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Reversing Dane's strategy: a new, concise, enantioselective synthesis of the steroid nucleus

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Abstract—Reversing the polarity of the cycloaddition partners in Dane's steroid synthesis provides ready access to enantiomerically pure, functionally-rich steroidal structures.

1. Introduction

In 1939 Dane described a strategy, now commonly described as the 'AB + D → ABCD' approach, for synthesising steroids based on the Diels–Alder addition of a vinyldihydronaphthalene **I** to an activated cyclopentenone **II**, as summarised in Figure 1.[1] This strategy has since been exploited many times in steroid synthesis in both racemic and enantioselective form.[2] Remarkably, the reverse of this approach, namely employing the AB component as the dienophile (e.g., **III**) and the D component as the diene **IV** has not been examined previously.[3] Herein, we disclose our results on the application of this new approach to the rapid, enantioselective synthesis of steroidal skeletons.[4–12]

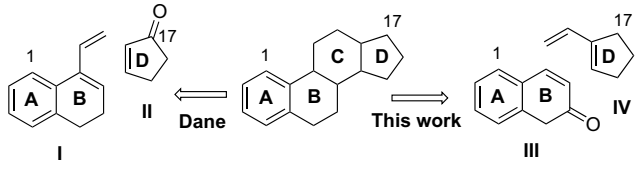

Figure 1. Retrosynthetic analyses of the tetracyclic core of steroids.

The synthetic equivalent of **III** (the dienophile component for the ultimate cycloaddition) was selected to be a 1,2-naphthoquinone.[13–19] For the synthesis of **IV**, we have disclosed a new two-step sequence of (i) nucleophilic addition and (ii) ring closing enyne metathesis (RCEM). The asymmetric aldol reaction was chosen for the nucleophilic addition in the first step as it (a) defines the absolute stereochemistry of the D-ring (most significantly that of C17 in steroids), (b) creates the enyne structure in one step and (c) should provide crystalline intermediates suitable for subsequent crystal structure determinations. The second step—RCEM—was anticipated to provide enantiomerically pure semi-cyclic dienes without disturbing the newly-created stereogenic centres.

2. Results and discussion

The synthesis of representative semi-cyclic dienes was first undertaken.

Thus, *syn*-selective aldol addition of alkenoyl sultam **1** to acetylenic aldehydes **2a**,[20] **2b**[21] and **2c**[22] (chosen for their differing electronic and steric properties) gave enynes **3a–c** in almost quantitative yields (unlike **3a**, a relatively high reaction temperature of −10 °C was required for successful additions with **3b** or **3c**). In each case, only the expected isomer was isolated. Ring closing enyne metathesis of **3a–c**, employing Mori's modification, (ethylene atmosphere)[23] gave excellent yields of the desired semi-cyclic dienes. These appear to be the first examples of such rearrangements of enantiomerically pure enynes constructed through asymmetric carbon–carbon bond formation rather than through alkylation of templates (typically derived from the chiral pool).[24,25] Gratifyingly, the aldol stereochemical integrity in the products was completely maintained (Scheme 1).

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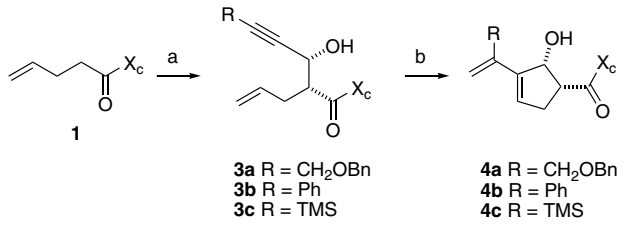
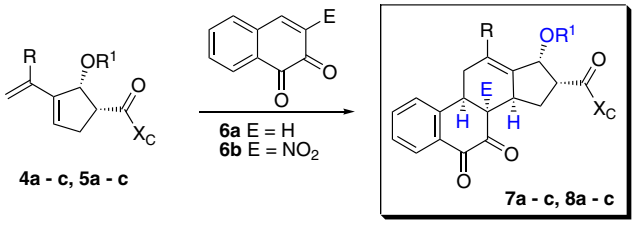


Scheme 1. Reagents and conditions: (a) Et_2BOTf, $Et_2(iPr)N$, CH_2Cl_2, −78 °C, then RCCCHO (at −78 °C for **3a** and −10 °C for **3b** or **3c**); (b) 2nd-generation Grubbs' cat., toluene, 80 °C, $CH_2{=}CH_2$.

In order to construct the steroid nucleus, we required a suitably reactive 1,2-naphthoquinone. Attempts to react dienes **4a–c** with 1,2-naphthoquinone **6a** ($E = H$) only returned starting materials. In order to improve the reactivity of the dienophile, 3-*nitro*-1,2-naphthoquinone **6b** ($E = NO_2$, Scheme 2) was prepared using Fieser's procedure.[26]



Scheme 2. Reagent and condition: (a) toluene, rt.

Dienophile **6b** proved to be remarkably reactive (Table 1), even at room temperature. Thus, free alcohol **4a** added to **6b** in good yield and with a diastereomeric ratio of 3:1 (Table 1, entry 1). Significantly, the reaction of the corresponding TES-protected diene **5a** gave adduct **8a** with an improved diastereomeric ratio (4:1 in toluene, entry 2 and 5:1 in CH_2Cl_2, entry 3).[27] This suggested that the extra steric bulk in the diene would increase the diastereoselection.

Table 1. Results from cycloadditions of semi-cyclic dienes to 3-nitro-1,2-naphthoquinone **6b** in toluene at room temperature

Entry	Diene	R	R^1	Product	dr[a]	Yield[b] (%)
1	**4a**	CH_2OBn	H	**7a**	3:1	73
2	**5a**	CH_2OBn	TES	**8a**	4:1	90[f]
3	**5a**	CH_2OBn	TES	**8a**	5:1	56[c]
4	**4b**	Ph	H	**7b**	1:1[d]	95[f]
5	**5b**	Ph	TES	**8b**	20:1	72[g]
6	**4c**	TMS	H	**7c**	—	0[e]
7	**5c**	TMS	TES	**8c**	—	NR

[a] Estimated by ^1H NMR spectroscopy.
[b] Isolated yield of the major diastereomer unless otherwise indicated.
[c] Reaction was run in dichloromethane.
[d] The minor component contained two diastereomers in a 3.5:1 ratio.
[e] Diene decomposed completely.
[f] Estimated conversion by ^1H NMR spectroscopy.
[g] Reaction run at 40 °C.

This effect was even more evident in additions involving phenyl-substituted dienes **4b** and **5b**. Thus, the addition of free alcohol **4b** proceeded with an excellent conversion but poor selectivity producing three diastereomers in an 11:7:2 ratio (entry 4). The corresponding TES-protected diene **5b** added to **6b** in good yield, producing only one detectable isomer (entry 5). We also investigated the additions of TMS-substituted semi-cyclic dienes **4c** and **5c**.[3] Exposure of the free alcohol **4c** to **6b** led to the decomposition of the diene (entry 6). In this case, no adduct was isolated. Somewhat surprisingly the corresponding TES–ether **5c** was completely unreactive towards **6b**, even under forcing conditions (entry 7).

Support for the stereochemistry of the major adducts shown in Scheme 2 comes from NOESY and 1D selective NOE experiments conducted on adduct **8b**. As shown in Figure 2, strong interactions were observed between H9 and H14 and H14 and H15a, establishing that these three hydrogens are all on the same face of the adduct. Strong interaction was also observed between H15b and H16, whereas there was negligible interaction between H14 and H15b.

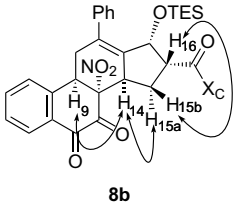
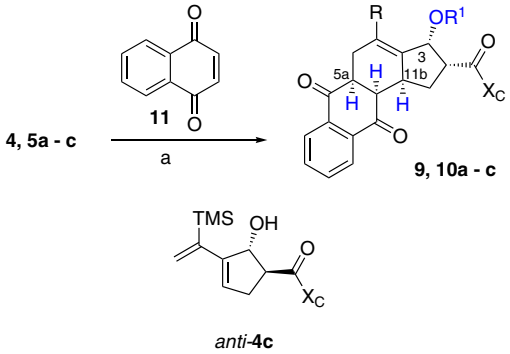


Figure 2. Selected NOE interactions observed for adduct **8b**.

Further support for the stereochemical assignment of the adducts from these reactions came from the additions of several of the semi-cyclic dienes to 1,4-naphthoquinones, generating anthrasteroidal structures of relevance to angucycline synthesis[28] (Scheme 3, Table 2). In terms of diastereoselectivity, the same trends were observed with each of the dienes in the free alcohol and TES-protected forms (compare entries 1 with 2 and 3 with 4).



Scheme 3. Reagent and condition: (a) toluene, 80 °C.

Additions with *syn*- and *anti*-TMS dienes proved instructive. Thus, unlike the complete decomposition, which occurred in the attempted addition to **6b**, diene **4c** reacted smoothly with 1,4-naphthoquinone **11** providing adduct **9c** in a good yield and with good diastereoselectivity (entry 5). The relative stereochemistry of the adjacent substituents in the cyclopentene ring is clearly critical as *anti*-**4c**[29] gave a

Table 2. Results from cycloadditions of semi-cyclic dienes to 1,4-naphthoquinone **11** in toluene at 80 °C

Entry	Diene	R	R[1]	Product	dr[a]	Yield[b] (%)
1	**4a**	CH_2OBn	H	**9a**	4:1[c]	57
2	**5a**	CH_2OBn	TES	**10a**	9:1	84
3	**4b**	Ph	H	**9b**	3:1[c]	54
4	**5b**	Ph	TES	**10b**	6:1	72
5	**4c**	TMS	H	**9c**	6:1	73
6	*anti*-**4c**	TMS	H	*anti*-**9c**	1.5:1:1	80[a]
7	**5c**	TMS	TES	**10c**	—	NR

[a] Estimated by ^{1}H NMR spectroscopy.
[b] Isolated yield of major diastereomer unless otherwise indicated.
[c] The minor component contained three diastereomers in a 3:1:1 ratio.

