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Generation and reactions of novel oxiranyl 'Remote' anions

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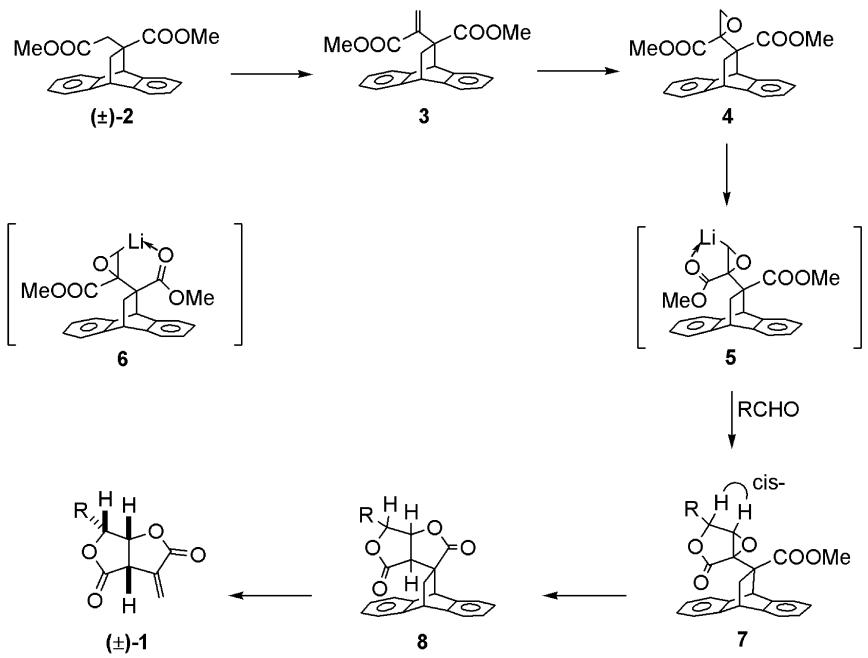
Abstract—Deprotonation of an oxiranyl β-proton takes place in a stereoselective manner providing the corresponding oxiranyl 'remote' anion. The anion is stabilized by chelation between the lithium and the carbonyl moiety of an ester, lactone, imide, or keto-group in the form of a five-membered cyclic intermediate. Certain ester-stabilized oxiranyl anions are stable and can be left in THF solution at −78°C for several hours. The generated anions undergo a stereoselective alkylation reaction to provide products, which could be useful intermediates in the synthesis of bioactive naturally occurring α-methylene bis-γ-butyrolactones.

1. Introduction

Among several approaches reported for the synthesis of naturally occurring α-methylene bis-γ-butyrolactones xylobovide **1a**,[1] canadensolide **1b**,[2] and sporothriolide **1c**,[3] metabolites from *Xylaria obovata*, *Penicillium canadense* and *Sporothrix sp*., respectively, the route shown in Scheme 1[4] which involved stereospecific deprotonation–aldol reaction



Scheme 1.

Keywords: oxiranyl anion; remote anion; oxirane β-lithiation; stereoselective deprotonation.
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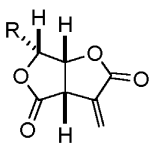
Table 1. Percent yields from reactions between the anions **5a** and **5b**, generated from **4a** and **4b**, respectively, and electrophiles

Electrophile	Product	% Yield from **4a**		% Yield from **4b**	
		9	**10**	**11**	**12**
(a) CD_3OD	E=D	58	–	64	–
(b) CH_3I	E=CH_3	76	–	77	–
(c) PhCHO	R^1=Ph; R^2=H	–	53	–	83
(d) C_2H_5CHO	I: R^1=C_2H_5; R^2=H	–	68	–	80
	II: R^1=H; R^2=C_2H_5	–	–	–	4
(e) *n*-C_4H_9CHO	I: R^1=*n*-C_4H_9; R^2=H	–	63	–	79
	II: R^1=H; R^2=*n*-C_4H_9	–	–	–	6
(f) *n*-$C_6H_{13}CHO$	I: R^1=*n*-C_6H_{13}; R^2=H	–	57	–	66
	II: R^1=H; R^2=*n*-C_6H_{13}	–	–	–	16
(g) PhCOPh	R^1=R^2=Ph	–	47	–	80
(h) CH_3COCH_3	R^1=R^2=CH_3	–	43	–	83
(i) CH_3COPh	I: R^1=CH_3; R^2=Ph	–	38	–	29
	II: R^1=Ph; R^2=CH_3	–	9	–	27
(j) Cyclohexanone	R^1–R^2=–$(CH_2)_5$–	–	50	–	62

of the epoxydiester **4** may be regarded as one of the most convenient methods to such deceptively simple molecules.[5]



1a : R = C_2H_5 ; Xylobovide
1b : R = *n*-C_4H_9 ; Canadensolide
1c : R = *n*-C_6H_{13} ; Sporothriolide

