reaction was then cooled to RT, and the solvent removed under reduced pressure to leave the crude product, which was purified by column chromatography (hexane/ethyl acetate 9:1) to afford **21b** as a colourless oil (0.071 g, 71%).

***rac*-(1a*S*,5b*R*,7a*S*,10a*R*,10b*S*,10c*R*)-1a,5b,6,7,7a,8,9,10,10b,10c-Decahydro-10a*H*-cyclopenta[1,2]phenanthro[9,10-*b*]oxiren-10a-ol (39)**: *m*CPBA (70%, 0.257 g, 1.05 mmol) was added to a solution of **23** (0.240 g, 1.00 mmol) in CH_2Cl_2 (1.5 mL) and the mixture was stirred at 0°C for 30 min, then at RT. After 8 h, the solution was diluted with CH_2Cl_2 (10 mL), washed with NaOH (4N) and with distilled water. The organic layer was separated, dried with $MgSO_4$, filtered and the solvent was evaporated to afford pure **39** as a colourless solid (0.256 g, quant.). M.p. 109–110°C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.37 (d, J = 7.4 Hz, 1H; Ar), 7.31–7.24 (m, 1H; Ar), 7.23–7.15 (m, 2H; Ar), 4.00 (dd, J = 4.3, 2.6 Hz, 1H; CH), 3.85 (d, J = 4.3 Hz, 1H; CH), 3.17–3.10 (m, 1H; CH), 2.75 (dd, J = 7.0, 2.6 Hz, 1H; CH), 2.45 (qd, J = 14.0, 3.2 Hz, 1H; CH_2), 2.01–1.91 (m, 1H; CH_2), 1.79–0.94 (m, 8H; CH_2, CH, OH), 0.82–0.69 ppm (m, 1H; CH_2); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 137.0, 133.1 (2s; Ar), 129.7, 128.8, 125.6, 124.3 (4d; Ar), 82.9 (s; C-10a), 55.6, 53.9, 49.5, 42.8 (4d; CH), 31.8 (t; CH_2), 31.1 (d; CH), 29.5, 28.3, 24.6, 20.0 ppm (4t; CH_2); IR (KBr): $\tilde{\nu}$ = 3365 (OH), 3065–2850 cm^{-1} (=C–H, C–H); elemental analysis calcd (%) for $C_{17}H_{20}O_2$ (256.4): C 79.65, H 7.86; found: C 79.88, H 7.84.

***rac*-(3a*S*,11a*S*)-2,3,3a,10,11,11a-Hexahydro-1*H*-cyclopenta[*a*]phenanthrene (40)**: Triethylsilane (0.027 g, 0.23 mmol) was added to a solution of **23** (0.050 g, 0.21 mmol) in CH_2Cl_2 (2 mL) at −78°C. Boron trifluoride etherate (0.032 g, 0.23 mmol) was then added dropwise and the mixture was stirred for 45 min at −78°C and then for 3 h at RT. It was quenched by addition of distilled water, the product was extracted in CH_2Cl_2, the combined organic layers were dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane 100%) to afford **40** as pale-yellow oil (0.043 g, 93%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.03, 7.82 (2d, J = 8.1 Hz, 1H each; Ar), 7.67 (d, J = 8.4 Hz, 1H; Ar), 7.52 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H; Ar), 7.45 (ddd, J = 8.1, 6.8, 1.1 Hz, 1H; Ar), 7.33 (d, J = 8.4 Hz, 1H; Ar), 3.25 (dt, J = 16.5, 4.6 Hz, 1H; CH_2), 3.24–3.17 (m, 1H; CH), 2.97 (ddd, J = 16.5, 10.8, 5.3 Hz, 1H; CH_2), 2.37 (m, 1H; CH), 2.28 (m, 1H; CH_2), 2.09–2.01 (m, 1H; CH_2), 1.94–1.86 (m, 1H; CH_2), 1.84–1.78 (m, 1H; CH_2), 1.75–1.65 ppm (m, 4H; CH_2);

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 137.7, 131.9, 131.8, 131.3 (4s; Ar), 128.5, 128.3, 128.2, 125.8, 124.6, 123.2 (6d; Ar), 43.8, 36.9 (2d; CH), 34.4, 32.0, 26.7, 24.8, 24.1 ppm (5t; CH_2); IR (film): $\tilde{\nu}$ = 3050–2870 (=C–H, C–H), 1600 cm^{-1} (C=C); MS (EI, 80 eV): *m/z* (%): 222 (100) $[M]^+$, 194 (52) $[M-C_2H_2]^+$, 179 (60) $[M-C_3H_7]^+$; HRMS (80 eV): calcd for $C_{17}H_{18}$: 222.1409; found: 222.1413.

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