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Samarium Diiodide Mediated Ketyl–Aryl Coupling Reactions – Influence of Substituents and Trapping Experiments

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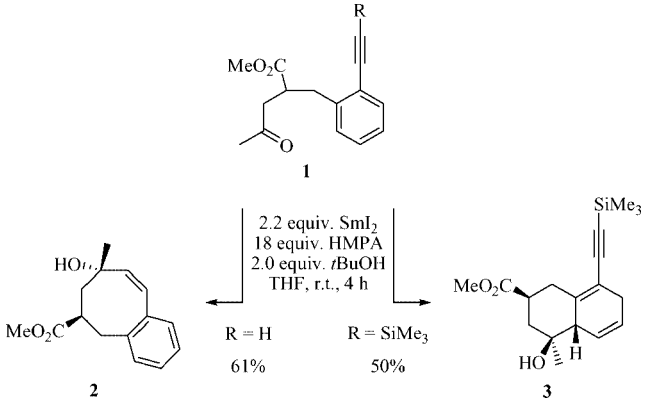
This comprehensive study describes the influence of substituents at the aryl moiety on SmI_2-mediated intramolecular ketyl–aryl coupling reactions. Differently substituted γ-aryl ketones were employed as precursors, which were directly prepared by Heck reactions of 4-penten-2-ol with the corresponding bromo- or iodobenzenes. After treatment with two equivalents of samarium diiodide γ-aryl ketones bearing electron-withdrawing substituents such as cyano, trifluoromethyl or carbonyl groups gave the expected hexahydronaphthalene derivatives as single diastereoisomers in most cases. The position of the substituents was also of crucial influence on the outcome; in several cases *ipso*-substitution leading to the formation of spiro compounds was observed. Electron-donating substituents at the aromatic moiety are less favourable for the ketyl–aryl couplings. They apparently impede the second electron transfer that is involved in this multi-step process. On the basis of these observations the mechanism of the SmI_2-promoted ketyl–aryl couplings is discussed in detail. For precursors with electron-withdrawing substituents in *m*-position fairly stabilized carbanionic intermediates of the SmI_2-promoted cyclization could be trapped with acetone or allyl bromide as electrophiles to regioselectively provide the corresponding addition products. Our results should be valuable for synthetic applications of the stereoselectively generated hexahydronaphthalene derivatives.

Introduction

Samarium diiodide is a powerful and versatile electron-transfer reagent[1] with many important applications in organic synthesis. Prominent examples are SmI_2-mediated ketyl-couplings with carbon–carbon multiple bonds which constitute an important methodology to create carbocycles and heterocycles.[2] During our investigations of intramolecular ketyl-alkynyl couplings of compounds such as **1** for the synthesis of benzannulated cyclooctanol derivatives like **2** we surprisingly gained access to hexahydronaphthalenes **3** by a novel ketyl–aryl coupling (Scheme 1).[3] Related, although not entirely equivalent SmI_2-induced ketyl–aryl couplings have been reported by Schmalz[4] and Fang,[5] whilst Shono[6] and Schäfer[7] successfully realized intramolecular couplings of γ-(hetero)aryl ketones by electrochemical methods. Our serendipitous discovery constituted a new method to convert easily available aromatic compounds into functionalized dearomatized products with high synthetic potential.[8] For this reason we started a systematic investigation of this SmI_2-induced reaction and successfully studied appropriately substituted ketones with aryl,[9] naphthyl,[10] pyrrolyl,[11] indolyl,[12] and quinolyl[13] groups as acceptors of samarium ketyls. This led to a variety of polycyclic compounds, including (hetero)steroid analogues and novel indole derivatives. In general, these cyclizations proceed in a highly stereoselective fashion.



Scheme 1. Dichotomy of SmI_2-induced cyclizations γ-aryl ketones **1** either leading to benzannulated cyclooctanol derivatives **2** or to hexahydronaphthalenes such as **3**.

The mechanism of the SmI_2-mediated ketyl–aryl coupling follows the pathway as illustrated in Scheme 2. Samariumketyl **B** is formed in equilibrium from samarium diiodide and γ-aryl ketone **A**. It then adds onto the aromatic ring via a six-membered chair-like transition structure. We as-

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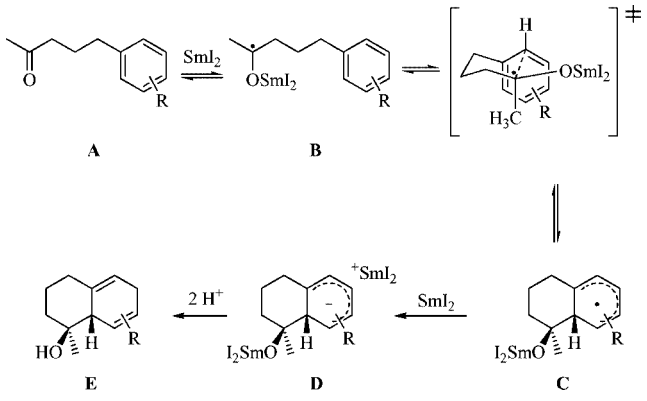
sume that the bulky samariumalkoxy group prefers an equatorial position and that the methyl group as well as the aryl hydrogen take axial positions. This arrangement explains the *cis*-configuration of this hydrogen and the resulting hydroxy group. Further reduction of the resulting radical **C** by another equivalent of samarium diiodide gives carbanion **D**, which is finally protonated analogously to the Birch reduction[14] to yield 1,4-diene **E**. It should be mentioned that in cyclohexanes the A-value of a methyl group is higher than the A-value of a hydroxy group.[15] Nevertheless, we assume that the samariumalkoxy group is fairly bulky and thus strongly prefers an equatorial position. We also investigated the influence of the spacer length between the aryl moiety and the carbonyl group. The formation of six-membered rings seems to be highly favoured since for β-phenyl and δ-phenyl ketones the expected cyclization products were not observed.[16,1j]



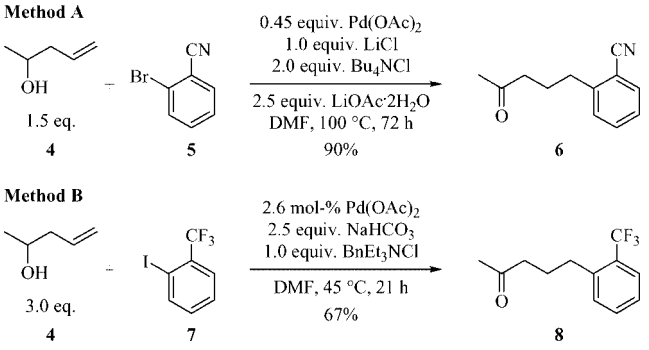
Scheme 2. Proposed mechanism and transition structure for the ketyl–aryl cyclization (HMPA ligands at samarium are omitted for simplicity).

Herein we report full details on the influence of substituents R of simple aryl derivatives **A** leading to bicyclic compounds **E**. In addition, we describe our attempts to trap the carbanions of type **D** with different electrophiles. These studies should also provide information about mechanistic details of this intriguing dearomatizing process.

Results and Discussion

Synthesis of Starting Materials

The γ-aryl ketones used as precursor were easily prepared by Heck reactions. Initially we applied the protocol of Taylor and Wang[17] (*method A*, Scheme 3), where the corresponding aryl bromide or iodide was heated in DMF at 100 °C for 24–72 h with 1.5 equiv. of homoallylic alcohol **4** and 0.45 equiv. of palladium(II) acetate. γ-Aryl ketones derived from bromobenzenes were isolated in 14–90% yield (e.g. compound **6**). Reactions employing substituted iodobenzenes yielded the γ-aryl ketones in 31–89%.[16]

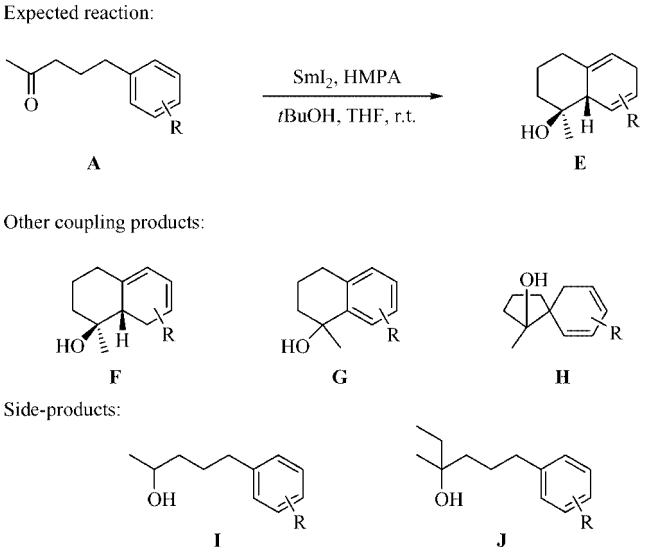


Scheme 3. Synthesis of γ-aryl ketones **6** and **8** by two different protocols of the Heck reaction employing 4-penten-2-ol (**4**).

Later we used Jeffery's conditions[18] (*method B*) which are more economically, since lower catalyst loading is required. Heating the corresponding iodobenzene and 3.0 equiv. of **4** together with 2–4 mol-% of palladium(II) acetate in DMF at 45 °C for 1–7 d furnished products such as **8** in 40–75% yield.[19] As minor components we isolated coupling products without fully migrated double bond (homoallylic and allylic alcohols) and traces of branched coupling products were also found.

Effect of Aryl Substituents on the SmI_2-Mediated γ-Aryl Ketone Cyclization

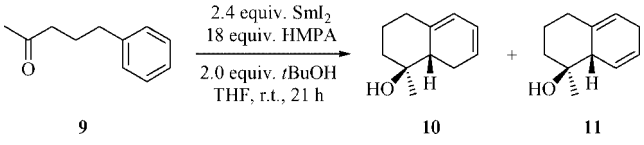
Studies of the SmI_2-HMPA-induced cyclizations of γ-aryl ketones **A** were performed at room temperature[20] under standard conditions employing 2.2–2.5 equiv. of samarium diiodide in THF along with an excess of HMPA (18 equiv.)[21] and 2 equiv. of *tert*-butyl alcohol as proton source. The investigation of substituent effects revealed that several side products can be formed (Scheme 4). In most cases the desired major component, bicyclic product **E**, was



Scheme 4. Products found in samarium diiodide promoted reactions of substituted γ-aryl ketones **A**: coupling products **E**, **F**, **G**, and **H**, reduction product **I** and ethene addition product **J**.

formed as a single diastereoisomer, however, occasionally we also observed coupling products such as 1,3-diene **F**, which probably arises by subsequent isomerization from **E**. The aromatized product **G** or the *ipso*-coupling product **H** was also formed in several cases. Finally, for substrates undergoing the anticipated cyclization very slowly or not at all, the reduction of the carbonyl group of **A** provided alcohol **I**. When samarium diiodide was prepared from samarium metal and 1,2-diiodoethane[22] the ethene generated can also undergo a coupling with the samarium ketyl **B**, which results in ethyl-substituted product **J** that was isolated in traces in several experiments.