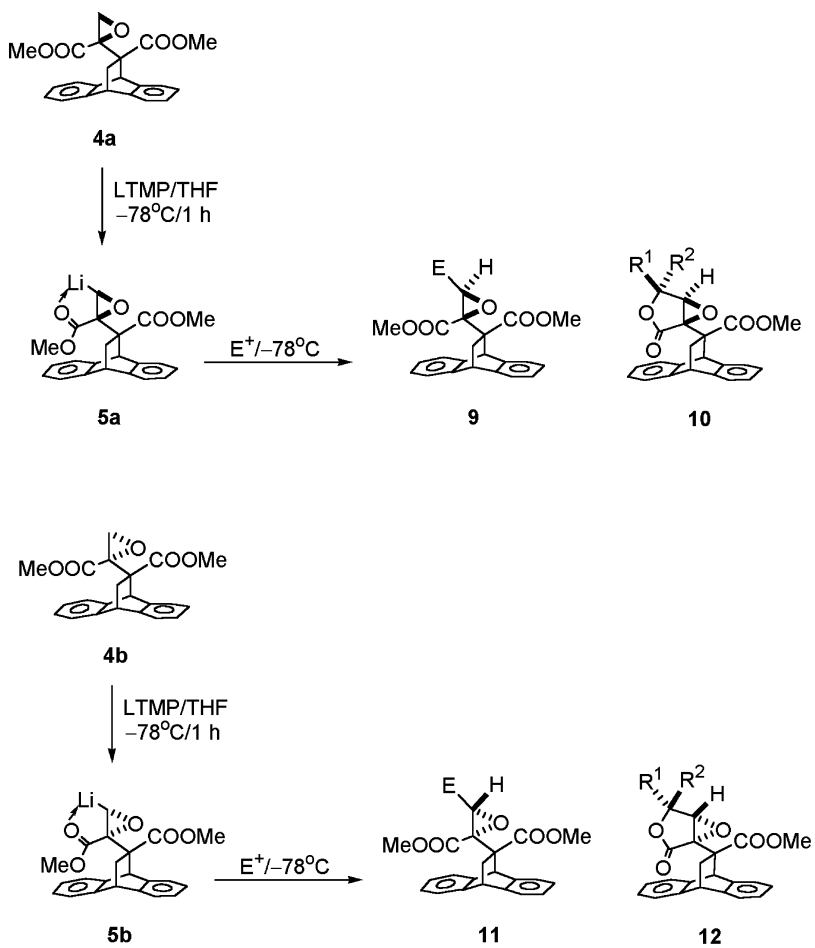
As revealed in our previous report, deprotonation of **4** provided the 'remote' anion which was stable in THF at −78°C, apparently due to the ester oxygen–lithium stabilization in the form of a five-membered cyclic intermediate **5**. Significantly, the six-membered chelated anion, stabilized by the second ester group, i.e. **6**, was not observed. The anion **5** reacted with aldehydes in a stereocontrolled fashion. Thus, a consecutive aldol–lactonization reaction of **5** provided the corresponding epoxyl-actone **7**, which could finally be converted efficiently into the corresponding α-methylene bis-γ-butyrolactone **1**.[4]

Utilization of the oxiranyl anion in natural product synthesis as demonstrated in Scheme 1 was very attractive and straightforward, however, questions concerning the nature of the intermediate anion needed to be addressed and further explored.[4,6] These involve factors governing the ease of generation and stability of the resulting anion because they would directly contribute to synthetic applications of the oxiranyl 'remote' anions. We would like to report our results, which would shed some light on these issues.