1.5:1:1 mixture of three diastereomeric adducts (entry 6). Diene **5c** again proved to be completely unreactive, failing to add to 1,4-naphthoquinone (entry 7).

Several of the 1,4-naphthoquinone adducts proved to be highly crystalline and the X-ray crystal structures of two of these **9b** and **9c** were determined and are shown in Figure 3.[†] In each case the *syn* relationship between hydrogens H5a, H11a, H11b at the newly-created stereocentres and the C3α–OH is clearly evident (these are shown in blue in Fig. 3).

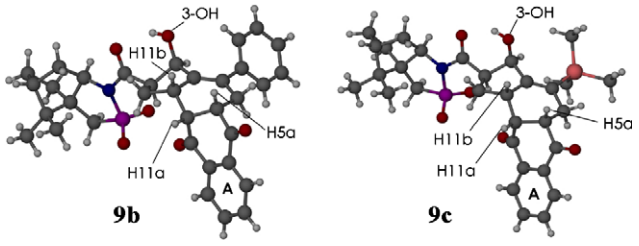


Figure 3. Crystal structures of the major adducts **9b** and **9c** from cycloaddition of semi-cyclic dienes **4b** and **4c** to 1,4-naphthoquinone.

All reports on the cycloadditions of semi-cyclic dienes indicate that this class of diene should react regioselectively whereby the less substituted terminus of the diene is the nucleophilic site in additions to unsymmetrical dienophiles ('δ^-' in Fig. 4).[30] The relative stereochemistry of the major adducts is the product of *endo–anti* addition. This is most likely due to steric hindrance in the approach of a dienophile *syn* to the two ring substituents leading to selective *anti* attack. This has some support from the results with *anti*-**4c**, which gave essentially random diastereoselection in additions to **11** (Table 2, entry 6) indicating that steric hindrance on both faces leads to poor selectivity.

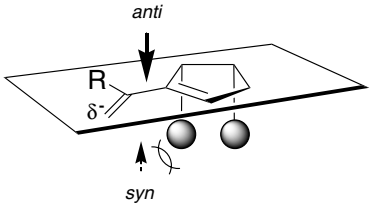


Figure 4. Predictive model for selective cycloadditions of semi-cyclic dienes prepared in this work.

[†] Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Numbers CCDC 610096 and 610097.

3. Conclusion

We have demonstrated that reversing the roles of the two components in the AB + D ⇐ ABCD strategy to steroid synthesis leads to a powerful new method for the synthesis of the steroid nucleus. In order to achieve this, a rapid technology for preparing enantiomerically pure semi-cyclic dienes has been developed. These new dienes undergo intermolecular cycloadditions with 1,2- and 1,4-naphthoquinone-based dienophiles to generate functionally-rich steroidal structures, with high levels of diastereoselectivity in a predictable manner. Studies on the manipulation of the stereochemistry and functionality of these adducts are currently underway and will be reported shortly.

4. Experimental

4.1. General experimental

Proton NMR spectra (^{1}H NMR) were recorded at 300 MHz on a Bruker AM 300 spectrometer or at 400 MHz on a Bruker Advance DRX 400 spectrometer. Carbon NMR spectra (^{13}C NMR) were recorded at 75 MHz on a Bruker AM 300 spectrometer or at 100 MHz on a Bruker Advance DRX 400 spectrometer. Protons and carbons on the chiral auxiliary are designated 'aux'. NOE experiments were performed on a Bruker Advance DRX 500 spectrometer. COSY, HSQC and HMBC spectra were used to aid assignment of some NMR spectra. Melting points were recorded on an Electrothermal melting point apparatus. Optical rotations were measured with a PolAAr 2001 automatic polarimeter at the sodium D-line (589 nm) using the solvents and concentrations (*c* g/100mL) indicated. IR spectra were recorded on a Perkin–Elmer 1600 series Fourier Transform spectrometer. Mass spectra (ESI) were recorded on a Micromass Platform QMS spectrometer. High resolution mass spectra (HRMS) were recorded on a Bruker BioApex 47e FTMS. Elemental microanalyses were performed by the University of Otago, Dunedin, New Zealand. Dichloromethane was distilled from P_2O_5 and toluene distilled from calcium hydride prior to use. Dimethylformamide (DMF) was dried over 4 Å molecular sieves. Reagents were purchased from the Aldrich Chemical Company unless otherwise stated. Compound *anti*-**3c** was synthesised according to the literature.[29]

4.2. General procedure A: *syn*-aldol additions

To a solution of triethylborane in hexanes (1.0 M, 2.2 equiv) was added, dropwise, triflic acid (freshly distilled from P_2O_5, 2.1 equiv) slowly, at room temperature and under an atmosphere of nitrogen. The mixture was stirred at approx. 40 °C for 30 min. The resulting homogeneous yel-

low solution was then cooled to −10 °C and the acyl sultam **1** (1 equiv) in dry CH_2Cl_2 (0.25 M) was added, followed by diisopropylethylamine (2.4 equiv). The solution was then stirred at −10 °C for 30 min before being cooled to −78 °C. The aldehyde (2.4 equiv) in dry CH_2Cl_2 was then added. The solution was then stirred at the appropriate temperature and time before being quenched with pH 7 phosphate buffer at −78 °C. The resulting mixture was then allowed to warm at room temperature after which it was diluted with ether. The aqueous phase was then separated and the organic phase was washed twice with saturated aqueous NH_4Cl, dried over $MgSO_4$, filtered and the filtrate concentrated in vacuo. Flash chromatography (ethyl acetate/hexanes) then yielded the pure adducts.

4.3. General procedure B: ring closing enyne metathesis

To the enyne and Grubbs' second generation catalyst (5 or 10 mol %) was added dry, degassed toluene (0.01 M) at room temperature and under an atmosphere of ethylene. The solution was then heated at 80 °C overnight before being cooled back to room temperature and concentrated in vacuo. Flash chromatography (ethyl acetate/hexanes) then yielded the pure products.

4.4. General procedure C: Diels–Alder additions

To the diene and dienophile (2 equiv) was added dry toluene (0.1 M) at room temperature and under an atmosphere of nitrogen. The reaction mixture was then stirred at the appropriate temperature and time before being concentrated in vacuo. Flash chromatography (ethyl acetate/hexanes) then yielded the pure adducts. Reaction selectivity was determined either by analysis of the crude ^{1}H NMR spectrum, or by flash chromatography.

4.5. *N*-(1*S*)-[(2*R*,3*R*)-6-Benzyloxy-3-hydroxy-2-allyl-hex-4-ynoyl]bornane-10,2-sultam 3a

Following general procedure A, the reaction between *N*-(1*S*)-(4-pentenoyl)bornane-10,2-sultam **1** (1.0 g, 3.4 mmol) and 4-benzyloxy-2,3-butynal **2a** (1.8 g, 10 mmol) was carried out by stirring at −78 °C for 5 h before being quenched. Flash chromatography (33% ethyl acetate/hexanes) yielded the title compound **3a** (1.5 g, 94% yield) as a viscous yellow oil, which was crystallised from ethyl acetate/hexanes to give colourless needles. Mp 104–105 °C. $[\alpha]_D = -52.0$ (*c* 0.50, chloroform). IR ($CDCl_3$) $\nu = 3482$b (O–H), 3017s, 2963s, 1688s (C=O), 1496w, 1455m, 1442m, 1414m, 1393m, 1337s, 1269s, 1237s, 1216s, 1166s, 1136s, 1070s, 993m, 923m, 876w, 754s, 699m, 668s cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.95$ and 1.14 (s, 3H, aux CH_3), 1.28–1.38 (m, 2H, aux), 1.82–2.02 (m, 5H, aux), 2.68–2.72 (m, 2H, H3), 3.41 and 3.50 (AB q, $J = 13.9$ Hz, 2H, aux H10), 3.45–3.50 (m, 1H, H2), 3.88 (t, $J = 6.4$ Hz, 1H, aux H2), 4.22 (d, $J = 1.7$ Hz, 2H, H4′), 4.59 (s, 2H, BnH), 4.82 (td, $J = 4.5$, 1.7 Hz, 1H, H1′), 4.99–5.14 (m, 2H, H5), 5.81–5.92 (m, 1H, H4), 7.27–7.37 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 20.0$ and 20.9 (aux CH_3), 33.3 (C3), 26.5, 33.0 and 38.4 (aux CH_2), 44.8 (aux CH), 47.8 and 48.3 (aux 4 °C), 49.9 (C2′), 53.3 (aux C10), 57.5 (C4′), 62.3 (C1′), 65.4 (aux C2), 71.6 (benzyl C), 82.2 and 84.7 (alkyne C), 118.0 (C5), 127.9, 128.2 and 128.5 (Ph C), 134.4 (Ph 4 °C), 137.7 (C4), 173.6 (C1). HRMS calcd for $(C_{26}H_{33}NNaO_5S)^+$: *m*/*z* 494.1977. Found: 494.1980. Anal. Calcd for $C_{26}H_{33}NO_5S$: C, 59.54; H, 7.85; N, 3.31. Found: C, 59.29; H, 7.83; N, 3.31.