The reductive cyclization of parent γ-aryl ketone **9** with samarium diiodide gave varying ratios (ca. 9:1 to ca. 1:9) of 1,3-diene **10** and its isomer 1,4-diene **11**. A typical experiment is outlined in Scheme 5, where we obtained 41% of **10** and ca. 4% of **11**. In this case, isomer **11** was not completely separated from by-products, in particular from ethene addition product of type **J**. We assume that the isomerization of **11** into **10** occurs during workup and that this substrate is particular sensitive to this (undesired) transformation. The relative configuration of **10** was proven by NOE and NOESY NMR experiments. As side reaction ketone **9** was reduced to the corresponding alcohol **I** (R = H) isolated in 7% yield. The ethene addition product of type **J** (R = H) was formed in 12% yield.

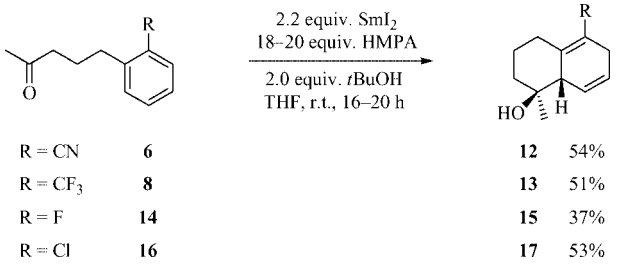


Scheme 5. Cyclization of parent substrate γ-aryl ketone **9** in the presence of SmI_2.

It should already be mentioned here that in many examples of this study the mass balance accounts only for 50–65% of the starting material. Very often yields of coupling products are around 50%. The formation of fragmentation products is possible, but it could not be proved. Higher molecular weight products were not isolated. Although an optimization of the reaction conditions, e.g. performance of the reactions at lower temperature, could lead to improved yields this was not the major issue of this study.

γ-Aryl Ketones with *o*-Substituents

While *o*-cyano-, *o*-trifluoromethyl- and *o*-chloro-substituted γ-aryl ketones **6**, **8**, and **16** afforded yields of 51–54% for the expected bicyclic products **12**, **13**, and **17**, only 37% of the *o*-fluoro compound **15** were obtained (Scheme 6). In this case also low amounts of the aromatized bicyclic products **G** (R = *o*-F, 5% and R = H, 3%) were isolated. In the reaction of trifluoromethyl-substituted precursor **8** the corresponding secondary alcohol **I** was isolated as by-product in 15% yield. Similarly, 11% of this type of alcohol was formed for the *o*-fluoro compound and 5% for the *o*-chloro substrate. Here also 6% of the dechlorinated alcohol **I** (R = H) was found.

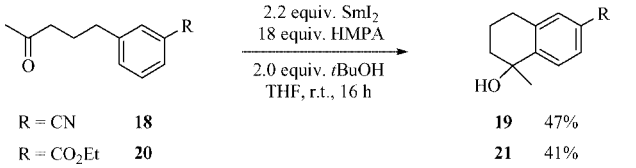


Scheme 6. SmI_2 promoted reactions of *o*-substituted γ-aryl ketones **6**, **8**, **14**, and **16** furnishing hexahydronaphthalene derivatives **12**, **13**, **15**, and **17**.

Electron-donating substituents in *o*-position gave less satisfying results (not shown). The *o*-methoxy-substituted γ-aryl ketone led to a mixture of the secondary alcohol **I** (R = *o*-OMe, 45%) and the corresponding bicyclic compound **E** (R = *o*-OMe, 20%), whilst *o*-methyl-substituted γ-aryl ketone only gave the secondary alcohol **I** (R = *o*-Me) in 57%.[16]

γ-Aryl Ketones with *m*-Substituents

m-Cyano- and *m*-ethoxycarbonyl-substituted γ-aryl ketones **18** and **20** surprisingly led to rearomatized bicyclic products **19** and **21** in 47% and 41% yield, respectively (Scheme 7). We assume that in these examples protonation by *t*BuOH is reversible due to the higher stability of the anionic intermediates (see intermediate **D** of Scheme 2). Reaction with air oxygen during workup transforms the expected products **E** into the isolated compounds of type **G**. Similar observations have been made with *m*-substituted aniline derivatives in the related cyclization reactions.[9b,9c]

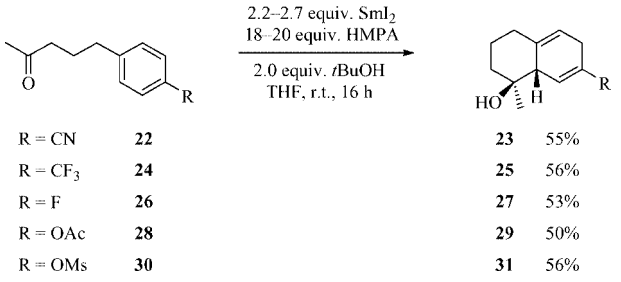


Scheme 7. SmI_2 promoted reactions of *m*-substituted γ-aryl ketones **18** and **20** furnishing rearomatized compounds **19** and **21**.

The results with other *m*-substituted γ-aryl ketones are not depicted here but just mentioned. *m*-Chloro-substituted γ-aryl ketone yielded dechlorinated products (15% of 1,4-diene **11** together with 13% of 1,3-diene **10**).[16] For *m*-fluoro- and *m*-methyl-substituted γ-aryl ketones no cyclization products could be observed, the corresponding secondary alcohols **I** were isolated in 27% (R = *m*-F) and 44% (R = *m*-Me). The *m*-fluoro-substituted precursor provided the coupling product with ethene **J** (R = *m*-F, 32% yield) as major component whilst 28% of the starting material was recovered. *m*-Methoxy-substituted γ-aryl ketone showed no reaction at all and the starting material was recovered, whereas *m*-trifluoromethyl-substituted γ-aryl ketone was partially defluorinated in the presence of samarium diiodide.[16,19]

γ-Aryl Ketones with *p*-Substituents

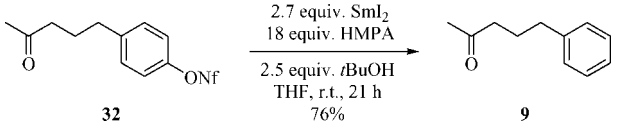
As expected, *p*-substituted γ-aryl ketones showed a fairly similar reactivity pattern as the corresponding *o*-substituted substrates. *p*-Cyano-, *p*-trifluoromethyl-, *p*-fluoro-, *p*-acetoxy- and *p*-mesyloxy-substituted γ-aryl ketones afforded the expected bicyclic products **23**, **25**, **27**, **29**, and **31** in 50–56% yield (Scheme 8). In the experiment with acetoxy-substituted precursor **28** 10% of alcohol **I** (R = *p*-OH) was isolated, where the acetyl group was removed. The conversion of mesylate **30** was not complete, 25% of starting material **30** was recovered.



Scheme 8. SmI_2 promoted reactions of *p*-substituted γ-aryl ketones **22**, **24**, **26**, **28**, and **30** affording hexahydronaphthalene derivatives **23**, **25**, **27**, **29**, and **31**.

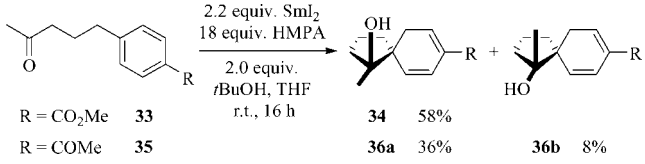
Again the less successful reactions are not illustrated here. The *p*-chloro-substituted γ-aryl ketone yielded 14% of the dechlorinated bicyclic 1,4-diene **11**, 9% of secondary alcohol **I** (R = *p*-Cl) and 22% of dechlorinated alcohol **I** (R = H). The reaction of *p*-methyl-substituted γ-aryl ketone furnished the expected bicyclic product **E** just in traces, whereas the secondary alcohol **I** (R = *p*-Me) was isolated in 32% yield. Treatment of *p*-hydroxy-substituted γ-aryl ketone with samarium diiodide only led to alcohol **I** (R = *p*-OH) in 68% yield. Similar results were obtained for the *p*-dimethylamino-substituted γ-aryl ketone, where the corresponding alcohol **I** (R = *p*-NMe_2) was isolated in 43%.[16] The *p*-methoxy-substituted γ-aryl ketone gave mixtures of 1,4-diene **E** (R = *p*-OMe), 1,3-diene **F** (R = *p*-OMe) and the secondary alcohol **I** (R = *p*-OMe) in varying ratios and yields (e.g. 65%, **E**/**F**/**I**, 37:22:41).[16,19]

To our surprise the *p*-nonafluorobutylsulfonyl-substituted γ-aryl ketone **32** was deoxygenated by samarium diiodide to yield 76% of the parent γ-aryl ketone **9** (Scheme 9). The mechanism of this transformation is not clear, since experiments of Yekta[23] demonstrated that these conditions can not generally be employed to reductively convert aryl- or alkenyl nonaflates into the corresponding deoxygenated species. A carbonyl moiety as present in γ-aryl ketone **32** seems to be essential for the reductive cleavage.[24]



Scheme 9. Reductive conversion of aryl nonaflate **32** into compound **9**.

The reaction of *p*-methoxycarbonyl-substituted γ-aryl ketone **33** with samarium diiodide afforded spiro compound **34** in 58% yield (Scheme 10). For the *p*-acetyl-substituted substrate **35** *ipso* attack was also observed, which led to spiro compound **36a** and its diastereoisomer **36b** in 36% and 8% yield, respectively. The conversion of **33** and related methoxycarbonyl-substituted aryl ketones with samarium diiodide into spiro compounds has been thoroughly investigated by Tanaka and co-workers.[25] They generally used five equivalents of samarium diiodide and hence compound **34** was obtained only as minor product. Under their conditions the electron-deficient double bond of **34** was further reduced to provide the major product with a cyclohexene moiety.