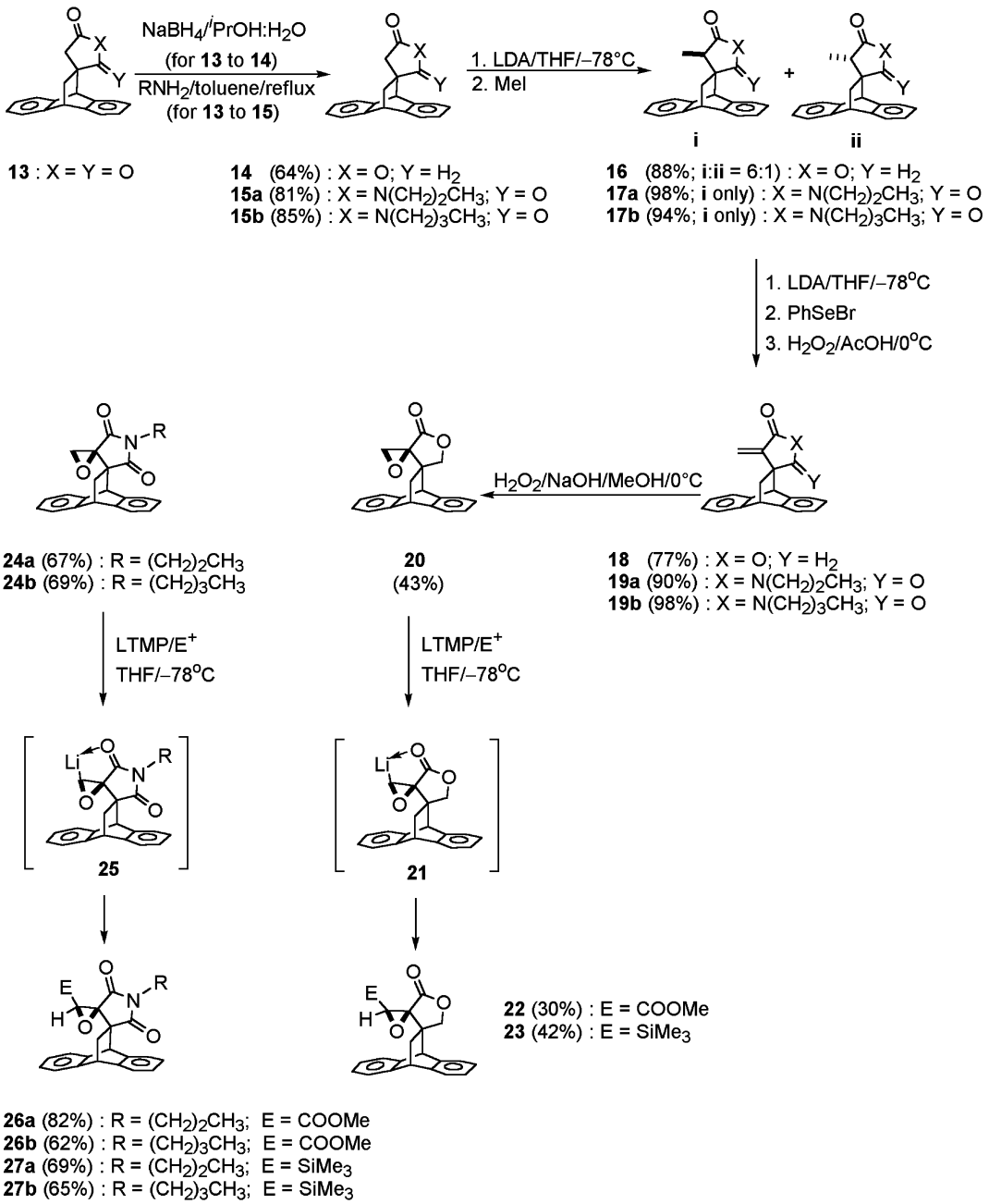
2. Results and discussion

2.1. Generation, stability and alkylation reactions of oxiranyl anion 5

Two stereomeric oxiranes **4a** and **4b** were obtained in equal



Scheme 2.



Scheme 3.

amounts from epoxidation of the methylene diester **3**, both of which underwent stereoselective deprotonation upon treatment with lithium 2,2,6,6-tetramethylpiperidide (LTMP) giving anions **5a** and **5b**, respectively.

The stereoselectivity of the deprotonation of **4a** and **4b** to provide oxiranyl anions, respectively, **5a** and **5b** and their subsequent alkylation reactions is evident from the structures of the products (Table 1). The results obtained also confirm that none of the six-membered stabilized anion, i.e. **6**, whereupon another ester group in the molecule is responsible for chelation of the lithium ion, was formed (Scheme 2).

Oxiranyl anions **5a** and **5b** were stable at −78°C, and they underwent stereoselective protonation (with CD_3OD), alkylation (CH_3I) and aldol reactions. For an unknown reason, it was noted that, in most cases, the anion **5b** provided better product yields than its isomeric counterpart, **5a**. As can be seen in Table 1, both anions underwent a consecutive aldol–lactonization reaction with aromatic and aliphatic aldehydes providing products **10c–f** and **12c–f**, respectively. Compounds **10d–f** and **12d–f** were successfully employed as intermediates in the syntheses of naturally occurring α-methylene bis-γ-butyrolactones xylobovide **1a**, canadensolide **1b** and sporothriolide **1c**.[4]

Interestingly, anions **5a** and **5b** reacted well with both non-enolizable (entry g) and enolizable (entries h–j) ketones to give epoxylactones **10g–j** and **12g–j** without the need for additional reagents such as Lewis acids. However, unlike the reaction with aldehydes, anions **5a** and **5b** reacted with

an unsymmetrical ketone to furnish two isomeric products having opposite stereochemistry at the γ-carbon of the lactone moiety. Thus **5a** reacted with acetophenone to give two separable isomers of **10i** and anion **5b** furnished a mixture of **12i**.

2.2. Lactone and imide stabilized oxiranyl anions

The carbonyl groups of the lactone and imide groups in compounds **20** and **24** have a direct influence on the acidity of the β-protons on the oxirane moieties and also on the stability of the emerging remote anions by providing a five-membered chelation. However, possibly due to the rigidity of the molecule, the stability of anion **21** was not as good as that of **5**. Thus, treatment of the epoxylactone **20** with excess LTMP in THF at −78°C followed by the addition of chlorotrimethylsilane provided a very low yield of the corresponding silylated product. Although TLC of the crude reaction mixture indicated a complete absence of the starting material, the mixture consisted of many unidentified materials. Improvement was made by introducing a mixture of the starting material **20** and electrophile into the LTMP/THF solution at −78°C whereupon products **22** and **23** were obtained in better isolated yields when dimethyl carbonate and chlorotrimethylsilane were, respectively, used as electrophiles (Scheme 3). Similar results were obtained with the epoxyimide **24** from which alkylated products **26a** and **27a**, and **26b** and **27b** were, respectively, obtained from **24a** and **24b**.