4.6. *N*-(1*S*)-[(2*R*)-2-((1*R*)-1-Hydroxy-3-phenyl-2-propyn-1-yl)-4-pentenoyl]bornane-10,2-sultam 3b

Following general procedure A, the reaction between *N*-(1*S*)-(4-pentenoyl)bornane-10,2-sultam **1** (1.0 g, 3.4 mmol) and phenylpropynal **2b** (1.0 mL, 8.2 mmol) was carried out by stirring at −10 °C for 3 h before being cooled to −78 °C for the quench. Flash chromatography (25% ethyl acetate/hexanes) yielded title compound **3b** (1.4 g, 93% yield) as a yellow foam. $[\alpha]_D^{21} = -91.0$ (*c* 0.73, chloroform). IR (nujol) $\nu = 3437$m (O–H), 1667s (C=O), 1641w, 1490m, 1444m, 1421w, 1393w, 1334m, 1269m, 1242m, 1221m, 1167m, 1134s, 1071s, 996m, 922s, 870w, 760s, 693m. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.97$ (s, 3H, aux CH_3), 1.16 (s, 3H, aux CH_3), 1.35 (m, 2H, aux), 1.90 (m, 3H, aux), 2.04 (m, 2H, aux), 2.77 (m, 2H, H3), 3.20 (d, $J = 3.3$ Hz, 1H, OH), 3.50 (m, 3H, H2 and aux H10), 3.92 (t, $J = 6.4$ Hz, 1H, aux H2), 4.99–5.18 (m, 3H, H5 and H1′), 5.91 (m, 1H, H4), 7.30 (m, 3H, Ph H3, Ph H4 and Ph H5), 7.46 (m, 2H, Ph H2 and Ph H6). ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 20.1$ and 21.1 (aux CH_3), 26.6 and 33.1 (aux CH_2), 33.4 (C3), 38.5 (aux CH_2), 44.9 (aux CH), 48.0 and 48.5 (aux 4 °C), 50.1 (C2), 53.4 (aux C10), 62.9 (C1′), 65.5 (aux C2), 86.2 (C3′), 87.2 (C2′), 118.1 (C5), 122.7 (Ph C1), 128.4 (Ph C3 and C5), 128.6 (Ph C4), 132.1 (Ph C2 and C6), 134.8 (C4), 174.0 (C=O). HRMS calcd for $(C_{24}H_{30}NO_4S)^+$: *m*/*z* 428.1896. Found: 428.1888. Anal. Calcd for $C_{24}H_{29}NO_4S$: C, 67.42; H, 6.84; N, 3.28. Found: C, 67.31; H, 6.90; N 2.97.

4.7. *N*-(1*S*)-[(2*R*)-2-((1*R*)-1-Hydroxy-3-trimethylsilyl-2-propyn-1-yl)-4-pentenoyl]bornane-10,2-sultam 3c

Following general procedure A, the reaction between *N*-(1*S*)-(4-pentenoyl)bornane-10,2-sultam **1** (1.0 g, 3.4 mmol) and trimethylsilylpropynal **2c** (0.97 g, 7.7 mmol) was carried out by stirring at −10 °C overnight before being cooled to −78 °C for the quench. Flash chromatography (20% ethyl acetate/hexanes) yielded the title compound **3c** (1.3 g, 87% yield) as a white solid. Mp 149–150 °C. $[\alpha]_D^{20} = -90.0$ (*c* 0.95, chloroform). IR (nujol) $\nu = 3502$m (O–H), 1667s (C=O), 1326s, 1274m, 1247m, 1222m, 1165m, 1137s, 1065s, 1034m, 992w, 949w, 919w, 845s, 801w, 772m, 760m. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.16$ (s, 9H, TMS CH_3), 0.96 (s, 3H, aux CH_3), 1.14 (s, 3H, aux CH_3), 1.33 (m, 2H, aux), 1.93 (m, 5H, aux), 5.37 (m, 2H, H3), 3.17 (d, $J = 3.2$ Hz, 1H, OH), 3.46 (m, 3H, H2 and aux H10), 3.89 (t, $J = 6.3$ Hz, 1H, aux H2), 4.76 (t, $J = 3.2$ Hz, 1H, H1′), 5.05 (m, 2H, H5), 5.88 (m, 1H, H4). ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = -0.1$ (TMS CH_3), 20.1 and 21.0 (aux CH_3), 26.6 (aux CH_2), 33.1 and 33.2 (C3 and aux CH_2), 38.5 (aux CH_2), 44.9 (aux CH), 47.9 and 48.4 (aux 4 °C), 49.6 (C2), 53.4 (aux C10), 62.7 (C1′), 65.5 (aux C2), 91.2 (C3′), 103.2 (C2′), 117.9 (C5), 134.9 (C4), 174.2 (C=O). ESI-MS *m*/*z* 406 $[M-OH]^+$,

424.3 $[M+H]^+$, 446.3 $[M+Na]^+$, 478.3 $[M+MeOH+Na]^+$. HRMS calcd for $(C_{21}H_{33}NO_4SSiNa)^+$: m/z 446.1792. Found: 446.1798. Anal. Calcd for $C_{21}H_{33}NO_4SSi$: C, 59.54; H, 7.85; N, 3.31. Found: C, 59.29; H, 7.86; N, 3.22.

4.8. *N*-(1*S*)-[1-[(1*R*,2*R*)-2-Hydroxy-3-(3-(benzyloxy)prop-1-en-2-yl)-3-cyclopentenyl]carbonyl]bornane-10,2-sultam 4a

Following general procedure B, enyne **3a** (150 mg, 0.32 mmol) and Grubbs' second generation catalyst (14 mg, 5 mol %) gave, after flash chromatography (50% ethyl acetate/hexanes), title compound **4a** (150 mg, 100% yield) as a brown oil. $[\alpha]_D = -29.2$ (c 0.25, chloroform). IR ($CHCl_3$) $\nu = 3483$br s (O–H), 2958s (C–H), 2883s (C–H), 1692 (C=O), 1602w, 1454m, 1392m, 1329s, 1269s, 1236s, 1211s, 1165m, 1132s, 1117s, 1063s, 996s, 831w, 751s, 699w, 617w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) $\delta = 0.98$ and 1.18 (s, 3H, aux CH_3), 1.28–1.46 (m, 2H, aux), 1.88–2.35 (m, 5H, aux), 2.66 (ddd, $J = 17.8$, 8.4, 2.9 Hz, 1H, H5), 2.84 (d, $J = 7.7$ Hz, 1H, OH), 3.01 (dd, $J = 17.8$, 7.0 Hz, 1H, H5), 3.48 and 3.55 (AB q, $J = 13.8$ Hz, 2H, aux H10), 3.86 (dt, $J = 8.4$, 7.0 Hz, 1H, H1), 3.97 (dd, $J = 7.7$, 5.1 Hz, 1H, aux H2), 4.16 and 4.23 (ABq, $J = 12.2$ Hz, 2H, $BnOCH_2$), 4.52 (s, 2H, Bn), 5.32–5.35 (m, 2H, H2 and H2′), 5.52 (s, 1H, H2′), 6.02 (t, $J = 2.9$ Hz, 1H, H4), 7.27–7.37 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 20.0$ and 21.1 (aux CH_3) 26.6 (aux CH_2), 33.0 (aux CH_2), 35.5 (C5), 38.8 (aux CH_2), 44.8 (aux CH), 47.7 (aux C10), 48.0 and 48.5 (aux 4 °C), 53.3 (aux CH_2), 65.7 (C2), 72.1 (Bn and $BnOCH_2$), 77.4 (aux C2), 115.9 (C2′), 127.7, 128.0 and 128.5 (Ph), 129.5 (C4), 138.1, 138.4, 141.8, 171.8 (C=O). HRMS calcd for $(C_{26}H_{33}NNaO_5S)^+$: m/z 494.1977. Found: 494.1975.

4.9. *N*-(1*S*)-[1-[(1*R*,2*R*)-2-Hydroxy-3-(1-phenylethen-1-yl)-3-cyclopentenyl]carbonyl]bornane-10,2-sultam 4b

Following general procedure B, enyne **3b** (700 mg, 1.6 mmol) and Grubbs' second generation catalyst (70 mg, 0.08 mmol) gave, after flash chromatography (30% ethyl acetate/hexanes), title compound **4b** (650 mg, 93% yield) as an off-white solid. Mp 167–170 °C. $[\alpha]_D^{21} = -24$ (c 0.70, chloroform). IR (nujol) $\nu = 3541$m (O–H), 1673s (C=O), 1629w (C=C), 1391m, 1362w, 1324s, 1314m, 1220m, 1167w, 1138m, 1121m, 1067s, 1050m, 994w, 954w, 933w, 884m, 839m, 773m, 702m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) $\delta = 0.99$ (s, 3H, aux CH_3), 1.18 (s, 3H, aux CH_3), 1.26–1.47 (m, 2H, aux), 1.89–2.19 (m, 5H, aux), 2.64 (ddd, $J = 17.7$, 8.4, 2.9 Hz, 1H, H5), 2.99 (m, 2H, H5 and OH), 3.50 and 3.56 (ABq, $J = 13.8$ Hz, 2H, aux H10), 3.96 (m, 2H, H1 and aux H2), 5.21 (s, 1H, H2′), 5.41 (t, $J = 7.3$ Hz, 1H, H2), 5.57 (s, 1H, H2′), 5.72 (t, $J = 2.9$ Hz, 1H, H4), 7.30 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 20.1$ and 21.2 (aux CH_3), 26.6 and 33.1 (aux CH_2), 35.4 (C5), 38.9 (aux CH_2), 44.9 (aux CH), 48.0 (aux 4 °C), 48.3 (C1), 48.6 (aux 4 °C), 53.4 (aux C10), 65.8 (aux C2), 77.4 (C2), 115.8 (C2′), 127.5 (Ph CH), 128.2 (Ph CH), 128.6 (Ph CH), 132.5 (C4), 141.9 (Ph 4 °C), 144.0 and 144.1 (C3 and C1′), 171.9 (C=O). ESI-MS m/z 410.4 $[M-OH]^+$, 450.4 $[M+Na]^+$. HRMS calcd for $(C_{24}H_{29}NO_4SNa)^+$: m/z 450.1710. Found: 450.1713. Anal. Calcd for $C_{24}H_{29}NO_4S$: C, 67.42; H, 6.84; N, 3.28. Found: C, 67.72; H, 6.84; N, 3.37.