Scheme 10. SmI_2-promoted reactions of *p*-substituted γ-aryl ketones **33** and **35** furnishing spiro compounds **34**, **36a**, and **36b**.

Discussion

To allow a brief overlook we summarized our results on samarium diiodide promoted cyclizations of monosubstituted γ-aryl ketones in Table 1. In general, reactions with electron-deficient aryl groups are more favourable. This is not unexpected since ketyl **B** (see Scheme 2) can be classified as an electron-rich nucleophilic radical and therefore the energy barrier between **B** and the first cyclization intermediate **C** is probably lower due to a better $HOMO_{radical}$-$LUMO_{arene}$-interaction.[26,27] As an additional crucial feature the stabilities of the resulting cyclohexadienyl radicals **C** have to be considered and the reduction of **C** to cyclohexadienyl anions **D** is also important.[28] In accordance with literature precedent[25] we suggest that formation of **B** and of **C** are reversible processes and that the second electron transfer yielding **D** is the reaction determining step. For cyano-, acetyl-, and alkoxycarbonyl-substituted precur-

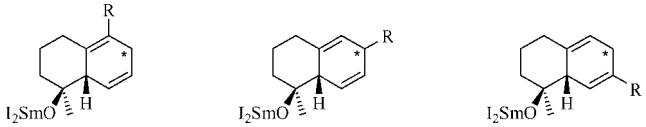
Table 1. Influence of substituents R in different positions of γ-aryl ketones on samarium diiodide promoted cyclizations (+ cyclization, – no cyclization).

Substituent R	*o*	*m*	*p*
H	+		
CN	+	+	+
COMe			+[a]
CO_2R	+[b]	+	+[a]
CF_3	+	–	+
F	+	–	+
Cl	+	–	–
OMs			+
OAc			+
OMe	+/–	–	+/–
Me	–	–	–

[a] Formation of spiro compound. [b] Ref.[25].

sors all these effects contribute to facilitate these steps.[29] Compounds with *p*-acetyl or *p*-alkoxycarbonyl groups preferentially undergo *ipso* attack leading to spiro systems, since the intermediate radicals and anions are better stabilized compared to the intermediates resulting from the alternative "normal" reaction mode. The case with an *o*-methoxycarbonyl substituent was studied by Tanaka et al.;[25] they report the *ipso* attack as major pathway together with minor formation of the fused product.

Whereas *o*- and *p*-trifluoromethyl-substituted substrates cyclize, the radical destabilizing effect of a trifluoromethyl group may inhibit the cyclization of the corresponding *m*-derivative. In Scheme 11 we depict the structures of intermediates **C** and **D** with substituents R in *o*-, *m*-, and *p*-positions. These formulas reveal that *m*-substituents should have the strongest effect on the stability of radicals and carbanions involved.



Scheme 11. Intermediates **C** and **D** (see Scheme 2) for the cyclizations of *o*-, *m*-, and *p*-substituted γ-aryl ketones (* could be a single electron or a negative charge).

Fluoro- and chloro-substituted precursors seem to be borderline cases; SmI_2-induced dehalogenations are severe side reactions. Nevertheless, the *o*- and *p*-substituted γ-aryl ketones provided the expected cyclization products. Possibly, the strong –I-effect of these substituents facilitates cyclization and the second electron transfer. In the case of methyl-substituted γ-aryl ketones, the +I-effect of the alkyl group together with its rather small stabilizing effect on radical **C** essentially inhibits the cyclization.

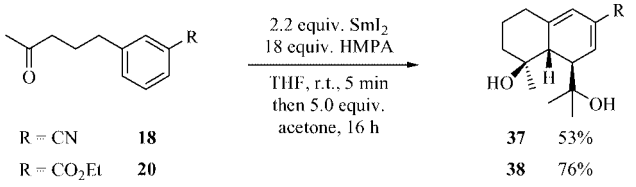
Alkoxy groups exert a strong +M-effect and therefore formation of carbanion **D** should be strongly disfavoured for the *m*-methoxy-substituted substrate. Indeed, no cyclization products were isolated in this case. From this failure we deduce our hypothesis that formation of radical **C** is reversible (at least for this case). Its generation from the *m*-methoxy-substituted substrate should be favourable due to the radical stabilizing effect of the alkoxy group, however, the disfavoured next electron transfer step determines the outcome of the overall process. For the *o*- and *p*-methoxy substituted substrates we observed cyclization to some extent. Possibly, the –I-effect allows formation of intermediate **D** in these cases. We have to admit that we do not fully understand the behaviour of methoxy-substituted γ-aryl ketones.

Not surprisingly, the *p*-dimethylamino- and *p*-hydroxy substituted γ-aryl ketones did not cyclize which may again be due to the disfavoured second electron transfer to provide intermediate **D**. However, it should be mentioned that *N*-acetylated β-anilino ketones, in which the cyclizing carbonyl group is connected via the nitrogen atom, are very good substrates for the aryl–ketyl reaction.[9] For the phenol derivative the formation of a samarium phenoxy species may additionally inhibit the cyclization of the ketyl. Thus, just reductions of the carbonyl groups were observed in these examples.

It should also be stressed here that the simplified discussion arguing with inductive and mesomeric effects of substituents completely neglects the influence of the samarium(II) and samarium(III) species being present in these solutions. The high oxophilicity of these ions has to be taken into account when discussing the reaction with oxygen containing substituents, yet these effects are difficult to quantify. Tanaka et al. also studied substrates with two or more substituents, in particular the combination of alkoxycarbonyl substituents and methoxy groups.[30] They could demonstrate that *in the absence of HMPA* the coordination of samarium(II) diiodide to *o*-methoxy groups has a strong influence on the reaction outcome, mainly leading to *ipso*-substitutions. In the presence of the strong ligand HMPA the interaction of Sm^{II} with the oxygen containing substituents should be less important.

Trapping of the Intermediate Cyclohexadienyl Samarium Species

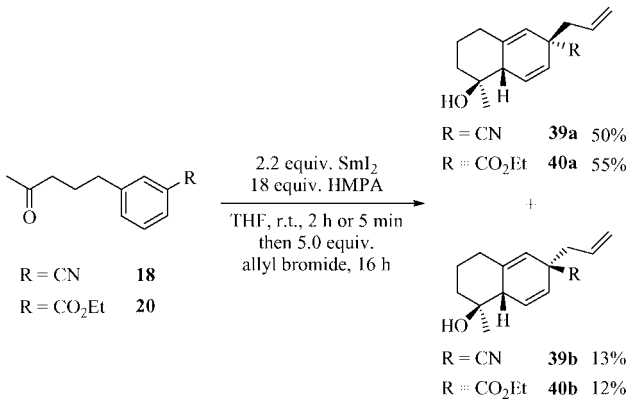
The cyclization of γ-aryl ketones with strongly electron-withdrawing groups in *m*-position such as **18** and **20** should lead to fairly stable cyclohexadienyl carbanions (see our arguments to explain the rearomatized products of Scheme 7). Therefore we also tried to trap these nucleophilic samarium species by suitable electrophiles.[9a] Indeed, when precursors **18** or **20** were treated under standard reaction conditions, *but without tBuOH as proton source*, addition of acetone to the resulting reaction mixture after a few minutes yielded the desired addition products **37** (R = CN: 53%; recovered starting material **18**: 22%) and **38** (R = CO_2Et, 76%). Both trapping products were isolated as single regio- and diastereoisomers (Scheme 12). Thus, three contiguous stereogenic centres can be controlled in this transformation. The configuration of **37** was unequivocally proven by X-ray analysis.[31]



Scheme 12. Trapping experiments with precursors **18** and **20** and acetone as electrophile providing adducts **37** and **38**.

Analogous reactions were performed by Tanaka and coworkers with *p*-substituted γ-aryl ketone **33**.[25] Interestingly, they did not observe any addition products when **33** was treated with samarium diiodide in the presence of acetone, which apparently only served as proton source in this case.

Trapping of the cyclohexadienyl anion was also achieved with allyl bromide as electrophile (Scheme 13). Here the electrophile was incorporated α to the electron-withdrawing group and only a moderate diastereoselectivity was observed. The cyano-substituted coupling–alkylation products **39a** and **39b** were isolated in 50% and 13% yield (*dr*: 3.8:1). The corresponding ethoxycarbonyl-substituted products **40a** and **40b** were received in 55% and 12% yield (*dr*: 4.6:1). This is in accordance with results of Tanaka and coworkers, where conversion of **33** with samarium diiodide followed by addition of different electrophiles (allyl bromide, benzyl bromide and methyl iodide) led to mixtures of diastereoisomers. As in our case, the electrophile was incorporated α to the electron-withdrawing substituent.[25] Experiments to trap the carbanion derived from **18** with methyl iodide or with benzaldehyde did not give clear results.[16] The regioselectivity of the incorporation of electrophiles follows entirely the rules well known for dienolates and related ambident carbanions. Carbonyl compounds as electrophiles prefer the γ-attack whereas alkylations generally occurs with preference at the α-carbon. Again, this discussion may be oversimplified since the influence of the samarium(III) counterion is completely neglected.



Scheme 13. Trapping experiments with precursors **18** and **20** and allyl bromide as electrophile providing adducts **39** and **40**.

Conclusions

We have demonstrated that in SmI_2-mediated cyclizations of γ-aryl ketones the substituent of the aromatic ring has its expected strong effect on the reaction outcome. Whereas various electron-withdrawing groups in different positions of the aryl group generally favour the ketyl–aryl cyclization, halogen substituents and in particular alkoxy groups are borderline cases. Alkyl groups seem to completely inhibit the cyclization. We could also demonstrate that at least for substrates with electron-withdrawing substituents trapping of the carbanion type intermediates **D** is possible. Our study gives new insights into mechanistic details of SmI_2-mediated ketyl–aryl couplings.[32] It should also facilitate further planning of synthetic applications of this new route to hexahydronaphthaline derivatives.[33]

Experimental Section

General Methods: Reactions were generally performed under argon in flame-dried flasks. Solvents and reagents were added by syringes. Solvents were dried using standard procedures. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone under argon. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride (130 °C, 12 mbar) and stored over molecular sieves (4 Å) under argon.