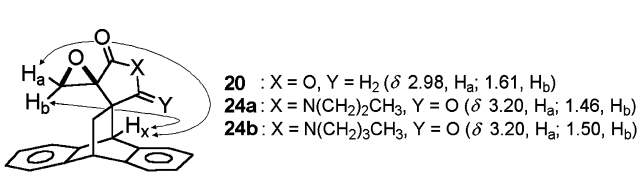
Several interesting and important observations concerning the experiments outlined in Scheme 3 deserve discussion here.

Lactone **14** was prepared by regiospecific borohydride reduction of the anhydride **13**, which, itself, was obtained from the diester **2**.[7] Methylation of **14** provided two isomers of **16** in a ratio of 6:1 while the imides **15a** and **15b**, also obtained from **13**, gave only a single product in each case. The methyl group was then converted into the methylene functionality by the one-pot selenoxide elimination strategy.[8] Other methylenation methods to convert **14** into **18** and **15** into **19** were investigated but it was found that the pathway described in Scheme 3 provided superior results. Basic hydrogen peroxide oxidation of **18** gave a single isomer of the oxirane **20** and, similarly, **19a** and **19b** furnished **24a** and **24b**, respectively. The explanation concerning stereoselectivity of the methylation (**14** into **16** and **15** into **17**) and epoxidation (**18** into **20**, and **19** into **24**) reactions which preferably took place on one side of the molecules can easily be made by inspection of molecular models. It is immediately apparent that the β-face of the anthracene adducts, i.e. **14** and **15** or **18** and **19**, is far less congested than the opposite.

Stereochemical identities of compounds **20**, **24a** and **24b** have been thoroughly proven by investigation of their NMR spectroscopic data. The two protons of the oxirane moiety resonate at different chemical shifts 1.5 ppm apart. The upfield shift of one proton is due to its close proximity to the aromatic nucleus and hence it experiences a strong shielding effect. Confirmation of the oxiranyl stereochemistry was obtained from NOE experiments in which correlation was observed between the oxiranyl protons and bridgehead proton of the anthracene adduct as shown in Figure 1.

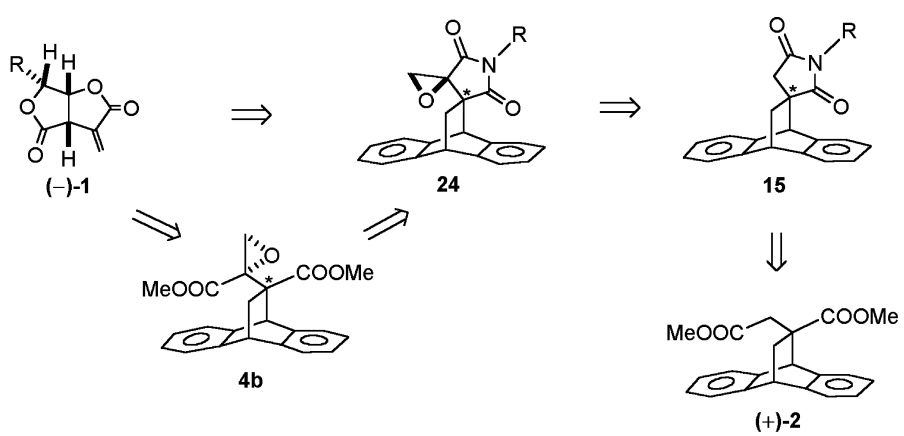
The NMR spectroscopic data of all products, **22**, **23**, **26a**,**b** and **27a**,**b** agreed well with the proposed stereostructures. In each case, the low field oxiranyl proton in the starting material was displaced by the electrophile, leaving the remaining high field proton intact. The results described indicated the stereoselective manner of the reactions between lactone and imide, **20** and **24**, respectively, with LTMP. Evidently, only the oxiranyl proton situated in close proximity (*cis*-) to the carbonyl group was affected by the base to provide corresponding oxiranyl anions, **21** and **25**. Alkylation reactions of these anions were also stereoselective giving a single diastereomeric product in each case.

The stereospecific epoxidation of **19** to yield only one product, **24**, caught our attention because it might have great potential in the enantiomeric synthesis of naturally occurring α-methylene bis-γ-butyrolactones, e.g. xylobovide **1a**, canadensolide **1b**, and sporothriolide **1c**. Our described

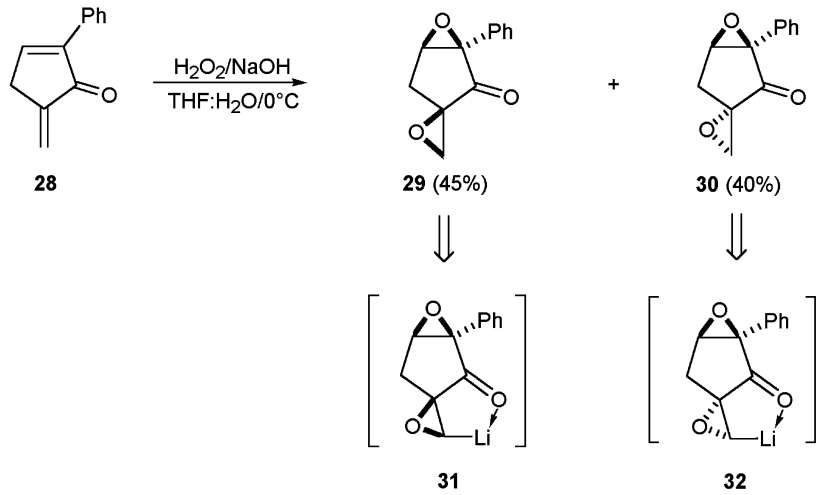


20 : X = O, Y = H_2 (δ 2.98, H_a; 1.61, H_b)
24a : X = $N(CH_2)_2CH_3$, Y = O (δ 3.20, H_a; 1.46, H_b)
24b : X = $N(CH_2)_3CH_3$, Y = O (δ 3.20, H_a; 1.50, H_b)

Figure 1.