4.10. *N*-(1*S*)-[1-[(1*R*,2*R*)-2-Hydroxy-3-(1-trimethylsilyl-ethen-1-yl)-3-cyclopentenyl]carbonyl]bornane-10,2-sultam 4c

Following general procedure B, enyne **3c** (620 mg, 1.5 mmol) and Grubbs' second generation catalyst (125 mg, 0.15 mmol) gave, after flash chromatography (25% ethyl acetate/hexanes), title compound **4c** (520 mg, 84% yield) as an off-white solid. Mp 139–142 °C. $[\alpha]_D^{20} = -34.5$ (c 0.48, chloroform). IR (nujol) $\nu = 3542$w (O–H), 1682s (C=O), 1333m, 1271w, 1248m, 1208w, 1167m, 1134m, 1117m, 1086m, 1055s, 1015w, 994w, 924w, 902w, 839s, 778w, 758w, 723w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) $\delta = 0.17$ (s, 9H, TMS CH_3), 0.98 (s, 3H, aux CH_3), 1.18 (s, 3H, aux CH_3), 1.35 (m, 2H, aux), 1.90 (m, 3H, aux), 2.12 (m, 2H, aux), 2.65 (ddd, $J = 17.5$, 8.4, 2.8 Hz, 1H, H5), 2.73 (d, $J = 7.6$ Hz, 1H, OH), 3.00 (dd, $J = 17.5$, 7.0 Hz, 1H, H5), 3.48 and 3.54 (AB q, $J = 13.8$ Hz, 2H, aux H10), 3.82 (dt $J = 8.4$, 7.0 Hz, 1H, H1), 3.97 (dd, $J = 7.7$, 5.1 Hz, 1H, aux H2), 5.32 (td, $J = 7.3$, 1.9 Hz, 1H, H2), 5.53 (d, $J = 2.6$ Hz, 1H, H2′), 5.85 (t, $J = 2.4$ Hz, 1H, H4), 6.03 (d, $J = 2.6$ Hz, 1H, H2′). ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = -0.5$ (TMS CH_3), 20.1 and 21.1 (aux CH_3), 26.6, 33.0, 35.6 and 38.8 (aux CH_2), 44.9 (aux C4), 47.7 (C1), 48.0 and 48.5 (aux 4 °C), 53.3 (aux C10), 65.7 (aux C2), 77.6 (C2), 127.1 (C2′), 129.9 (C4), 144.2 and 145.5 (C1′ and C3), 172.0 (C=O). ESI-MS m/z 406.5 $[M-OH]^+$, 446.5 $[M+Na]^+$. HRMS calcd for $(C_{21}H_{33}NO_4SSiNa)^+$: m/z 446.1792. Found: 446.1791. Anal. Calcd for $C_{21}H_{33}NO_4SSi$: C, 59.54; H, 7.85; N, 3.31. Found: C, 59.80; H, 7.78; N, 3.31.

4.11. *N*-(1*S*)-[1-[(1*S*,2*R*)-2-Hydroxy-3-(1-trimethylsilyl-ethen-1-yl)-3-cyclopentenyl]carbonyl]bornane-10,2-sultam *anti*-4c

Following general procedure B, enyne *anti*-**3c** (150 mg, 0.35 mmol) and Grubbs' second generation catalyst (30 mg, 10 mol %) gave, after flash chromatography (25% ethyl acetate/hexanes), title compound *anti*-**4c** (150 mg, 100% yield) as a white solid. Mp 110–114 °C. $[\alpha]_D = -72.9$ (c 1.1, $CHCl_3$). IR (powder) $\nu = 3509$bm (O–H), 3008s, 2958m, 1686s (C=O), 1482w, 1456m, 1411m, 1392m, 1376m, 1326s, 1265s, 1248s, 1235s, 1211s, 1164s, 1132s, 1116s, 1067s, 1042s, 997m, 838s, 750s, 637w cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.16$ (s, 9H, TMS), 0.99 (s, 3H, aux CH_3), 1.20 (s, 3H, aux CH_3), 1.37–1.44 (m, 2H, aux CH_2), 1.80–2.35 (m, 5H, aux CH_2 and CH), 2.75 (d, $J = 4.6$ Hz, 1H, OH), 2.81–2.84 (m, 2H, H5), 3.46–3.62 (m, 3H, H1 and aux H10), 3.92 (dd, $J = 7.1$, 5.5 Hz, 1H, aux H2), 5.08–5.11 (m, 1H, H2), 5.51 (d, $J = 2.8$ Hz, 1H, H2′), 5.82 (t, $J = 2.6$, 1H, H4), 5.94 (d, $J = 2.8$ Hz, 1H, H2′). ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.6 (TMS) 20.0 (aux CH_3), 21.0 (aux CH_3), 26.6 and 32.9 (aux CH_2), 33.4 (C5), 38.6 (aux CH_2), 44.7 (aux CH), 47.9 and 48.6 (aux 4 °C), 53.2 (C1), 53.3 (aux C10), 65.7 (aux C2), 82.0 (C2), 126.7 (C2′), 130.3 (C4), 144.2 and 144.6 (C1′ and C3), 172.9 (C=O). HRMS calcd for $(C_{21}H_{33}NNaO_4SSi)^+$: m/z 446.1797. Found: 446.1791. Anal. Calcd for

$C_{21}H_{33}NO_4SSi0.08CH_2Cl_2$: C, 58.82; H, 7.76; N, 3.25. Found: C, 58.80; H, 7.79; N, 3.30.

4.12. *N*-(1*S*)-[(2*R*,3*R*)-6-Benzyloxy-3-triethylsilyloxy-2-propen-3-yl-hex-4-ynoyl]bornane-10,2-sultam 3a-TES

To a solution of alcohol **3a** (470 mg, 1.0 mmol) in 0.15 mL ethyl acetate were added imidazole (140 mg, 2.0 mmol) and DMF (0.5 mL) under an atmosphere of nitrogen. Chlorotriethylsilane (0.21 mL, 2.0 mmol) was then added and the reaction mixture was stirred for 4 h at an ambient temperature. The suspension was diluted with 5 mL ethyl acetate, washed four times with water, dried ($MgSO_4$), filtered and the filtrate concentrated in vacuo. Flash chromatography (10% ethyl acetate/hexanes) yielded the title compound (400 mg, 69%) as a colourless oil. $[\alpha]_D = -27.2$ (*c* 1.04, chloroform). IR ($CDCl_3$) $\nu = 2959$s (C–H), 2877s (C–H),1687s (C=O), 1641w, 1457s, 1414m, 1386s, 1339s, 1265s, 1237s, 1214s, 1166s, 1136s, 1090s, 1003m, 912s, 828w, 742s, 850s, 517s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) $\delta = 0.65$–0.73 (m, 6H, TES CH_2), 0.94–1.01 (m, 12H, TES CH_3 and aux CH_3), 1.14 (s, 3H, aux CH_3), 1.26–1.28 (m, 2H, aux CH_2), 1.82–1.85 (m, 3H, aux), 2.02–2.05 (m, 2H, aux), 2.51–2.69 (m, 2H, H3), 3.34 and 3.45 (ABq, $J = 13.8$ Hz, 2H, aux H10), 3.49–3.54 (m, 1H, H2), 3.81 (t, $J = 6.4$ Hz, 1H, aux H2), 4.20 (d, $J = 1.7$ Hz, 2H, H4′), 4.58 (s, 2H, BnH), 4.72 (dt, $J = 8.4$ and 1.7 Hz, 1H, H1′), 4.98–5.11 (m, 2H, H5), 5.75–5.89 (m, 1H, H4), 7.27–7.38 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 5.1$ (TES CH_2), 6.9 (TES CH_3), 20.1 and 21.0 (aux CH_3), 26.6 (aux CH_2), 33.0 (aux CH_2), 34.4 (C3), 38.7 (aux CH_2), 44.7 (aux CH), 47.8 and 48.2 (aux 4 °C), 52.4 (C2), 53.2 (aux C10), 57.7 (C4′), 62.3 (C1′), 65.4 (aux C2), 71.2 (Bn C), 81.5 (C3′), 86.6 (C2′), 117.8 (C5), 127.8 (Ph), 128.2 and 128.4 (Ph), 134.4 (C4), 138.1 (Ph 4 °C), 171.8 (C1). HRMS calcd for $(C_{32}H_{47}NNaO_5SSi)^+$: *m*/*z* 608.2842. Found: 608.2828.