Warning: *HMPA has been identified as a carcinogenic reagent. Appropriate glove protection is required during handling. Reactions and chromatography should be performed in a well-vented hood.*

1,2-Diiodoethane was dried at 50 °C for 3 h in vacuo. SmI_2 was freshly prepared in THF (see general procedure) or taken from a previously prepared stock solution (0.1 M in THF). Other reagents were purchased and were used as received without further purification unless otherwise stated. Products were purified by flash chromatography on silica gel (230–400 mesh, Merck or Fluka) or HPLC (Nucleosil 50–5). Unless otherwise stated, yields refer to analytically pure samples. NMR spectra were recorded on Bruker (AM 270, AC 300, AC 500) and JOEL (Eclipse 500) instruments. Chemical shifts are reported relative to TMS (^{1}H: δ = 0.00 ppm) and $CDCl_3$ (^{13}C: δ = 77.0 ppm). Integrals are in accordance with assignments; coupling constants are given in Hz. All ^{13}C spectra are proton-decoupled. For detailed peak assignments 2D spectra were measured (COSY, HMQC, HMBC, NOESY and NOE if necessary). IR spectra were measured with a Nicolet 5 SXC FT-IR spectrometer or with a Nexus FT-IR spectrometer equipped with a Nicolet Smart DuraSamplIR ATR. MS and HRMS analyses were performed with Finnigan MAT 711 (EI, 80 eV, 8 kV), MAT CH7A (EI, 80 eV, 3 kV) and Varian Ionspec QFT-7 (ESI-FT ICRMS) instruments. Elemental analyses were carried out with CHN-Analyzer 2400 (Perkin–Elmer), Vario EL or Vario EL III. Melting points were measured with a Reichert apparatus Thermovar and are uncorrected.

5-(2-Cyanophenyl)pentan-2-one (6): 2-Bromobenzonitrile (0.910 g, 5.00 mmol), 4-penten-2-ol (0.646 g, 7.50 mmol), nBu$_4$NCl (2.78 g, 10.0 mmol), LiCl (0.212 g, 5.00 mmol), LiOAc·2H$_2$O (1.30 g, 12.5 mmol) and $Pd(OAc)_2$ (0.500 g, 2.25 mmol) were suspended in DMF (10 mL) and heated at 100 °C for 72 h. Then, brine (50 mL) was added and the mixture was extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried with Na_2SO_4 and the solvent was removed under reduced pressure. Purification by flash-chromatography on silica gel (hexane/ethyl acetate, 4:1) afforded compound **6** (0.839 g, 90%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96 (quint, J = 7.6 Hz, 2 H, 4-H), 2.16 (s, 3 H, 1-H), 2.52, 2.85 (2t, J = 7.6 Hz, 2 H each, 3-H, 5-H), 7.28–7.35 (m, 2 H, Ar), 7.52 (br. t, $J \approx$ 7.5 Hz, 1 H, Ar), 7.62 (br. d, $J \approx$ 7.5 Hz, 1 H, Ar) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.6 (t, C-4), 29.9 (q, C-1), 33.7, 42.6 (2t, C-3, C-5), 112.3 (s, CN), 118.0 (s, Ar), 126.6, 129.5, 132.7, 132.8 (4d, Ar), 145.6 (s, Ar), 208.0 (s, C=O) ppm. IR (film): $\tilde{\nu}$ = 3100–2870 (=C–H, C–H), 2225 (CN), 1715 (C=O), 1600 (C=C) cm^{-1}. $C_{12}H_{13}NO$ (187.2): calcd. C 76.97, H 7.00, N 7.48; found C 76.94, H 7.00, N 7.85.

5-[2-(Trifluoromethyl)phenyl]pentan-2-one (8): 1-Iodo-2-(trifluoromethyl)benzene (2.74 g, 10.1 mmol), 4-penten-2-ol (3.1 mL, 2.6 g, 30 mmol), $NaHCO_3$ (2.10 g, 25.0 mmol), $BnEt_3NCl$ (2.28 g, 10.0 mmol) and $Pd(OAc)_2$ (60 mg, 0.26 mmol) were suspended in DMF (10 mL) and heated at 45 °C for 21 h. The mixture was diluted with CH_2Cl_2 (250 mL) and washed with H_2O (2 × 30 mL, 2 × 20 mL) and brine (2 × 20 mL), then dried with Na_2SO_4. The solvent was removed under reduced pressure. Purification by flash-

chromatography on silica gel (pentane/ethyl acetate, 6:1) afforded compound **8** (1.55 g, 67%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.91 (quint, $J \approx 7.5$ Hz, 2 H, 4-H), 2.12 (s, 3 H, 1-H), 2.49, 2.77 (2 t, J = 7.3 Hz, J = 8.0 Hz, 2 H each, 3-H, 5-H), 7.25–7.29 (m, 1 H, Ar), 7.35 (d, J = 7.7 Hz, 1 H, Ar), 7.45 (t, J = 7.7 Hz, 1 H, Ar), 7.59 (d, J = 7.7 Hz, 1 H, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.2 (t, C-4), 29.6 (q, C-1), 31.5 (qt, $^4J_{C,F}$ = 1.8 Hz, C-5), 42.8 (t, C-3), 124.5 (q, $^1J_{C,F}$ = 273.7 Hz, CF_3), 125.7 (qd, $^3J_{C,F}$ = 5.8 Hz, Ar), 125.9 (d, Ar), 128.2 (q, $^2J_{C,F}$ = 29.3 Hz, Ar), 130.8 (d, Ar), 131.7, 140.4 (q, qd, $J_{C,F}$ = 1.1, $J_{C,F}$ = 1.6 Hz, Ar), 207.9 (s, C=O) ppm. IR (film): $\tilde{\nu}$ = 3100–2885 (=C–H, C–H), 1715 (C=O), 1610 (C=C), 1585 (C=C), 1495 (C=C) cm^{-1}. $C_{12}H_{13}F_3O$ (230.2): calcd. C 62.60, H 5.69; found C 62.13, H 5.35.

General Procedure for Samarium Diiodide-Induced Cyclizations: Samarium (2.4–3.0 equiv.) and 1,2-diiodoethane or iodine (2.2–2.7 equiv.) were suspended in THF (16–24 mL/mmol SmI_2) under argon atmosphere and stirred at room temp. until the colour of the solution turned into dark blue (1–5 h). The flask was then gently evacuated to remove ethene (when 1,2-diiododethane was used as the iodine source), purged with argon and HMPA (18–20 equiv.) was added. The corresponding γ-aryl ketone (1 equiv.) and *t*BuOH (2.0–2.5 equiv.) were dissolved in THF (22–32 mL/mmol γ-aryl ketone) and argon was bubbled through the solution for 20–30 min. The solution was added to the deep violet solution of SmI_2 in THF/HMPA. The mixture was stirred at room temp. for 0.5–16 h (in most cases SmI_2 was consumed after a few minutes, the colour of the mixture turned from violet to grey). Saturated aq. sodium hydrogen carbonate solution was added, the organic layer was separated and the aq. layer was extracted three times with Et_2O. The combined organic layers were washed with water and brine, dried with Na_2SO_4 and the solvent was removed under reduced pressure to give the crude product, which was contaminated with HMPA. Flash-chromatography on silica gel and in singular cases additional purification by HLPC yielded the pure compounds.

Alternatively SmI_2 was taken from a previously prepared stock solution (0.1 M in THF), which was prepared according to the following procedure: 1,2-diiodoethane or iodine (15 mmol, 1 equiv.) and samarium (18 mmol, 1.2 equiv.) were suspended in THF (150 mL, 10 mL/mmol ICH_2CH_2I or I_2) under argon atmosphere and stirred at room temp. until the colour of the solution turned into dark blue (1–5 h). The flask was then wrapped in aluminium foil to exclude light and stored at room temp.

***rac*-(1*S*,8a*S*)-1-Methyl-1,2,3,4,8,8a-hexahydronaphthalen-1-ol (10):** According to the general procedure, samarium diiodide (0.1 M in THF, 15 mL, 1.5 mmol, 2.4 equiv.), HMPA (1.95 mL, 1.99 g, 11.1 mmol), **9** (0.100 g, 0.616 mmol), *t*BuOH (0.12 mL, 0.091 g, 1.2 mmol) and THF (10 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 3:1) and HPLC (hexane/ethyl acetate, 7.3:1) compound **10** (0.041 g, 41%) as a colourless solid and highly contaminated compound **11** as a colourless oil (12 mg, ca. 4%).

10: M.p. 86–87 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (s, 3 H, CH_3), 1.39* (br. s, 1 H, OH), 1.41* (tq, J = 4.2, 13.1 Hz, 1 H, 3-H), 1.55 (dt, J = 4.2, 13.1 Hz, 1 H, 2-H), 1.73–1.84 (m, 2 H, 2-H, 3-H), 2.01 (dt, J = 4.9, 13.1 Hz, 1 H, 4-H), 2.20 (tdd, J = 2.0, 4.2, 13.1 Hz, 1 H, 4-H), 2.38 (dd, J = 4.8, 13.2 Hz, 1 H, 8a-H), 2.50 (tdd, J = 3.5, 13.2, 19.5 Hz, 1 H, 8-H), 2.61 (dtd, J = 1.0, 4.8, 19.5 Hz, 1 H, 8-H), 5.52 (ddd, J = 3.5, 4.8, 9.3 Hz, 1 H, 7-H), 5.58 (br. d, $J \approx 5$ Hz, 1 H, 5-H), 5.61–5.65 (m, 1 H, 6-H) ppm. *Overlapping signals. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.4 (q, CH_3), 22.4 (t, C-8), 24.6 (t, C-3), 35.0 (t, C-4), 42.9 (t, C-2), 47.0 (d, C-8a), 75.1 (s, C-1), 117.3 (d, C-7), 121.9 (d, C-6), 123.4 (d, C-5), 138.4 (s, C-4a) ppm. IR (ATR): $\tilde{\nu}$ = 3230 (O–H), 3050–2835 (=C–H, C–H), 1660, 1605 (C=C) cm^{-1}. MS (EI, 80 eV, 30 °C): *m*/*z* (%) = 164 (33) [M$^+$], 131 (21), 106 (100), 104 (57), 91 (47), 71 (21), 43 (19). HRMS: $C_{11}H_{16}O$: calcd. 164.12012; found 164.12012.