Scheme 4.



Scheme 5.

synthesis of these metabolites, as shown in Scheme 1, involved the epoxydiester **4** as a key intermediate. However, epoxidation of **3** was not highly stereoselective whereupon two stereoisomers, **4a** and **4b**, were obtained in equal amounts. Therefore, the route to optically active **1**, having identical absolute configuration to that of the natural product, was not efficient because it would involve successive resolution of **2** and separation of diastereomeric **4a** and **4b**. We anticipated that, according to the route shown in Scheme 3, preparation of optically active imide **15** and epoxide **24** from enantiomerically pure anhydride would be straightforward,[7] hence the process shown in Scheme 4 would finally lead to (−)-**1**.

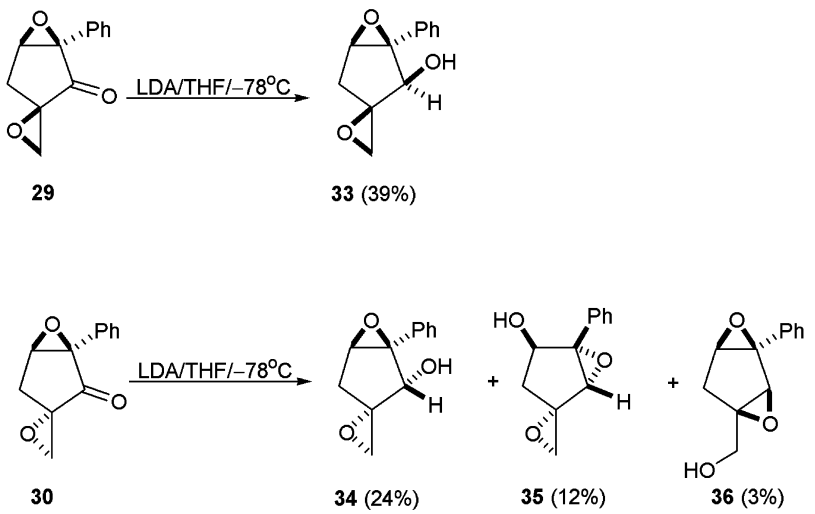
However, numerous attempts to convert **24** into **4b** (and hence **1**)[4] or attempted manipulation of **24** to the natural product, **1**, by other methods has so far been unsuccessful.

2.3. Keto- vs ester stabilized oxiranyl anions

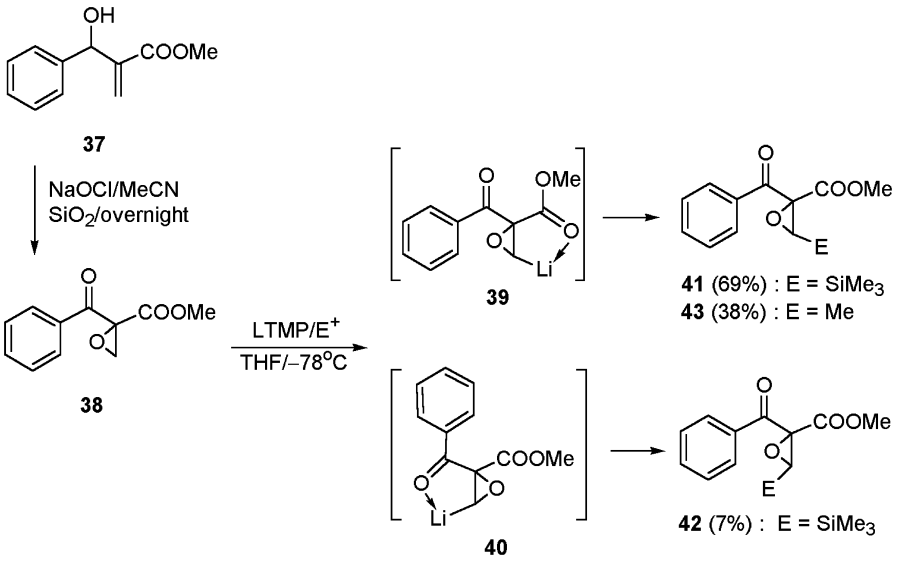
Since it has already been shown that the oxiranyl anions can be stabilized by ester, lactone and imide functionalities, it was of interest to investigate the stabilization ability of the keto-group with regards to the generation and behavior of remote oxiranyl anions.