4.13. *N*-(1*S*)-[1-[(1*R*,2*R*)-2-Triethylsilyloxy-3-(3-(benzyloxy)prop-1-en-2-yl)-3-cyclopentenyl]carbonyl]bornane-10,2-sultam 5a

Following general procedure B, enyne **3a-TES** (400 mg, 0.69 mmol) and Grubbs' second generation catalyst (29 mg, 5 mol %) gave, after flash chromatography (20% diethyl ether/hexanes), the title compound **5a** (400 mg, 100% yield) as a dark oil. $[\alpha]_D = +18.1$ (*c* 0.30, chloroform). IR ($CDCl_3$) *v* 2959s (C–H), 2930s (C–H), 2875s (C–H), 1698s (C=O), 1637w, 1604w, 1496w, 1456s, 1414m, 1384s, 1330s, 1294w, 1265m, 1234m, 1208s, 1165m, 1132s, 1108s, 1010m, 970w, 915s, 852w, 805w, 720s, 850s, 619m cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.54$–0.64 (m, 6H, TES CH_2), 0.82–1.06 (m, 9H, TES CH_3), 0.98 (s, 3H, aux CH_3), 1.18 (s, 3H, aux CH_3), 1.30–1.42 (m, 2H, aux), 1.86–1.96 (m, 3H, aux), 2.06–2.36 (m, 2H, aux), 2.49 (ddd, $J = 17.1$, 7.5 and 3.3 Hz, 1H, H5), 3.14 (ddd, $J = 17.1$, 8.1, 0.8 Hz, 1H, H5), 3.45 and 3.52 (ABq, $J = 13.8$ Hz, 2H, aux H10), 3.65 (td, $J = 7.8$ and 5.9 Hz, 1H, H1), 3.88 (dd, $J = 7.8$ and 5.1 Hz, 1H, aux H2), 4.14 and 4.22 (ABq, $J = 12.8$ Hz, 2H, $BnOCH_2$), 4.45 (s, 2H, Bn), 5.33 (s, 1H, H2′), 5.35 (s, 1,H, H2′), 5.49 (dd, $J = 5.9$ and 1.3 Hz, 1H, H2), 5.97 (m, 1H, H4), 7.27–7.37 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 5.2$ (TES CH_2), 7.2 (TES CH_3), 21.2 and 20.0 (aux CH_3), 26.5 (aux CH_2), 33.4 (aux CH_2), 35.0 (C5), 38.8 (aux CH_2), 44.8 (aux CH), 48.5 and 47.8 (aux 4 °C), 50.3 (C1), 53.3 (aux C10), 66.1 (aux C2), 71.8 ($BnOCH_2$), 71.9 (Bn), 77.4 (C2), 114.3 (C2′), 127.7 and 127.8 and 128.5 (Ph CH), 129.5 (C4), 138.5, 138.6, 142.8, 169.0 (C=O). HRMS calcd for $(C_{32}H_{47}NNaO_5SSi)^+$: *m*/*z* 608.2842. Found: 608.2830.

4.14. *N*-(1*S*)-[1-[(1*R*,2*R*)-2-Triethylsilyloxy-3-(1-phenylethen-1-yl)-3-cyclopentenyl]carbonyl]bornane-10,2-sultam 5b

To a solution of the alcohol **4b** (300 mg, 0.70 mmol) in 1.5 mL dry DMF were added imidazole (92 mg, 1.4 mmol) followed by chlorotriethylsilane (170 μL, 1.0 mmol) under an atmosphere of nitrogen. A precipitate formed almost immediately upon addition of the chlorotriethylsilane. The suspension was diluted with 20 mL CH_2Cl_2, washed three times with water, dried ($MgSO_4$), filtered and the filtrate concentrated in vacuo to yield an off-white solid. Flash chromatography (7.5% ethyl acetate/hexanes) yielded the title compound **5b** (340 mg, 90%) as a white solid. Mp 153–155 °C. $[\alpha]_D^{22} = +58$ (*c* 1.0, chloroform). IR (nujol) $\nu = 1686$s (C=O), 1630w (C=C), 1362m, 1332m, 1294m, 1278m, 1245w, 1209s, 1164m, 1134m, 1116m, 1072m, 1021w, 997w, 968w, 942w, 917w, 904w, 864w, 856w, 827w, 776m, 744m, 701m cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.52$ (m, 6H, TES CH_2), 0.87 (t, $J = 7.9$ Hz, 9H, TES CH_3), 0.98 (s, 3H, aux CH_3), 1.18 (s, 3H, CH_3), 1.35 (m, 2H, aux), 1.91 (m, 3H, aux), 2.17 (m, 2H, aux), 2.48 (ddd, $J = 17.0$, 7.6, 3.2 Hz, 1H, H5), 3.14 (m, 1H, H5), 3.45 and 3.53 (ABq, $J = 13.8$ Hz, 2H, aux H10), 3.77 (td, $J = 7.6$ and 6.1 Hz, 1H, H1), 3.89 (m, 1H, aux H2), 5.29 (s, 1H, H2′), 5.36 (s, 1H, H2′), 5.44 (d, $J = 6.1$ Hz, 1H, H2), 5.75 (m, 1H, H4), 7.40 (m, 5H, Ph H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 5.6$ (TES CH_2), 7.2 (TES CH_3), 20.1 and 21.4 (aux CH_3), 26.6 and 33.5 (aux CH_2), 35.0 (C5), 39.0 (aux CH_2), 45.0 (aux CH), 47.9 and 48.6 (aux 4 °C), 50.6 (C1), 53.4 (aux H10), 66.2 (aux C2), 77.6 (C2), 114.9 (C2′), 127.7 (Ph CH), 126.2 (Ph CH), 128.3 (Ph CH), 132.7 (C4), 141.3, 144.3, 145.3, 169.1 (C=O). ESI-MS *m*/*z* 410.4 $[M-OTES]^+$, 546.4 $[M+Na]^+$. HRMS calcd for $(C_{30}H_{43}NO_4SSiNa)^+$: *m*/*z* 564.2580. Found: 564.2578. Anal. Calcd for $C_{30}H_{43}NO_4SSi$: C, 66.50; H, 8.00; N, 2.59. Found: C, 66.14; H, 7.68; N, 2.50.

4.15. *N*-(1*S*)-[16-[(8*R*,9*R*,14*R*,16*R*,17*R*)-12-(Benzyloxymethyl)-17-hydroxy-8-nitro-6,7-dioxo-7,8,9,11,14,15,16,17-Octahydro-6*H*-cyclopenta[*a*]phenanthrene]carbonyl]bornane-10,2-sultam 7a

Following general procedure C, diene **4a** (100 mg, 0.21 mmol) and 3-nitro-1,2-naphthoquinone (86 mg, 0.42 mmol) were stirred at room temperature for 3 h before flash chromatography (50–60% ethyl acetate/hexanes) yielded the major diastereomer of title compound **7a** (97 mg, 73% yield) as a red amorphous solid. Reaction selectivity: 75:25. Minor diastereomers were detected but not characterised. Mp 78–81 °C. $[\alpha]_D = +9.5$ (*c* 0.15, chloroform). IR ($CDCl_3$) $\nu = 3460$s (O–H), 2962s (C–H), 2885s

(C–H), 1719s (C=O), 1700s (C=O), 1684s (C=O), 1594m, 1550m, 1455w, 1393m, 1335m, 1296m, 1270m, 1239m, 1219m, 1167w, 1135m, 1117m, 1070w, 949w, 772w, 642m cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.98$ (s, 3H, aux CH_3), 1.13 (s, 3H, aux CH_3), 1.30–1.46 (m, 2H, aux), 1.89–2.33 (m, 7H, H11, H15 and aux), 2.63 (ddd, $J = 13.0$, 8.6, 7.6 Hz, 1H, H15), 2.99 (m, 1H, H11), 3.47 and 3.55 (AB q, $J = 13.8$ Hz, 2H, aux H10), 3.90–4.16 (m, 6H, aux H2, $BnOCH_2$, H9, H16 and H14), 4.34 and 4.38 (ABq, $J = 11.9$ Hz, 2H, BnH), 5.10 (d, $J = 4.9$ Hz, 1H, H17), 7.24–7.39 (m, 6H, H1 and Ph), 7.47 (td, $J = 7.7$, 0.9 Hz, 1H, H3), 7.49 (td, $J = 7.7$, 1.2 Hz, 1H, H2), 8.12 (dd, $J = 7.8$, 1.2 Hz, 1H, H4). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 20.0$ and 21.1 (aux CH_3), 26.6 (C11), 28.0 (aux CH_2), 33.0 (aux CH_2), 37.3 (C15), 38.7 (aux CH_2), 44.7 (aux CH), 44.8 (C9), 46.8 (C14), 47.4 (C16), 48.0 and 48.7 (aux 4 °C), 53.2 (aux C10), 65.4 (aux C2), 68.4 (Bn), 72.1 ($BnOCH_2$), 72.3 (C17), 96.9, 127.9 (Ph), 128.0, 128.2 (Ph), 128.6 (Ph), 129.2 and 129.0 (C2 and C3), 130.2 (C4), 130.7, 136.3 (C1), 138.0, 138.3, 142.4, 173.5 (aux C=O), 180.0 and 183.3 (C6 and C7). HRMS calcd for $(C_{36}H_{38}N_2NaO_9S)^+$: m/z 697.2196. Found: 697.2198.