11: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.00 (s, 3 H, CH_3), 1.34 (tq, J = 4.1, 13.0 Hz, 1 H, 3-H), 1.57–1.99 (m, 5 H, 2-H, 3-H, 4-H, OH), 2.13 (m_c, 1 H, 4-H), 2.59–2.63 (m, 3 H, 6-H, 8a-H), 5.42 (br. s, 1 H, 5-H), 5.75, 5.83 (AB system, J_{AB} = 12.2 Hz, 1 H each, 7-H, 8-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.8 (q, CH_3), 24.1 (t, C-3), 26.7 (t, C-6), 34.9 (t, C-4), 41.9 (t, C-2), 48.9 (d, C-8a), 74.5 (s, C-1), 118.3, 124.0, 125.8 (3 d, C-5, C-7, C-8), 136.0 (s, C-4a) ppm. The ^{1}H NMR and ^{13}C NMR spectroscopic data are in accordance with those given in the literature.[32]

***rac*-(4a*S*,5*S*)-5-Hydroxy-5-methyl-2,4a,5,6,7,8-hexahydronaphthalene-1-carbonitrile (12):** According to the general procedure, samarium (0.180 g, 1.20 mmol), 1,2-diiodoethane (0.310 g, 1.10 mmol), HMPA (1.6 mL, 1.6 g, 9.0 mmol), **6** (0.094 g, 0.50 mmol), *t*BuOH (0.095 mL, 0.074 g, 1.00 mmol) and THF (25 mL + 13 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 9:1→4:1) compound **12** (0.051 g, 54%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (s, 3 H, CH_3), 1.47 (td, J = 3.9, 13.4 Hz, 1 H, 7-H), 1.60 (br. s, 1 H, OH), 1.72 (dt, J = 4.1, 13.4 Hz, 1 H, 6-H), 1.85–1.90 (m, 2 H, 6-H, 7-H), 2.02 (br. t, $J \approx 12.2$ Hz, 1 H, 8-H), 2.82–2.88 (m, 3 H, 2-H, 4a-H), 2.93 (br. d, $J \approx 12.2$ Hz, 1 H, 8-H), 5.81, 5.89 (AB system, J_{AB} = 12.3 Hz, 1 H each, 3-H, 4-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.0 (t, C-7), 23.3 (q, CH_3), 28.3 (t, C-2), 33.3 (t, C-8), 41.2 (t, C-6), 49.5 (d, C-4a), 75.0 (s, C-5), 103.6 (s, C-1), 118.3 (s, CN), 122.9, 123.4 (2d, C-3, C-4), 154.0 (s, C-8a) ppm. IR (film): $\tilde{\nu}$ = 3460 (O–H), 3100–2850 (=C–H, C–H), 2225 (CN), 1600 (C=C) cm^{-1}. $C_{12}H_{15}NO$ (189.2): calcd. C 76.16, H 7.99, N 7.40; found C 75.82, H 7.93, N 7.45.

***rac*-(1*S*,8a*S*)-1-Methyl-5-(trifluoromethyl)-1,2,3,4,6,8a-hexahydronaphthalen-1-ol (13):** According to the general procedure, samarium (0.376 g, 2.50 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.6 mL, 3.7 g, 20 mmol), **8** (0.232 g, 1.00 mmol), *t*BuOH (0.18 mL, 0.14 g, 0.19 mmol) and THF (50 mL + 25 mL) afforded after purification by flash-chromatography on silica gel (pentane/ethyl acetate, 6:1) compound **13** (0.118 g, 51%) as a colourless solid; m.p. 68 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (s, 3 H, CH_3), 1.41 (tq, J = 3.9, 13.4 Hz, 1 H, 3-H), 1.49 (br. s, 1 H, OH), 1.68 (dt, J = 4.4, 13.4 Hz, 1 H, 2-H), 1.74–1.90 (m, 3 H, 2-H, 3-H, 4-H), 2.78–2.84, 2.90 (m, qdd, J = 1.9, 3.7, 13.4 Hz, 3 H, 1 H, 6-H_2, 8a-H, 4-H), 5.83–5.90 (m, 2 H, 7-H, 8-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.7 (t, C-3), 23.6 (q, CH_3), 25.8 (qt, $^3J_{CF}$ = 3.3 Hz, C-6), 30.5 (qt, $^4J_{CF}$ = 1.9 Hz, C-4), 41.4 (t, C-2), 50.7 (d, C-8a), 75.4 (q, $^5J_{CF}$ = 1.0 Hz, C-1), 119.9 (q, $^2J_{CF}$ = 28.7 Hz, C-5), 123.1 (d, C-8), 124.2 (qd, $^4J_{CF}$ = 1.0 Hz, C-7), 124.5 (q, $^1J_{CF}$ = 275.6 Hz, CF_3), 142.7 (q, $^3J_{CF}$ = 3.6 Hz, C-4a) ppm. IR (KBr): $\tilde{\nu}$ = 3370 (O–H), 3040–2835 (=C–H, C–H), 1690 (C=C), 1655 (C=C) cm^{-1}. $C_{12}H_{15}F_3O$ (232.2): calcd. C 62.06, H 6.51; found C 61.94, H 6.16.

***rac*-(1*S*,8a*S*)-5-Fluoro-1-methyl-1,2,3,4,6,8a-hexahydronaphthalen-1-ol (15):** According to the general procedure, samarium diiodide (0.1 M in THF, 22 mL, 2.2 mmol, 2.2 equiv.), HMPA (3.2 mL, 3.2 g, 18 mmol), **14** (0.180 g, 1.00 mmol), *t*BuOH (0.19 mL, 0.15 g, 2.0 mmol) and THF (10 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 2:1) and HPLC (hexane/ethyl acetate, 4:1) compound **15** (0.067 g, 37%) as a colourless solid; m.p. 83 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (s, 3 H, CH_3), 1.35 (ddq, J = 3.9, 4.1, 13.4 Hz, 1 H, 3-H), 1.48 (br. s, 1 H, OH), 1.52–1.60 (m, 2 H, 2-H, 4-H), 1.71–1.77 (m, 1 H, 3-H),

1.81 (dtd, J = 1.4, 3.2, 12.5 Hz, 1 H, 2-H), 2.78–2.89 (m, 4 H, 4-H, 6-H_2, 8a-H), 5.73–5.79 (m, 1 H, 7-H), 5.85–5.86 (m, 1 H, 8-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6, 23.1 (q, t, CH_3, C-3), 23.5 (dt, $^3J_{CF}$ = 6.9 Hz, C-4) 27.1 (dt, $^2J_{CF}$ = 27.8 Hz, C-6), 41.6 (t, C-2), 50.4 (dd, $^3J_{CF}$ = 4.2 Hz, C-8a), 74.1 (d, $^4J_{CF}$ = 2.8 Hz, C-1), 111.7 (d, $^2J_{CF}$ = 11.1 Hz, C-4a), 123.6 (dd, $^3J_{CF}$ = 11.1 Hz, C-7), 124.7 (dd, $^4J_{CF}$ = 2.8 Hz, C-8), 150.9 (d, $^1J_{CF}$ = 248.3 Hz, C-5) ppm. IR (KBr): $\tilde{\nu}$ = 3315 (O–H), 3040–2830 (=C–H, C–H), 1650 (C=C) cm^{-1}. $C_{11}H_{15}FO$ (182.2): calcd. C 72.50, H 8.30; found C 72.73, H 8.18.

***rac*-(1*S*,8a*S*)-5-Chloro-1-methyl-1,2,3,4,6,8a-hexahydronaphthalen-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 (3.2 mL, 3.2 g, 18 mmol), **16** (0.197 g, 1.00 mmol), *t*BuOH (0.19 mL, 0.15 g, 2.0 mmol) and THF (50 mL + 25 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 3:1) compound **17** (0.105 g, 53%) as a colourless solid; m.p. 98–99 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.02 (s, 3 H, CH_3), 1.34 (m_c, 1 H, 3-H), 1.59 (dt, J = 3.7, 12.9 Hz, 1 H, 2-H), 1.64–1.76 (m, 2 H, 3-H, 4-H), 1.81 (br. d, $J \approx$ 13 Hz, 1 H, 2-H), 1.87 (br. s, 1 H, OH), 2.77–2.82 (m, 1 H, 8a-H), 2.91–2.95 (m, 2 H, 6-H), 2.96–3.02 (m, 1 H, 4-H), 5.73 (dtd, J = 1.6, 3.3, 10.2 Hz, 1 H, 7-H), 5.81–5.86 (m, 1 H, 8-H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.6 (q, CH_3), 22.8 (t, C-3), 29.4 (t, C-4), 34.7 (t, C-6), 41.5 (t, C-2), 51.4 (d, C-8a), 74.6 (s, C-1), 123.6 (s, C-5), 124.0 (d, C-8), 124.6 (d, C-7), 131.0 (s, C-4a) ppm. IR (KBr): $\tilde{\nu}$ = 3410 (O–H), 3050–2830 (=C–H, C–H) cm^{-1}. $C_{11}H_{15}ClO$ (198.7): calcd. C 66.50, H 7.61; found C 66.63, H 7.46.

5-Hydroxy-5-methyl-5,6,7,8-tetrahydronaphthalene-2-carbonitrile (19): According to the general procedure, samarium (0.180 g, 1.20 mmol), 1,2-diiodoethane (0.310 g, 1.10 mmol), HMPA (1.6 mL, 1.6 g, 9.0 mmol), **18** (0.094 g, 0.50 mmol), *t*BuOH (0.095 mL, 0.074 g, 1.00 mmol) and THF (25 mL + 13 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 4:1) compound **19** (0.044 g, 47%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54 (s, 3 H, CH_3), 1.84 (br. s, 1 H, OH), 1.82–1.99 (m, 4 H, 7-H, 8-H), 2.81 (m_c, 2 H, 6-H), 7.38 (br. s, 1 H, 1-H), 7.48 (br. d, $J \approx$ 8 Hz, 1 H, 3-H), 7.70 (d, J = 8.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 30.8 (q, CH_3), 20.1, 29.3, 39.2 (3t, C-6, C-7, C-8), 70.5 (s, C-5), 110.7 (s, C-2), 118.9 (s, CN), 127.3, 129.7, 132.5 (3 d, C-1, C-3, C-4), 137.3, 148.2 (2 s, C-8a, C-4a) ppm. IR (film): $\tilde{\nu}$ = 3510 (O–H), 3060–2840 (=C–H, C–H), 2225 (CN), 1600 (C=C) cm^{-1}. $C_{12}H_{13}NO$ (187.2): calcd. C 76.97, H 7.00, N 7.48; found C 76.78, H 7.06, N 7.80.