Ketoepoxides **29** and **30**, prepared directly by epoxidation of the known methylene cyclopentenone **28**[9] using basic hydrogen peroxide oxidation, were chosen for our study. It was hoped that this study would offer us a better understanding of keto-stabilized oxiranyl anions and the alkylation reaction of the remote anions **31** and **32** would present us with a good method for cyclopentenone functionalization. However, we failed to detect the presence of keto-stabilized oxiranyl anion, i.e. **31**, either by treatment of the *cis*-diepoxide **29** with LTMP at −78°C followed by addition of electrophile or in situ trapping of the emerging anion with the electrophile. TLC and NMR spectral data of the crude reaction mixtures from the experiments described above revealed the presence of unreacted starting material together with many unidentified compounds.

Likewise, the *trans*-diepoxide **30** also failed to give any useful products, which could be derived from the oxiranyl anion, i.e. **32**, when treated with LTMP (Scheme 5).



Scheme 6.



Scheme 7.

Interestingly, during the course of our study to generate oxarinyl anions **31** and **32**, we treated the epoxide **29** with LDA (2 equiv.) in THF at −78°C and obtained a low yield of alcohol **33** as the only isolable product. Similar treatment of **30** provided **34** (24%), **35** (12%) and **36** (3%) (Scheme 6). Obviously, LDA did not act as a base but, instead, as a hydride donor to trigger the Meerwein–Ponndorf–Verley type hydride transfer reduction[10] yielding the observed alcohols. Apparently, LDA only approached the carbonyl group in **29** from the opposite side of the *cis*-diepoxide, however, in the case of *trans*-diepoxide **30**, reduction took place randomly. The β-approach provided alcohol **34** which underwent Payne rearrangement[11] to give **35**, while the minor product, **36**, resulted from reduction on the α-face followed by rearrangement. Spectroscopic data (together with NOE experiments) of all products described agreed well with the proposed stereostructures.

The failure to detect the strained keto-stabilized oxiranyl anions, i.e. **31** or **32**, did not deter us from our plan to investigate the behavior of epoxyketoester **38**,[12] prepared from epoxidation of the alcohol **37**. The latter was readily obtained by the Baylis–Hillman reaction between benzaldehyde and methyl acrylate.[13] Ketoester **38**, having an oxirane group flanked by a ketone and an ester, provided us with an excellent opportunity to directly investigate the chelation abilities of these two carbonyl groups.

Upon treatment of the epoxyketoester **38** with LTMP in THF at −78°C followed by addition of excess TMSCl, only a trace amount of the silylated product **41** was identified together with many unidentified materials. However, when a mixture of **38** and excess TMSCl in THF was added to LTMP/THF solution at −78°C and the reaction mixture was left stirring at −78°C for 5 h, two silylated products, **41** and **42**, were obtained, in 69 and 7% yields, respectively, after PLC separation. However, when CH_3I was used instead of TMSCl as the electrophile in the above reaction, the corresponding methylated product **43** was the only product isolated from the reaction mixture.

The results shown in Scheme 7 can be summarized by suggesting that two reaction pathways were involved when epoxyketoester **38** was treated with LTMP. The major reaction path involved abstraction of a proton *cis*- to the ester group to provide the ester-stabilized oxiranyl anion **39**, while the alternative, abstraction of proton *cis*- to the keto-group to provide the keto-stabilized anion **40**, was the minor reaction pathway. Isolation of major and minor products, **41** and **42**, respectively, from silylation and product **43** from methylation strongly indicated that the keto-group exerted a weaker chelation ability compared to the ester.

3. Conclusion

In conclusion, we have shown that oxiranyl remote anions can be generated and employed in alkylation reactions. These anions were stabilized by chelation between the lithium and carbonyl moieties of ester, lactone, imide or keto-groups in a five-membered cyclic intermediate. The ester group provided a good chelation effect: ester-stabilized oxiranyl anions **5a** and **5b** were stable and could be left in THF solution at −78°C for several hours. In the system **38**, designed for direct competition of chelation abilities of the keto- and ester groups, it was found that the keto-group provided only a weak chelation effect compared to that of the ester functionality. Oxiranyl anions **5a** and **5b** underwent consecutive aldol–lactonization reation with aldehydes to provide the corresponding epoxylactones, **10d–f** and **12d–f**, which could be further employed in the stereoselective synthesis of naturally occurring α-methylene bis-γ-butyrolactones, **1a–c**.

4. Experimental

4.1. General

Melting points were determined by Electrothermal Melting Point apparatus and were uncorrected. ^1H NMR spectra

were recorded on Bruker DPX 300, 400 and 500 MHz spectrometers in $CDCl_3$ using TMS as internal standard. Infrared spectra were recorded on an FT-IR system 2000 (Perkin–Elmer) spectrometer. Elemental analyses were performed on a Perkin–Elmer Elemental Analyzer 2400 CHN and mass spectra were recorded on Bruker Esquire and Finnigan MAT INCOS 50 mass spectrometers. Merck silica gel 60 PF_{254} was used for PLC, Merck silica gel 60 and Merck silica gel 60H were employed for the column chromatography. Solvents were distilled before used. Dried oxygen free THF (distilled with sodium/benzophenone) was used in all experiments. Lithium 2,2,6,6-tetramethylpiperidide (LTMP) and lithium diisopropylamide (LDA) employed in the experiments were prepared according to the standard method using the corresponding amine and *n*-butyllithium (purchased from Metallgesellschaft AG; molarity was determined by titration with 2,5-dimethoxybenzyl alcohol).