4.16. *N*-(1*S*)-[16-[(8*R*,9*R*,14*R*,16*R*,17*R*)-17-Hydroxy-8-nitro-6,7-dioxo-12-phenyl-7,8,9,11,14,15,16,17-octahydro-6*H*-cyclopenta[*a*]phenanthrene]carbonyl]bornane-10,2-sultam 7b

Following general procedure C, diene **4b** (50 mg, 0.12 mmol), 3-nitro-1,2-naphthoquinone (45 mg, 0.22 mmol) and a small amount of potassium carbonate were stirred at room temperature for 3 h. Reaction selectivity: 55:35:10. Flash chromatography (30–40% ethyl acetate/hexanes) yielded an inseparable mixture of the two major diastereomers (40 mg, 53% yield) together with decomposition products (the minor diastereomer was not isolated). Characterisation was performed on the mixture; *major* and *minor* refer to the diastereomer ratio in the crude reaction mixture. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.96$ (s, 6H, aux CH_3 *major* and *minor*), 1.12 (s, 3H, aux CH_3 *minor*), 1.13 (s, 3H, aux CH_3 *major*), 1.35 (m, aux), 1.89 (m, aux), 1.93–2.12 (m, aux), 2.15–2.36 (m, H15 *minor* and aux), 2.40 (ddd partially obscured, $J = 19.2$, 4.0, 1.3 Hz, 1H, H11 *major*), 2.47 (ddd, $J = 18.8$, 11.6, 3.7 Hz, 1H, H11 *minor*), 2.66 (ddd, $J = 13.0$, 9.1, 4.5 Hz, 1H, H15 *minor*), 2.93 (d, $J = 8.4$ Hz, 1H, OH *major*), 3.03 (ddd, $J = 18.8$, 6.8, 1.7 Hz, 1H, H11 *minor*), 3.11 (m, 1H, H15 *major*), 3.21 (ddd, $J = 19.2$, 7.4, 1.1 Hz, 1H, H11 *major*), 3.40–3.51 (m, 6H, H14 *major*, H16 *major* and aux H10 *major* and *minor*), 3.90 (m, 3H, H16 *minor* and aux H2 *major* and *minor*), 4.14 (m, 1H, H14 *minor*), 4.23 (m, 2H, H9 *major* and *minor*), 4.59 (s, 1H, OH *minor*), 4.84 (d, $J = 3.5$ Hz, 1H, H17 *minor*), 5.17 (m, 1H, H17 *major*), 7.20–7.31 (m, 10H, Ph *major* and *minor*), 7.36 (m, 2H, H1 *major* and *minor*), 7.49 (m, 2H, H3 *major* and *minor*), 7.66 (m, 2H, H2 *major* and *minor*), 8.16 (m, 2H, H4 *major* and *minor*). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 20.0$, 21.0, 21.1, 26.5, 26.6, 27.5, 28.1, 29.6, 29.8, 29.9, 32.1, 33.0, 33.1, 38.6, 38.7, 40.2, 42.1, 44.3, 44.8, 44.9, 46.7, 47.0, 47.1, 47.5, 48.0, 48.7, 48.8, 49.5, 53.1, 53.3, 65.1, 65.9, 72.1, 73.7, 96.2, 97.4, 127.6, 127.7, 128.0, 128.3, 128.5, 128.6, 129.0, 129.1, 129.3, 129.4, 130.3, 130.4, 130.7, 130.8, 130.9, 133.7, 136.4 136.5, 137.3, 138.0, 138.5, 138.6, 142.0, 142.1, 169.5, 174.6, 179.9, 180.1, 183.0, 183.7. ESI-MS m/z 653.1 $[M+Na]^+$, 685.2 $[M+MeOH+Na]^+$. HRMS calcd for $(C_{34}H_{34}N_2O_8SNa)^+$: m/z 653.1928. Found: 653.1929.

4.17. *N*-(1*S*)-[16-(8*R*,9*R*,14*R*,16*R*,17*R*)-12-(Benzyloxymethyl)-8-nitro-6,7-dioxo-17-(triethylsilyloxy)-7,8,9,11,14,15,16,17-octahydro-6*H*-cyclopenta[*a*]phenanthrene]carbonyl]bornane-10,2-sultam 8a

Following general procedure C, diene **5a** (68 mg, 0.12 mmol) and 3-nitro-1,2-naphthoquinone (47 mg, 0.23 mmol) were stirred at room temperature for 3 h before flash chromatography (10–20% ethyl acetate/hexanes) yielded the major diastereomer of title compound **8a** (52 mg, 56% yield) as an amorphous solid. Reaction selectivity: 80:20 (toluene) and 85:15 (CH_2Cl_2). The minor diastereomer was detected but not characterised. Mp 77–79 °C. $[\alpha]_D = +30.1$ (*c* 1.0, chloroform). IR ($CHCl_3$) $\nu = 2956$s (C–H), 2876 (C–H), 1698br s (C=O), 1600w, 1549s, 1456m, 1387m, 1331s, 1267m, 1238m, 1209m, 1165m, 1132m, 1086m, 1066m, 1004m, 746m cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.56$–0.67 (m, 6H, TES CH_2), 0.81–0.97 (m, 12H, TES CH_3 and aux CH_3), 1.15 (s, 3H, aux CH_3), 1.33–1.45 (m, 2H, aux), 1.86–1.93 (m, 3H, aux), 1.98–2.32 (m, 4H, aux, H15 and H11), 2.68–2.80 (m, 1H, H15), 2.96 (ddd, $J = 19.0$, 6.9, 1.6 Hz, 1H, H11), 3.41 and 3.50 (ABq, $J = 13.8$ Hz, 2H, aux H10), 3.75–3.99 (m, 2H, H14 and aux H2), 4.00–4.11 (m, 4H, H9, H16 and BnH), 4.25 and 4.38 (ABq, $J = 11.4$ Hz, 2H, $BnOCH_2$), 5.55 (d, $J = 3.3$ Hz, 1H, H17), 7.27–7.33 (m, 5H, Ph), 7.39 (d, $J = 7.4$ Hz, 1H, H1), 7.47 (t, $J = 7.7$ Hz, 1H, H3), 7.65 (td, $J = 7.5$, 1.4 Hz, 1H, H2), 8.11 (dd, $J = 7.9$, 1.3 Hz, 1H, H4).^{13}C NMR (100 MHz $CDCl_3$) $\delta = 5.0$ (TES CH_2), 7.0 (TES CH_3), 20.0 and 21.0 (aux CH_3), 26.2 (C11), 26.6 (aux CH_2), 33.1 (aux CH_2), 37.1 (C15), 38.7 (aux CH_2), 42.8 (C9), 44.6 (aux CH), 46.5 (C16), 48.0 and 48.7 (aux 4 °C), 50.0, (C14), 53.2 (aux C10), 65.9 (aux C2), 69.2 ($PhCH_2O$), 72.5 ($BnOCH_2$), 72.5 (C17), 97.5, 124.9, 127.8 (Ph), 128.1 and 128.5 (Ph), 128.9 and 129.1 (C2 and C3), 130.2 (C4), 130.7, 136.3 (C1), 138.0, 140.8, 142.5, 168.5 (aux C=O), 180.2 and 183.6 (C6 and C7). HRMS calcd for $(C_{42}H_{52}N_2NaO_9SSi)^+$: m/z 811.3060. Found: 811.3052.

4.18. *N*-(1*S*)-[16-[(8*R*,9*R*,14*R*,16*R*,17*R*)-8-Nitro-6,7-dioxo-12-phenyl-17-triethylsilyloxy-7,8,9,11,14,15,16,17-octahydro-6*H*-cyclopenta[*a*]phenanthrene]carbonyl]bornane-10,2-sultam 8b

Following general procedure C, diene **5b** (200 mg, 0.37 mmol) 3-nitro-1,2-naphthoquinone (150 mg, 0.74 mmol) and a small amount of potassium carbonate were stirred at approx. 40 °C for 9 h before flash chromatography (15% ethyl acetate/hexanes) yielded the major diastereomer of title compound **8b** (200 mg, 73% yield) as a yellow foam. Reaction selectivity: 95:5. The minor diastereomer was not isolated. $[\alpha]_D^{22} = +51$ (*c* 1.0, chloroform). IR (nujol) $\nu = 1698$s (C=O), 1599w (C=C), 1548s, 1332m, 1271w, 1237w, 1208w, 1133w, 1071m, 1011w, 939w, 889w, 750s,

707m cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.26$ (m, 6H, TES CH_2), 0.76 (t, $J = 7.9$ Hz, 9H, TES CH_3), 0.97 (s, 3H, aux CH_3), 1.18 (s, 3H, aux CH_3), 1.31 (m, 2H, aux), 1.88 (m, 3H, aux), 2.04–2.20 (m, 3H, H11 and aux), 2.28 (ddd, $J = 13.1$, 8.3, 3.8 Hz, 1H, H15), 2.84 (m, 1H, H15), 3.26 (ddd, $J = 19.2$, 7.0, 2.0 Hz, 1H, H11), 3.41 and 3.52 (ABq, $J = 13.8$ Hz, 2H, aux H10), 3.79 (m, 1H, aux H2), 3.86 (m, 1H, H14), 4.17 (m, 2H, H9 and H16), 5.48 (d, $J = 3.1$ Hz, 1H, H17), 7.17 (m, 2H, Ph H), 7.22–7.34 (m, 3H, Ph H), 7.46 (m, 2H, H1 and H3), 7.66 (td, $J = 7.5$, 1.4 Hz, 1H, H2), 8.10 (dd, $J = 8.1$, 1.4 Hz, 1H, H4). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 4.67$ (TES CH_2), 6.87 (TES CH_3), 20.12 and 21.04 (aux CH_3), 26.69 (aux CH_2), 27.02 (C15), 33.10 and 38.71 (aux CH_2), 41.33 (C11), 42.78 (C14), 44.61 (aux CH), 47.14 (C9), 48.06 and 48.78 (aux 4 °C), 49.53 (C16), 53.20 (aux C10), 65.87 (aux C2), 73.37 (C17), 97.57 (C8), 128.15, 128.53, 128.74, 128.74, 128.96, 129.21, 130.28, 130.77, 136.33, 138.29, 139.66, 142.38, 168.78 (aux C=O), 180.12 (C6), 183.37 (C7). ESI-MS *m/z* 613.4 $[M-OTES]^+$, 767.4 $[M+Na]^+$. HRMS calcd for $(C_{40}H_{48}N_2O_8SSiNa)^+$: *m/z* 767.2793. Found: 767.2796. Anal. Calcd for $C_{40}H_{48}N_2O_8SSi$: C, 64.49; H, 6.49; N, 3.76. Found: C, 64.68; H, 6.40; N, 3.31.