Ethyl 5-Hydroxy-5-methyl-5,6,7,8-tetrahydronaphthalene-2-carboxylate (21): According to the general procedure, samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.2 mL, 3.2 g, 18 mmol), **20** (0.234 g, 1.00 mmol), *t*BuOH (0.19 mL, 0.15 g, 2.0 mmol) and THF (50 mL + 25 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 4:1) compound **21** (0.096 g, 41%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (t, J = 7.0 Hz, 3 H, OCH_2CH_3), 1.49 (s, 3 H, CH_3), 1.72–1.82, 1.84–1.94 (2m, 1 H, 3 H, 7-H, 8-H), 2.20 (br. s, 1 H, OH), 2.74–2.79 (m, 2 H, 6-H), 4.30 (q, J = 7.0 Hz, 2 H, OCH_2), 7.59 (d, J = 8.1 Hz, 1 H, 4-H), 7.68 (br. s, 1 H, 1-H), 7.77 (dd, J = 1.9, 8.1 Hz, 1 H, 3-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (q, OCH_2CH_3), 30.7 (q, 5-CH_3), 20.3, 29.6, 39.4 (3t, C-6, C-7, C-8), 60.8 (t, OCH_2), 70.5 (s, C-5), 126.4, 130.0, 127.2 (3d, C-1, C-3, C-4), 128.8, 136.2, 147.8 (3s, C-2, C-4a, C-8a), 166.6 (s, C=O) ppm. IR (film): $\tilde{\nu}$ = 3480 (O–H), 3010–2850 (=C–H, C–H), 1700 (C=O), 1610 (C=C) cm^{-1}. $C_{14}H_{18}O_3$ (234.3): calcd. C 71.77, H 7.74; found C 71.41, H 7.60.

***rac*-(8*S*,8a*S*)-8-Hydroxy-8-methyl-3,5,6,7,8,8a-hexahydronaphthalene-2-carbonitrile (23):** According to the general procedure, samarium (0.180 g, 1.20 mmol), 1,2-diiodoethane (0.310 g, 1.10 mmol), HMPA (1.6 mL, 1.6 g, 9.0 mmol), **22** (0.094 g, 0.50 mmol), *t*BuOH (0.095 mL, 0.074 g, 1.00 mmol) and THF (25 mL + 13 mL) afforded after purification by HPLC (hexane/ethyl acetate, 1:1) compound **23** (0.052 g, 55%) as a colourless oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.05 (s, 3 H, CH_3), 1.32–2.00 (m, 6 H, 5-H, 6-H_2, 7-H_2, OH), 2.23 (br. d, $J \approx$ 14 Hz, 1 H, 5-H), 2.80–2.87 (m, 3 H, 3-H, 8a-H), 5.46 (br. s, 1 H, 4-H), 6.82 (br. s, 1 H, 1-H) ppm. ^{13}C NMR (68 MHz, $CDCl_3$): δ = 22.0 (t, C-6), 23.3 (q, CH_3), 28.3 (t, C-3), 35.0 (t, C-5), 42.4 (t, C-7), 49.5 (d, C-8a), 74.0 (s, C-8), 109.8 (s, C-2), 116.0 (d, C-4), 118.9 (s, CN), 134.7 (s, C-4a), 142.2 (d, C-1) ppm. IR (film): $\tilde{\nu}$ = 3450 (O–H), 3100–2850 (=C–H, C–H), 2220 (CN), 1605 (C=C) cm^{-1}. $C_{12}H_{15}NO$ (189.3): calcd. C 76.16, H 7.99, N 7.40; found C 75.73, H 7.78, N 7.52.

***rac*-(1*S*,8a*S*)-1-Methyl-7-(trifluoromethyl)-1,2,3,4,6,8a-hexahydronaphthalen-1-ol (25):** According to the general procedure, samarium (0.180 g, 1.20 mmol), 1,2-diiodoethane (0.310 g, 1.10 mmol), HMPA (1.6 mL, 1.6 g, 9.0 mmol), **24** (0.115 g, 0.500 mmol), *t*BuOH (0.095 mL, 0.074 g, 1.00 mmol) and THF (25 mL + 13 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 19:1→4:1) and HPLC compound **25** (0.065 g, 56%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.97 (s, 3 H, CH_3), 1.31 (tq, J = 4.3, 12.6 Hz, 1 H, 3-H), 1.53–2.00 (m, 5 H, 4-H, 3-H, 2-H, OH), 2.23 (m_c, 1 H, 4-H), 2.55–2.80 (m, 3 H, 6-H, 8a-H), 5.46 (br. s, 1 H, 5-H), 6.47 (br. s, 1 H, 8-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.8 (t, C-3), 23.6 (qt, $^3J_{CF}$ = 1.4 Hz, C-6), 34.0 (t, C-4), 25.7 (q, CH_3), 42.1 (t, C-2), 74.0 (s, C-1), 48.7 (d, C-8a), 116.5 (d, C-5), 126.8 (q, $^2J_{CF}$ = 30.2 Hz, C-7), 127.4 (q, $^1J_{CF}$ = 231.5 Hz, CF_3), 127.5 (qd, $^3J_{CF}$ = 5.7 Hz, C-8), 134.8 (s, C-4a) ppm. IR (film): $\tilde{\nu}$ = 3380 (O–H), 3050–2840 (=C–H, C–H) cm^{-1}. MS (EI, 80 eV, 30 °C): m/z (%) = 232 (1) [M$^+$], 215 (100), 187 (23) 159 (28), 18 (89). HRMS: $C_{12}H_{15}F_3O$: calcd. 232.10750; found 232.10731.

***rac*-(1*S*,8a*S*)-7-Fluoro-1-methyl-1,2,3,4,6,8a-hexahydronaphthalen-1-ol (27):** According to the general procedure, samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.2 mL, 3.2 g, 18 mmol), **26** (0.182 g, 1.00 mmol), *t*BuOH (0.19 mL, 0.15 g, 2.00 mmol) and THF (50 mL + 25 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 9:1→4:1) and HPLC compound **27** (0.097 g, 53%) as a colourless solid; m.p. 79–80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (s, 3 H, CH_3), 1.34 (tq, J = 4.1, 13.5 Hz, 1 H, 3-H), 1.52–1.63 (m, 2 H, 2-H, OH), 1.70–1.76 (m, 1 H, 3-H), 1.81 (br. d, $J \approx$ 13 Hz, 1 H, 2-H), 1.94 (m_c, 1 H, 4-H), 2.22 (tdd, J = 2.1, 4.3, 13.5 Hz, 1 H, 4-H), 2.73–2.86 (m, 3 H, 6-H, 8a-H), 5.35–5.41 (m, 2 H, 5-H, 8-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.8 (t, C-3), 24.1 (q, CH_3), 27.2 (dt, $^2J_{CF}$ = 27.0 Hz, C-6), 34.1 (t, C-4), 41.6 (t, C-2), 50.2 (dd, $^3J_{CF}$ = 6.7 Hz, C-8a), 74.6 (d, $^4J_{CF}$ = 1.6 Hz, C-1), 99.7 (dd, $^2J_{CF}$ = 15.1 Hz, C-8), 116.5 (dd, $^3J_{CF}$ = 10.9 Hz, C-5), 136.4 (d, $^4J_{CF}$ = 2.6 Hz, C-4a), 159.9 (d, $^1J_{CF}$ = 253.8 Hz, C-7) ppm. IR (KBr): $\tilde{\nu}$ = 3380 (O–H), 3050–2840 (=C–H, C–H) cm^{-1}. $C_{11}H_{15}FO$ (182.2): calcd. C 72.50, H 8.30; found C 72.00, H 8.46.

***rac*-(8*S*,8a*S*)-(8-Hydroxy-8-methyl-3,5,6,7,8,8a-hexahydronaphthalen-2-yl)acetate (29):** According to the general procedure, samarium (0.205 g, 1.36 mmol), iodine (0.311 g, 1.23 mmol), HMPA (1.45 mL, 1.46 g, 8.17 mmol), **28** (0.100 g, 0.454 mmol), *t*BuOH (0.08 mL, 0.07 g, 0.9 mmol) and THF (20 mL + 10 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 4:1→3:1) compound **29** (0.050 g, 50%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (s, 3 H, CH_3), 1.37

(tq, J = 4.1, 13.4 Hz, 1 H, 6-H), 1.57 (br. s, 1 H, OH), 1.61 (dt, J = 4.5, 13.4 Hz, 1 H, 7-H), 1.74 (ttd, J = 2.2, 4.5, 13.4 Hz, 1 H, 6-H), 1.83 (dddd, J = 1.5, 2.3, 4.1, 13.4 Hz, 1 H, 7-H), 1.95 (tdt, $J \approx$ 2, 4.5, 13.4 Hz, 1 H, 5-H), 2.14 [s, 3 H, O(C=O)CH_3], 2.23 (tdd, J = 2.2, 4.1, 13.4 Hz, 1 H, 5-H), 2.75–2.79 (m, 2 H, 3-H), 2.88 (dt, J = 3.5, 7.6 Hz, 1 H, 8a-H), 5.41 (tt, J = 1.7, 3.5 Hz, 1 H, 4-H), 5.56 (td, J = 1.7, 3.5 Hz, 1 H, 1-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.0, 21.7 (2q, CH_3), 24.0 (t, C-6), 28.2 (t, C-3), 34.0 (t, C-5), 41.5 (t, C-7), 50.2 (d, C-8a), 74.5 (s, C-8), 111.9 (d, C-1), 116.8 (d, C-4), 135.6 (s, C-4a), 147.2 (s, C-2), 169.3 (s, C=O) ppm. IR (film): $\tilde{\nu}$ = 3435 (O–H), 3045–2835 (=C–H, C–H), 1755 (C=O), 1670 (C=C) cm^{-1}. HRMS (ESI): $C_{13}H_{18}NaO_3$: calcd. 245.1154; found 245.1169.