4.2. Generation of oxiranyl anions 5a and 5b and their reactions with electrophiles

A solution of the oxirane **4a** (0.14 mmol) in THF (10 mL) was introduced to the solution of LTMP (0.42 mmol) in THF (0.6 mL) at −78°C and the mixture was stirred at that temperature for 1 h. Then, electrophile (1.40 mmol) was added to the anion solution at −78°C after which the reaction mixture was left stirring for 4 h. After quenching with saturated aqueous NH_4Cl solution, the crude mixture was extracted several times with CH_2Cl_2. The combined organic extract was washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by PLC using 20% EtOAc in hexane as eluent followed by crystallization to obtain the products (Scheme 2, Table 1).

Oxirane **4b** was also subjected to the reaction described above to yield corresponding products (Scheme 2, Table 1).

Physical data of **9a**,**b**, **10c**–**f**, **11a**,**b** and **12c**–**f** have already been described.[4]

4.2.1. 11-Carbomethoxy-11-(4′,4′-diphenyl-3′,6′-dioxa-2′-oxobicyclo[3.1.0]hex-1′-yl)-9,10-dihydro-9,10-ethanoanthracene (10g). 33.8 mg (47%), white solid, mp 257–259°C; [Found: C, 79.01; H, 5.24. $C_{34}H_{26}O_5$ requires C, 79.36; H, 5.09%]; ν_{max} (KBr) 3031, 3013, 2955, 1787, 1747, 1459, 1279, 1086 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.48–6.99 (18H, m, Ph), 5.18 (1H, s, C*H*Ph), 4.32 (1H, dd, *J*=2.8, 2.5 Hz, CHHC*H*), 3.86 (1H, s, OCH), 3.50 (3H, s, OMe), 2.72 (1H, dd, *J*=12.7, 2.8 Hz, C*H*HCH), 1.46 (1H, dd, *J*=12.7, 2.5 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 171.4, 169.4, 144.2, 143.3, 139.5, 139.4, 139.3, 137.9, 128.7, 128.6, 128.5, 128.4, 126.8, 126.7, 126.1, 126.0, 125.9, 125.5, 124.5, 123.6, 123.2, 85.8, 63.4, 62.9, 52.7, 50.2, 47.5, 43.5, 34.7; *m*/*z* (ES) 538.4 (29, $[M+1+Na]^+$), 537.5 (100, $[M+Na]^+$).

4.2.2. 11-Carbomethoxy-11-(4′,4′-dimethyl-3′,6′-dioxa-2′-oxobicyclo[3.1.0]hex-1′-yl)-9,10-dihydro-9,10-ethanoanthracene (10h). 23.5 mg (43%), white solid, mp 235–237°C; [Found: C, 73.87; H, 5.70. $C_{24}H_{22}O_5$ requires C, 73.83; H, 5.68%]; ν_{max} (KBr) 3029, 3013, 2955, 1778, 1747, 1460, 1388, 1373, 1286, 1090 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.47–7.09 (8H, m, Ph), 5.37 (1H, s, C*H*Ph), 4.38 (1H, dd, *J*=2.7, 2.5 Hz, CHHC*H*), 3.63 (3H, s, OMe), 3.01 (1H, s, OCH), 2.62 (1H, dd, *J*=12.6, 2.7 Hz, C*H*HCH), 1.57 (1H, dd, *J*=12.6, 2.5 Hz, CH*H*CH), 1.31 (3H, s, CH_3CCH_3), 1.22 (3H, s, CH_3CCH_3); δ_C (75 MHz, $CDCl_3$) 172.3, 169.6, 143.9, 143.5, 139.8, 139.3, 126.7, 126.6, 126.1, 125.9, 124.8, 123.5, 123.1, 80.3, 63.2, 62.1, 52.7, 50.7, 47.4, 43.7, 34.7, 24.6, 21.3; *m*/*z* (ES) 803.5 (29, $[2M+Na]^+$), 414.1 (23, $[M+1+Na]^+$), 413.1 (100, $[M+Na]^+$).

4.2.3. 11-Carbomethoxy-11-(4′-methyl-4′-phenyl-3′,6′-dioxa-2′-oxobicyclo[3.1.0]hex-1′-yl)-9,10-dihydro-9,10-ethanoanthracene (10i-I). 10i-I and **10i-II** were separated by PLC (20% EtOAc in hexane as eluent) followed by crystallization. 24.0 mg (38%), white solid, mp 185–187°C; [Found: C, 76.95; H, 5.31. $C_{29}H_{24}O_5$ requires C, 76.97; H, 5.34%]; ν_{max} (KBr) 3031, 2954, 1783, 1746, 1459, 1373, 1248, 1088 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.38–6.95 (13H, m, Ph), 5.18 (1H, s, C*H*Ph), 4.17 (1H, dd, *J*=2.8, 2.6 Hz, CHHC*H*), 3.32 (3H, s, OMe), 3.30 (1H, s, OCH), 2.44 (1H, dd, *J*=12.6, 2.8 Hz, C*H*HCH), 1.52 (3H, s, $PhCCH_3$), 1.28 (1H, dd, *J*=12.6, 2.6 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 171.6, 169.7, 144.0, 143.4, 139.7, 139.5, 139.3, 128.8, 128.5, 126.7, 126.0, 125.9, 124.7, 124.2, 123.5, 123.1, 82.9, 62.8, 62.4, 52.6, 50.5, 47.4, 43.5, 34.5, 22.7; *m*/*z* (ES) 927.6 (50, $[2M+Na]^+$), 476.1 (33, $[M+1+Na]^+$), 475.1 (100, $[M+Na]^+$).