4.19. *N*-(1*S*)-[2-[(2*R*,3*R*,5a*S*,11a*R*,11b*S*)-4-(Benzyloxymethyl)-3-hydroxy-6,11-dioxo-2,3,5,5a,6,11,11a,11b-octahydro-1*H*-cyclopenta[*a*]anthracene]carbonyl]bornane-10,2-sultam 9a

Following general procedure C, diene **4a** (100 mg, 0.17 mmol) and 1,4-naphthoquinone (54 mg, 0.34 mmol) were stirred at 80 °C overnight before flash chromatography (20% ethyl acetate/hexanes) yielded the major diastereomer of title compound **9a** (87 mg, 57% yield) as an amorphous solid. Reaction selectivity: 80:15:5 where the 5% contains two diastereomers. Minor diastereomers were detected but not characterised. Mp 62–65 °C. $[\alpha]_D = +12.5$ (*c* 0.30, chloroform). IR ($CHCl_3$) $\nu = 3504$br s (O–H), 2958s (C–H), 1692br s (C=O), 1592w, 1454w, 1392m, 1332m, 1251s, 1213s, 1165m, 1134s, 1116s, 1065s, 964w, 910w, 788w, 750s, 699m, 666w, 626w cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.99$ (s, 3H, aux CH_3), 1.19 (s, 3H, aux CH_3), 1.38–1.46 (m, 2H, aux), 1.89–1.95 (m, 3H, aux), 2.13–2.36 (m, 5H, H1, H5, aux), 2.51–2.57 (m, 1H, H5), 2.78 (dd, $J = 7.4$, 4.3 Hz, 1H, H1), 3.22 (m, 1H, H11b), 3.38 (ddd, $J = 11.3$, 7.0, 4.4 Hz, 1H, H5a), 3.50 and 3.55 (ABq, $J = 13.8$ Hz, 2H, aux H10), 3.62 (t, $J = 4.4$ Hz, 1H, H11a), 3.96 (m, 1H, aux H2), 4.02–4.15 (m, 3H, H2, $BnOCH_2$), 4.30 (s, 2H, BnH), 5.10 (d, $J = 4.5$ Hz, 1H, H3), 7.00–7.26 (m, 5H, Ph), 7.70 (m, 2H, H8 and H9), 7.94–7.96 (m, 1H, H10), 8.03–8.05 (m, 1H, H7). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 20.0$ and 21.2 (aux CH_3), 26.5 (aux CH_2), 28.1 (C5), 30.7 (C1), 33.1 (aux CH_2), 38.6 (C11b), 38.8 (aux CH), 44.9 (aux CH_2), 47.7 and 47.9 (aux 4 °C), 48.5 (C11a), 48.9 (C5a), 49.8 (C2), 53.3 (aux C10), 65.4 (aux C2), 68.9 ($PhCH_2O$), 71.4 ($BnOCH_2$), 72.6 (C3), 126.6, 127.1 (C10), 127.3 (C7), 127.6, 128.0 and 128.4 (Ph), 132.7, 134.2 and 134.4 (C8 and C9), 135.7, 138.3, 141.0, 174.7 (aux C=O), 197.1 and 198.6 (C6 and C11). ESI-MS calcd for $(C_{36}H_{39}NNaO_7S)^+$: *m/z* 652.2. Found: 652.3.

4.20. *N*-(1*S*)-[2-[(2*R*,3*R*,5a*S*,11a*R*,11b*S*)-3-Hydroxy-6,11-dioxo-4-phenyl-2,3,5,5a,6,11,11a,11b-octahydro-1*H*-cyclopenta[*a*]anthracene]carbonyl]bornane-10,2-sultam 9b

Following general procedure C, diene **4b** (100 mg, 0.23 mmol) and 1,4-naphthoquinone (75 mg, 0.47 mmol) were stirred at 80 °C overnight before flash chromatography (30–40% ethyl acetate/hexanes) yielded the major diastereomer of title compound **9b** (73 mg, 54% yield) as an off-white solid. Reaction selectivity 75:15:5:5. The minor diastereomers were also partially isolated and their identities were confirmed by low resolution mass spec. Mp 129–131 °C. $[\alpha]_D^{21} = -21.2$ (*c* 0.58, chloroform). IR ($CDCl_3$) $\nu = 3440$brw (O–H), 2963 (C–H), 2882 (C–H), 1692s (C=O), 1667m (C=O), 1595w (C=C), 1456w, 1390m, 1377m, 1340s, 1267m, 1254s, 1236m, 1215m, 1166w, 1136m, 1113w, 1045w, 1008w cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.97$ (s, 3H, aux CH_3), 1.16 (s, 3H, aux CH_3), 1.38 (m, 2H, aux), 1.91 (m, 3H, aux), 2.12 (m, 2H, aux), 2.38 (m, 1H, H1), 2.59 (m, 2H, H5), 2.66 (ddd, $J = 12.3$, 9.0, 4.7 Hz, 1H, H1), 3.34 (m, 1H, H11b), 3.49 (m, 3H, H5a and aux H10), 3.74 (t, $J = 4.8$ Hz, 1H, H11a), 3.93 (m, 2H, H2 and aux H2), 4.52 (s, 1H, OH), 4.79 (d, $J = 3.5$ Hz, 1H, H3), 7.23 (m, 5H, Ph H), 7.40 (m, 2H, H8 and H9), 8.04 (m, 2H, H7 and H10). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 20.09$ and 21.19 (aux CH_3), 26.60 (aux CH_2), 31.02 (C1 and C5), 33.14 (aux CH_2), 38.07 (C11), 38.78 (aux CH_2), 44.94 (aux CH), 47.43 (C2), 47.97 and 48.58 (aux 4 °C), 49.56 (C5a), 49.97 (C11a), 53.26 (aux C10), 65.37 (aux C2), 73.72 (C3), 126.99 and 127.35 (C7 and C10), 127.58 and 127.86 and 128.25 (Ph CH), 130.48, 132.87, 134.24 and 134.56 (C8 and C9), 135.80, 139.36, 140.05, 175.65 (aux C=O), 196.66 (C11), 198.41 (C6). ESI-MS *m/z* 608.3 $[M+Na]^+$. HRMS calcd for $(C_{34}H_{35}NO_6SNa)^+$: *m/z* 608.2077. Found: 608.2088. Anal. Calcd for $C_{34}H_{35}NO_6S0.2CH_2Cl_2$: C, 68.18; H, 5.92; N, 2.32. Found: C, 67.81; H, 6.09; N, 2.45.

4.21. *N*-(1*S*)-[2-[(2*R*,3*R*,5a*S*,11a*R*,11b*S*)-3-Hydroxy-6,11-dioxo-4-trimethylsilyl-2,3,5,5a,6,11,11a,11b-octahydro-1*H*-cyclopenta[*a*]anthracene]carbonyl]bornane-10,2-sultam 9c

Following general procedure C, diene **4c** (200 mg, 0.47 mmol) and 1,4-naphthoquinone (160 mg, 1.0 mmol) were stirred at 80 °C overnight before flash chromatography (30% ethyl acetate/hexanes) yielded the major diastereomer of the title compound **9c** (200 mg, 73% yield) as an off-white solid. Reaction selectivity: 85:15 (two diastereomers constitute the 15%). Minor diastereomers were detected but not characterised. Mp 259–261 °C. $[\alpha]_D^{21} = +37$ (*c* 0.80, chloroform). IR (nujol) $\nu = 3416$m (O–H), 1703s (C=O), 1687s (C=O), 1649s (C=O), 1597m (C=C), 1338m, 1290m, 1258m, 1251m, 1218m, 1166w, 1135m, 1081w, 1049w, 1026w, 1012w, 960w, 926m, 900w, 869s, 836s, 774w, 754m, 739w, 720w, 696w, 652w, 616w cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.09$ (s, 9H, TMS CH_3), 0.99 (s, 3H, aux CH_3), 1.19 (s, 3H, CH_3), 1.36 (m, 2H, aux), 1.93 (m, 3H, aux), 2.05 (ddd, $J = 18.3$, 11.2, 3.6 Hz, 1H, H5), 2.14 (m, 2H, aux), 2.38 (ddd, $J = 12.4$, 8.7, 5.2, 1H, H1), 2.67 (ddd, $J = 18.3$, 6.8, 2.6 Hz, 1H, H5), 2.60 (td, $J = 11.9$, 9.5 Hz, 1H, H1), 3.13 (m, 1H, H11b), 3.32 (ddd, $J = 11.2$, 6.8, 4.7 Hz, 1H, H5a), 3.49 and 3.55

(ABq, $J = 13.8$ Hz, 2H, aux H10), 3.63 (t, $J = 4.7$ Hz, 1H, H11a), 3.96 (m, 2H, aux H2 and OH), 4.03 (td, $J = 9.1$, 4.0 Hz, 1H, H2), 4.99 (m, 1H, H3), 7.71 (m, 2H, H8 and H9), 7.96 (m, 1H, H10), 8.05 (m, 1H, H7). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = -0.3$ (TMS CH_3), 20.1 and 21.3 (aux CH_3), 26.6 (aux CH_2), 30.3 (C5), 30.5 (C1), 33.2 (aux CH_2), 38.1 (C11b), 38.8 (aux CH_2), 44.9 (aux CH), 47.5 (C2), 48.0 (C11a), 48.6 and 49.0 (aux 4 °C), 50.0 (C5a), 53.3 (aux C10), 65.5 (aux C2), 74.7 (C3), 126.8 and 127.3 (C7 and C10), 129.9, 132.8, 134.1 and 134.5 (C8 and C9), 135.9, 151.6, 175.3 (aux C=O), 197.0 (C11) 199.2 (C6). HRMS calcd for $(C_{31}H_{39}NO_6SSiNa)^+$: m/z 604.2160. Found: 604.2161. Anal. Calcd for $C_{31}H_{39}NO_6SSi$: C, 64.00; H, 6.76; N, 2.41. Found: C, 64.18; H, 6.87; N, 2.46.