***rac*-(8*S*,8a*S*)-(8-Hydroxy-8-methyl-3,5,6,7,8,8a-hexahydronaphthalen-2-yl)methanesulfonate (31):** According to the general procedure, samarium (0.140 g, 0.930 mmol), iodine (0.213 g, 0.840 mmol), HMPA (0.98 mL, 1.0 g, 5.6 mmol), **30** (0.080 g, 0.31 mmol), *t*BuOH (0.07 mL, 0.06 g, 0.8 mmol) and THF (20 mL + 10 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 8:1→1:1) compound **31** (0.045 g, 56%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.09 (s, 3 H, CH_3), 1.36 (tq, J = 4.1, 13.5 Hz, 1 H, 6-H), 1.63 (ddt, J = 0.7, 4.1, 13.1 Hz, 1 H, 7-H), 1.72–1.80 (m, 2 H, 6-H, OH), 1.84 (m_c, 1 H, 7-H), 1.95 (m_c, 1 H, 5-H), 2.24 (tdd, J = 2.1, 4.2, 13.4 Hz, 1 H, 5-H), 2.89–2.96 (m, 3 H, 3-H, 8a-H), 3.13 [s, 3 H, O(SO_2)CH_3], 5.40–5.42 (m, 1 H, 4-H), 5.85–5.87 (m, 1 H, 1-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.0 (q, CH_3), 23.8 (t, C-6), 29.3 (t, C-3), 33.9 (t, C-5), 38.0 [q, O(SO_2)CH_3], 41.7 (t, C-7), 50.5 (d, C-8a), 74.4 (s, C-8), 114.4 (d, C-1), 116.7 (d, C-4), 135.4 (s, C-4a), 147.0 (s, C-2) ppm. IR (film): $\tilde{\nu}$ = 3420 (O–H), 3030–2835 (=C–H, C–H), 1660 (C=C) cm^{-1}. MS (EI, 80 eV, 60 °C): m/z (%) = 258 (43) [M$^+$], 240 (24), 238 (100), 200 (23), 198 (25), 161 (80), 159 (54), 131 (17), 121 (29), 120 (20), 91 (21), 85 (18). HRMS: $C_{12}H_{18}O_4S$: calcd. 258.09259; found 258.09210.

5-Phenylpentan-2-one (9): According to the general procedure, samarium (0.079 g, 0.52 mmol), iodine (0.118 g, 0.465 mmol), HMPA (0.55 mL, 0.56 g, 3.1 mmol), **32** (0.079 g, 0.17 mmol), *t*BuOH (0.04 mL, 0.03 g, 0.4 mmol) and THF (20 mL + 10 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 8:1→2:1) compound **9** (0.021 g, 76%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.91 (quint, J = 7.5 Hz, 2 H, 4-H), 2.12 (s, 3 H, 1-H), 2.44 (t, J = 7.5 Hz, 2 H, 3-H), 2.62 (t, J = 7.5 Hz, 2 H, 5-H), 7.15–7.21 (m, 3 H, Ar), 7.26–7.30 (m, 2 H, Ar) ppm. The ^{1}H NMR spectroscopic data are in accordance with those given in the literature.[34]

***rac*-(1*S*,5*S*)-Methyl 1-Hydroxy-1-methylspiro[4.5]deca-6,8-diene-8-carboxylate (34):** According to the general procedure, samarium (0.180 g, 1.20 mmol), 1,2-diiodoethane (0.310 g, 1.10 mmol), HMPA (1.6 mL, 1.6 g, 9.0 mmol), **33** (0.110 g, 0.500 mmol), *t*BuOH (0.095 mL, 0.074 g, 1.00 mmol) and THF (25 mL + 13 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 9:1→7:3) compound **34** (0.064 g, 58%) as colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19 (s, 3 H, 1-CH_3), 1.47 (br. s, 1 H, OH), 1.50–1.93 (m, 6 H, CH_2), 2.31 (dd, J = 5.2, 19.4 Hz, 1 H, 10-H), 2.69 (dd, J = 4.3, 19.4 Hz, 1 H, 10-H), 3.71 (s, 3 H, OCH_3), 5.55 (dd, J = 0.7, 10.0 Hz, 1 H, 6-H), 6.37 (dd, J = 1.5, 10.0 Hz, 1 H, 7-H), 6.91 (m_c, 1 H, 9-H) ppm. The ^{1}H NMR spectroscopic data are in accordance with those given in the literature.[25]

***rac*-1-(1*S*,5*S*)- and 1-[(1*R*,5*S*)-1-Hydroxy-1-methylspiro[4.5]deca-6,8-dien-8-yl]ethanone (36a and 36b):** According to the general procedure, samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.2 mL, 3.2 g, 18 mmol), **35** (0.204 g, 1.00 mmol), *t*BuOH (0.19 mL, 0.15 g, 2.0 mmol) and THF (50 mL + 25 mL) afforded after purification by flash-chromatography on silica gel (hexane/ethyl acetate, 19:1→9:1) compound **36a** (0.074 g, 36%) and compound **36b** (0.017 g, 8%) as colourless oils.

36a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (s, 3 H, 1-CH_3), 1.48 (br. s, 1 H, OH), 1.53–1.94 (m, 6 H, CH_2), 2.23 (s, 3 H, $COCH_3$), 2.31 (dd, J = 5.4, 19.5 Hz, 1 H, 10-H), 2.73 (dd, J = 4.4, 19.5 Hz, 1 H, 10-H), 5.55 (d, J = 10.2 Hz, 1 H, 6-H), 6.37 (dd, $J \approx$ 1, 10.2 Hz, 1 H, 7-H), 6.81 (m_c, 1 H, 9-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.9 (t, CH_2), 23.4, 25.2 (2q, CH_3), 30.0 (t, C-10), 38.6* (2t, CH_2), 48.4 (s, C-5), 83.0 (s, C-1), 119.6 (d, C-6), 133.6 (d, C-7), 135.6 (s, C-8), 138.4 (d, C-9), 196.8 (s, C=O) ppm. *Signal has higher intensity.

36b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (s, 3 H, 1-CH_3), 1.38 (br. s, 1 H, OH), 1.54–1.90 (m, 6 H, CH_2), 2.25 (s, 3 H, $COCH_3$), 2.31 (dd, J = 4.9, 18.8 Hz, 1 H, 10-H), 2.46 (dd, J = 4.6, 18.8 Hz, 1 H, 10-H), 5.85 (d, J = 10.2 Hz, 1 H, 6-H), 6.56 (dd, J = 1.4, 10.2 Hz, 1 H, 7-H), 6.72 (m_c, 1 H, 9-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.1 (t, CH_2), 23.5, 25.2 (2q, CH_3), 32.7 (t, C-10), 36.8 (t, CH_2), 38.0 (t, CH_2), 47.9 (s, C-5), 83.4 (s, C-1), 121.7 (d, C-6), 132.3 (d, C-7), 136.1 (s, C-8), 136.9 (d, C-9), 196.4 (s, C=O) ppm. The relative configurations or **36a** and **36b** were assigned by comparison with the literature known compound **34**. Due to the low stability of **36a**/**36b** and their rapid decomposition no further characterization was possible.

***rac*-(4*R*,4a*S*,5*S*)-5-Hydroxy-4-(1-hydroxy-1-methylethyl)-5-methyl-4,4a,5,6,7,8-hexahydronaphthalene-2-carbonitrile (37):** According to the general procedure, but without *t*BuOH. Samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.2 mL, 3.2 g, 18 mmol), **21** (0.187 g, 1.00 mmol), and THF (50 mL) afforded a solution which was treated with acetone (0.290 g, 5.00 mmol) in THF (25 mL) after 5 min. Purification by flash-chromatography on silica gel (hexane/ethyl acetate, 9:1→1:1) furnished compound **37** (0.130 g, 53%) as a colourless solid; m.p. 106–110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03, 1.05, 1.34 (3s, 3 H each, CH_3), 1.44 (m_c, 1 H, 7-H), 1.68 (dt, J = 4.2, 12.9 Hz, 1 H, 6-H), 1.81–1.86 (m, 1 H, 7-H), 1.89 (br. d, $J \approx$ 13 Hz, 1 H, 6-H), 2.03 (dt, J = 4.6, 12.9 Hz, 1 H, 8 H), 2.17 (br. s, 1 H, OH), 2.27 (m_c, 1 H, 8-H), 2.31 (br. s, 1 H, OH), 2.61–2.63 (m, 1 H, 4a-H), 2.75 (t, J = 5.0 Hz, 1 H, 4-H), 5.60 (s, 1 H, 1-H), 6.31 (d, J = 5.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.5 (q, CH_3), 24.1 (t, C-7), 24.2, 29.0 (2q, CH_3), 34.7 (t, C-8), 42.7 (t, C-6), 45.1 (d, C-4), 47.1 (d, C-4a), 77.0 (s, *C*-C-4), 77.3 (s, C-5), 110.9 (s, C-2), 112.8 (d, C-1), 118.8 (s, CN), 138.3 (d, C-3), 142.8 (s, C-8a) ppm. IR (KBr): $\tilde{\nu}$ = 3440 (O–H), 3055–2865 (=C–H, C–H), 2225 (CN), 1600 (C=C) cm^{-1}. $C_{15}H_{21}NO_2$ (247.3): calcd. C 72.84, H 8.56, N 5.66; found C 72.24, H 8.56, N 5.78.

***rac*-Ethyl (4*R*,4a*S*,5*S*)-5-Hydroxy-4-(1-hydroxy-1-methylethyl)-5-methyl-4,4a,5,6,7,8-hexahydronaphthalene-2-carboxylate (38):** According to the general procedure, but without *t*BuOH. Samarium (0.361 g, 2.40 mmol), 1,2-diiodoethane (0.620 g, 2.20 mmol), HMPA (3.2 mL, 3.2 g, 18 mmol), **23** (0.234 g, 1.00 mmol) and THF (50 mL) afforded a solution, which was treated with acetone (0.290 g, 5.00 mmol) in THF (25 mL) after 5 min. Purification by flash-chromatography on silica gel (hexane/ethyl acetate, 9:1→7:3) provided compound **38** (0.224 g, 76%) as a colourless solid; m.p. 127–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99, 1.02 (2 s, 3 H each, CH_3), 1.29 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 1.36 (s, 3 H, CH_3), 1.34–1.49 (m, 1 H, 7-H), 1.68 (dt, J = 4.3, 13.2 Hz, 1 H, 6-H), 1.75–1.81 (m, 1 H, 7-H), 1.86 (br. d, $J \approx$ 13 Hz, 1 H, 6-H), 2.01 (dt, J = 4.9, 12.9 Hz, 1 H, 8-H), 2.29 (br. d, $J \approx$ 13 Hz, 1 H, 8-H),

2.57 (br. s, 1 H, 4a-H), 3.31 (br. s, 2 H, OH), 2.75 (dd, *J* = 4.1, 5.2 Hz, 1 H, 4-H), 4.16–4.24 (m, 2 H, OCH_2), 6.07 (br. s, 1 H, 1-H), 6.62 (d, *J* = 5.2 Hz, 1 H, 3-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3 (q, OCH_2CH_3), 20.5 (q, CH_3), 24.2 (t, C-7), 24.4, 29.2 (2q, CH_3), 35.1 (t, C-8), 43.0 (t, C-6), 45.5 (d, C-4), 47.8 (d, C-4a), 60.7 (t, OCH_2), 74.0, 74.6 (2 s, C-5, 4-C), 113.9 (d, C-1), 127.9 (s, C-2), 133.6 (d, C-3), 140.5 (s, C-8a), 166.2 (s, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3410, 3255 (O–H), 2970–2800 (=C–H, C–H), 1720 (C=O), 1615 (C=C) cm^{-1}. MS (EI, 80 eV): *m*/*z* (%) = 276 (17) [$M^+ - H_2O$], 236 (38) [$M^+ - C_3H_6O$], 218 (65) [$M^+ - C_3H_5OH - H_2O$], 190 (100) [$M^+ - C_3H_6O - C_2H_5OH$].

***rac*-(2*R*,4a*S*,5*S*)- and (2*S*,4a*S*,5*S*)-2-Allyl-5-hydroxy-5-methyl-2,4a,5,6,7,8-hexahydronaphthalene-2-carbonitrile (39a and 39b):** According to the general procedure, but without *t*BuOH. Samarium (0.181 g, 1.20 mmol), 1,2-diiodoethane (0.310 g, 1.10 mmol), HMPA (1.6 mL, 1.6 g, 9.0 mmol), **21** (0.094 g, 0.50 mmol) and THF (25 mL) afforded a solution, which was treated with allyl bromide (0.302 g, 2.50 mmol) in THF (13 mL) after 2 h. Purification by flash-chromatography on silica gel (hexane/ethyl acetate, 17:3) and separation of the diastereomers by HPLC furnished compounds **39a** (0.057 g, 50%) and **39b** (0.015 g, 13%) as colourless oils.

39a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02 (s, 3 H, CH_3), 1.35 (tq, *J* = 4.1, 13.2 Hz, 1 H, 7-H), 1.60 (dt, *J* = 3.9, 13.2 Hz, 1 H, 6-H), 1.69–1.87 (m, 3 H, 6-H, 7-H, OH), 1.95 (dt, *J* = 5.6, 13.5 Hz, 1 H, 8-H), 2.15–2.21 (m, 1 H, 8-H), 2.34–2.42 (m, 2 H, 1′-H), 2.49 (br. s, 1 H, 4a-H), 5.07–5.18 (m, 2 H, 3′-H), 5.34 (br. s, 1 H, 1-H), 5.65–5.78 (m, 2 H, 2′-H, 3-H), 6.08 (dd, *J* = 3.5, 10.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.1 (q, CH_3), 23.8 (t, C-7), 34.3 (t, C-8), 37.6 (s, C-2), 41.9 (t, C-6), 45.0 (t, C-1′), 48.8 (d, C-4a), 74.7 (s, C-5), 118.0 (d, C-1), 120.1 (t, C-3′), 121.0 (s, CN), 124.9 (d, C-3), 127.9 (d, C-4), 131.2 (d, C-2′), 139.8 (s, C-8a) ppm. IR (film): $\tilde{\nu}$ = 3470 (O–H), 3060–2800 (=C–H, C–H), 2230 (CN), 1600 (C=C) cm^{-1}. $C_{15}H_{19}NO$ (229.3): calcd. C 78.56, H 8.35, N 6.11; found C 78.87, H 8.22, N 6.02.

39b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (s, 3 H, CH_3), 1.36 (tq, *J* = 4.1, 13.0 Hz, 1 H, 7-H), 1.50 (br. s, 1 H, OH), 1.66 (dt, *J* = 4.1, 13.0 Hz, 1 H, 6-H), 1.73–1.89 (m, 2 H, 6-H, 7-H), 2.06 (dt, *J* = 5.1, 13.4 Hz, 1 H, 8-H), 2.20–2.31 (m, 1 H, 8-H), 2.38–2.46 (m, 2 H, 1′-H), 2.71 (m_c, 1 H, 4a-H), 5.13–5.26 (m, 2 H, 3′-H), 5.42 (m_c, 1 H, 1-H), 5.71–5.93 (m, 2 H, 2′-H, 3-H), 6.14 (dd, *J* = 3.1, 10.0 Hz, 1 H, 4-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.2 (q, CH_3), 23.7 (t, C-7), 34.3 (t, C-8), 37.8 (s, C-2), 41.9 (t, C-6), 45.8 (t, C-1′), 48.6 (d, C-4a), 73.8 (s, C-5), 118.1 (d, C-1), 120.2 (t, C-3′), 121.0 (s, CN), 124.7 (d, C-3), 127.7 (d, C-4), 131.4 (d, C-2′), 139.5 (s, C-8a) ppm. IR (film): $\tilde{\nu}$ = 3470 (O–H), 3055–2800 (=C–H, C–H), 2230 (CN) cm^{-1}.

***rac*-Ethyl (2*R*,4a*S*,5*S*)- and Ethyl (2*S*,4a*S*,5*S*)-2-Allyl-5-hydroxy-5-methyl-2,4a,5,6,7,8-hexahydronaphthalene-2-carboxylate (40a and 40b):** According to the general procedure, but without *t*BuOH. Samarium (0.721 g, 4.80 mmol), 1,2-diiodoethane (1.24 g, 4.40 mmol), HMPA (6.3 mL, 6.4 g, 36 mmol), **23** (0.469 g, 2.00 mmol) and THF (100 mL) afforded a solution, which was treated with allyl bromide (1.21 g, 10.0 mmol) in THF (50 mL). Purification by flash-chromatography on silica gel (hexane/ethyl acetate, 9:1) afforded a mixture of **40a** and **40b** (0.480 g, 87%). Separation by HPLC gave compounds **40a** (0.303 g, 55%) and **40b** (0.067 g, 12%) as colourless oils.

40a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (s, 3 H, CH_3), 1.14 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.35 (tq, *J* = 4.0, 13.1 Hz, 1 H, 7-H), 1.57 (dt, *J* = 4.0, 13.1 Hz, 1 H, 6-H), 1.61–1.68 (m, 1 H, 7-H), 1.73 (br. d, *J* ≈ 12.5 Hz, 1 H, 6-H), 1.92 (dt, *J* = 5.0, 13.3 Hz, 1 H, 8-H), 2.15 (m_c, 1 H, 8-H), 2.32 (m_c, 2 H, 1′-H), 2.44 (br. s, 1 H, OH), 2.55 (br. s, 1 H, 4a-H), 4.03 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.93, 4.95 (2m_c, 1 H each, 3′-H), 5.38 (d, *J* = 1.9 Hz, 1 H, 1-H), 5.51–5.59 (m, 1 H, 2′-H), 5.73 (td, *J* = 1.9, 10.2 Hz, 1 H, 3-H), 5.95 (dd, *J* = 3.4, 10.2 Hz, 1 H, 4-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (q, OCH_2CH_3), 21.8 (q, CH_3), 24.0 (t, C-7), 34.6 (t, C-8), 41.9 (t, C-6), 44.2 (t, C-1′), 48.7 (s, C-2), 49.2 (d, C-4a), 60.7 (t, OCH_2), 74.5 (s, C-5), 117.9 (t, C-3′), 121.2 (d, C-2′), 125.7 (d, C-4), 128.1 (d, C-3), 133.4 (d, C-1), 137.4 (s, C-8a), 174.2 (s, C=O) ppm. IR (film): $\tilde{\nu}$ = 3435 (O–H), 3075–2845 (=C–H, C–H), 1720 (C=O), 1610 (C=C) cm^{-1}. $C_{17}H_{24}O_3$ (276.4): calcd. C 73.88, H 8.75; found C 73.57, H 8.60.

40b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.00 (s, 3 H, CH_3), 1.23 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.30–1.40 (m, 1 H, 7-H), 1.62 (dt, *J* = 4.0, 13.0 Hz, 1 H, 6-H), 1.66 (br. s, 1 H, OH), 1.71–1.77 (m, 1 H, 7-H), 1.82 (br. d, *J* ≈ 13 Hz, 1 H, 6-H), 1.92 (dt, *J* = 5.0, 13.1 Hz, 1 H, 8-H), 2.23 (m_c, 1 H, 8-H), 2.34–2.44 (m, 2 H, 1′-H), 2.62 (br. s, 1 H, 4a-H), 4.11 (q, *J* = 7.1 Hz, 2 H, OCH_2), 5.04–5.09 (m, 2 H, 3′-H), 5.53 (d, *J* = 1.9 Hz, 1 H, 1-H), 5.64–5.72 (m, 1 H, 2′-H), 5.89 (td, *J* = 2.1, 10.3 Hz, 1 H 3-H), 6.01 (dd, *J* = 3.2, 10.3 Hz, 1 H, 4-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (q, OCH_2CH_3), 22.3 (q, CH_3), 24.0 (t, C-7), 34.6 (t, C-8), 42.0 (t, C-6), 45.3 (t, C-1′), 48.6 (s, C-2), 48.9 (d, C-4a), 60.8 (t, OCH_2), 74.1 (s, C-5), 118.1 (t, C-3′), 121.4 (d, C-2′), 125.5 (d, C-4), 128.2 (d, C-3), 133.4 (d, C-1), 137.1 (s, C-8a), 174.1 (s, C=O) ppm. IR (film): $\tilde{\nu}$ = 3435 (O–H), 3085–2800 (=C–H, C–H), 1715 (C=O), 1610 (C=C) cm^{-1}. $C_{17}H_{24}O_3$ (276.4): calcd. C 73.88, H 8.75; found C 73.47, H 8.76.

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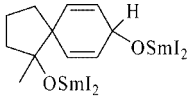

X

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