4.22. *N*-(1*S*)-[2-[(2*S*,3*R*)-3-Hydroxy-6,11-dioxo-4-(trimethylsilyl)-2,3,5,5a,6,11,11a,11b-octahydro-1*H*-cyclopenta[*a*]anthracene]carbonyl]bornane-10,2-sultam *anti*-9c

Following general procedure C, diene *anti*-**4c** (50 mg, 0.12 mmol) and 1,4-naphthoquinone (37 mg, 0.24 mmol) were stirred at 80 °C overnight. Reaction selectivity: 1.5:1:1. Due to the lack of selectivity, separation of the diastereomers was not attempted. ^{1}H NMR resonances of the diagnostic proton H3 are given below. Unreacted diene *anti*-**4c** was also detected. Crude ^{1}H NMR (400 MHz, $CDCl_3$) diagnosties H3 resonances only: $\delta = 4.65$ (s), 4.75 (d, $J = 4.1$ Hz) 4.78 (m). ESI-MS shows peaks corresponding to the diene *anti*-**4c** calculated for $(C_{21}H_{33}NNaO_4SSi)^+$: m/z 446.2 found 446.3 and the adduct *anti*-**9c** calculated for $(C_{31}H_{39}NNaO_6SSi)^+$: m/z 604.2, found 604.2. HRMS calcd for $(C_{31}H_{39}NNaO_6SSi)^+$: m/z 604.2165. Found: 604.2156.

4.23. *N*-(1*S*)-[2-[(2*R*,3*R*,5a*S*,11a*R*,11b*S*)-4-(Benzyloxymethyl)-3-triethylsilyloxy-6,11-dioxo-2,3,5,5a,6,11,11a,11b-octahydro-1*H*-cyclopenta[*a*]anthracene]carbonyl]bornane-10,2-sultam 10a

Following general procedure C, diene **5a** (100 mg, 0.17 mmol) and 1,4-naphthoquinone (54 mg, 0.34 mmol) were stirred at 80 °C overnight before flash chromatography (20% ethyl acetate/hexanes) yielded the major diastereomer of title compound **10a** (110 mg, 84% yield) as an oil. Reaction selectivity: 90:10. The minor diastereomer was detected but not characterised. $[\alpha]_D = +5.1$ (c 0.40, chloroform). IR ($CHCl_3$) $\nu = 2955$s (C–H), 2875s (C–H), 1695br s (C=O), 1593w, 1455w, 1413w, 1377w, 1330m, 1249m, 1206m, 1164w, 1132w, 1062m, 1003m, 914w, 820w, 744m, 699w cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.52$–0.59 (m, 6H, TES CH_2), 0.90–0.96 (m, 12H, TES CH_3 and aux CH_3), 1.19 (s, 3H, aux CH_3), 1.31–1.45 (m, 2H, aux), 1.85–1.92 (m, 3H, aux), 2.19–2.33 (m, 4H, aux, H1 and H5), 2.44 (ddd, $J = 18.3$, 6.8, 2.2 Hz, 1H, H5), 2.76 (td, $J = 12.1$, 9.9 Hz, 1H, H1), 3.10 (m, 1H, H11b), 3.35 (ddd, $J = 11.3$, 6.8, 4.6 Hz, 1H, H5a), 3.43 and 3.50 (ABq, $J = 13.7$ Hz, 2H, aux H10), 3.65 (t, $J = 4.6$ Hz, 1H, H11a), 3.86 (dd, $J = 7.7$, 5.1 Hz, 1H, aux H2), 4.01 (dt, $J = 3.4$ and 9.2 Hz, 1H, H2), 4.04 and 4.18 (ABq, $J = 11.8$ Hz, 2H, BnH), 4.21 and 4.31 (ABq, $J = 11.3$ Hz, 2H, $BnOCH_2$), 5.52 (d, $J = 3.5$ Hz, 1H, H3), 7.15–7.23 (m, 5H, Ph), 7.67–7.74 (m, 2H, H8 and H9), 7.92–7.94 (m, 1H, H10), 8.01–8.05 (m, 1H, H7). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 5.1$ (TES CH_2), 6.9 (TES CH_3), 20.1 and 21.2 (aux CH_3), 26.6 (aux CH_2), 27.8 (C5), 28.7 (C1), 33.2 (aux CH_2), 36.6 (C11b), 38.9 (aux CH), 44.6 (aux CH_2), 47.9 and 48.6 (aux 4 °C), 49.1 (C11a), 49.7 (C5a), 50.2 (C2), 53.2 (aux C10), 66.0 (aux C2), 69.8 ($PhCH_2O$), 71.6 ($BnOCH_2$), 72.6 (C3), 124.0, 126.5 (C10), 127.3 (C7), 127.4, 128.0 and 128.3 (Ph), 132.8, 134.1 and 134.4 (C8 and C9), 136.0, 138.5, 143.3, 169.7 (aux C=O), 197.2 and 198.8 (C6 and C11). HRMS calcd for $(C_{42}H_{53}NNaO_7SSi)^+$: m/z 766.3210. Found: 766.3202.

4.24. *N*-(1*S*)-[2-[(2*R*,3*R*,5a*S*,11a*R*,11b*S*)-3-Triethylsilyloxy-6,11-dioxo-4-phenyl-2,3,5,5a,6,11,11a,11b-octahydro-1*H*-cyclopenta[*a*]anthracene]carbonyl]bornane-10,2-sultam 10b

Following general procedure C, diene **5b** (65 mg, 0.12 mmol) and 1,4-napthoquinone (40 mg, 0.25 mmol) were stirred at 80 °C overnight before flash chromatography (10–30% ethyl acetate/hexanes) yielded the major diastereomer of the title compound **10b** (72% average yield) as a brown oil. Reaction selectivity: 85:15. The minor diastereomer was also partially isolated and its identity was confirmed by low resolution mass spec. $[\alpha]_D^{21} = +38.4$ (c 1.1, chloroform). IR ($CDCl_3$) $\nu = 2956$m (C–H), 2872m (C–H), 1694s (C=O), 1595w (C=C), 1455w, 1415w, 1377w, 1331m, 1250m, 1027m, 1172w, 1133w, 1063m, 1014w, 876w cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.23$ (m, 6H, TES CH_2), 0.73 (t, $J = 7.9$ Hz, 9H, TES CH_3), 0.98 (s, 3H, aux CH_3), 1.23 (s, 3H, aux CH_3), 1.36 (m, 2H, aux), 1.81 (m, 3H, aux), 2.08–2.31 (m, 3H, H5 and aux), 2.40 (ddd, $J = 12.3$, 8.3, 4.0, 1H, H1), 2.87 (m, 2H, H1 and H5), 3.17 (m, 1H, H11b), 3.48 (m, 3H, H5a and aux H10), 3.71 (t, $J = 4.7$ Hz, 1H, H11a), 3.82 (dd, $J = 7.8$ and 5.1 Hz, 1H, aux H2), 4.12 (dd, $J = 8.3$, 3.2 Hz, 1H, H2), 5.46 (d, $J = 3.2$ Hz, 1H, H3), 7.19 (m, 3H, Ph H), 7.31 (m, 2H, Ph H), 7.68 (m, 2H, H8 and H9), 7.94 (m, 1H, H10), 8.01 (m, 1H, H7). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 4.7$ (TES CH_2), 6.9 (TES CH_3), 20.2 and 21.2 (aux CH_3), 26.7 (aux CH_2), 29.4 (C1), 31.8 (C5), 33.2 (aux CH_2), 36.4 (C11), 38.9 (aux CH_2), 44.7 (aux CH), 48.0 and 48.6 (aux 4 °C), 48.8 (C2), 49.8 (C5a), 50.4 (C11a), 53.2 (aux C10), 66.0 (aux C2), 73.5 (C3), 126.7 and 127.2 (C7 and C10), 127.5 (Ph CH), 127.9, 128.3 and 128.7 (Ph CH), 132.7, 134.1 and 134.6 (C8 and C9), 136.2, 140.0, 141.9, 170.0 (aux C=O), 197.1 (C11), 198.8 (C6). ESI-MS m/z 722.3 $[M+Na]^+$. HRMS calcd for $(C_{40}H_{49}NO_6SSiNa)^+$: m/z 722.2942. Found: 722.2915.

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