4.2.4. 11-Carbomethoxy-11-(4′-methyl-4′-phenyl-3′,6′-dioxa-2′-oxobicyclo[3.1.0]hex-1′-yl)-9,10-dihydro-9,10-ethanoanthracene (10i-II). 5.7 mg (9%), white solid, mp 215–217°C; ν_{max} (KBr) 3030, 3012, 2928, 2856, 1784, 1721, 1460, 1379, 1280, 1085 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.33–6.95 (13H, m, Ph), 5.19 (1H, s, C*H*Ph), 3.50 (3H, s, OMe), 3.20 (1H, s, OCH), 4.25 (1H, dd, *J*=2.8, 2.6 Hz, CHHC*H*), 2.55 (1H, dd, *J*=12.8, 2.8 Hz, C*H*HCH), 1.49 (1H, dd, *J*=12.8, 2.6 Hz, CH*H*CH), 1.37 (s, 3H); δ_C (75 MHz, $CDCl_3$) 172.3, 169.3, 144.0, 143.6, 139.8, 139.3, 138.3, 128.6, 128.3, 126.9, 126.8, 126.2, 126.1, 126.0, 125.1, 124.8, 123.6, 123.2, 82.8, 62.2, 52.8, 50.8, 47.6, 43.7, 38.2, 34.8, 26.2; *m*/*z* (ES) 453 (9, $[M+1]^+$), 178 (100); ESITOF: $[M+Na]^+$, found: 475.1514. $C_{29}H_{24}O_5$ requires 475.1521.

4.2.5. 11-Carbomethoxy-11-{spiro[cyclohexane-1″,4′-(3′,6′)-dioxa-2′-oxobicyclo[3.1.0]hexan]-1′-yl}-9,10-dihydro-9,10-ethanoanthracene (10j). 30.1 mg (50%), white solid, mp 245–246°C; ν_{max} (KBr) 3074, 3029, 2945, 2865, 1775, 1747, 1459, 1285, 1094 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.46–7.08 (8H, m, Ph), 5.31 (1H, s, C*H*Ph), 4.38 (1H, dd, *J*=2.9, 2.5 Hz, CHHC*H*), 3.63 (3H, s, OMe), 3.05 (1H, s, OCH), 2.65 (1H, dd, *J*=12.5, 2.9 Hz, C*H*HCH), 1.68–1.26 (10H, m, $(CH_2)_5$), 1.56 (1H, dd, *J*=12.5, 2.5 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 172.2, 169.8, 143.9, 143.5, 139.8, 139.4, 126.7, 126.6, 126.0, 125.9, 124.7, 123.5, 123.1, 82.1, 62.7, 61.0, 52.7, 50.6, 47.5, 43.7, 34.9, 34.0, 30.5, 24.8, 22.1, 21.6; *m*/*z* (ES) 883.7 (2, $[2M+Na]^+$), 454.5 (27, $[M+1+Na]^+$), 453.5 (100, $[M+Na]^+$); HRMS (FAB^+): $[M+1]^+$, found: 431.1858. $C_{27}H_{26}O_5$ requires 431.1859.

4.2.6. 11-Carbomethoxy-11-(4′,4′-diphenyl-3′,6′-dioxa-2′-oxobicyclo[3.1.0]hex-1′-yl)-9,10-dihydro-9,10-ethanoanthracene (12g). 57.6 mg (80%), white solid, mp

224–226°C; [Found: C, 79.03; H, 5.13. $C_{34}H_{26}O_5$ requires C, 79.36; H, 5.09%]; ν_{max} (KBr) 3030, 3013, 2955, 1786, 1753, 1459, 1280, 1086 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.46–6.63 (18H, m, Ph), 4.65 (1H, s, C*H*Ph_2), 4.35 (1H, dd, *J*=2.6, 2.4 Hz, CHHC*H*), 4.29 (1H, s, OCH), 3.46 (3H, s, OMe), 2.69 (1H, dd, *J*=13.6, 2.6 Hz, C*H*HCH), 2.02 (1H, dd, *J*=13.6, 2.4 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 171.6, 169.4, 143.6, 143.5, 140.2, 139.5, 138.9, 138.8, 128.8, 128.5, 128.4, 128.3, 126.6, 126.5, 126.3, 125.8, 125.7, 125.2, 124.4, 123.4, 123.1, 86.6, 65.2, 64.5, 52.5, 49.9, 49.3, 43.6, 35.2; *m/z* (ES) 1051.3 (18, $[2M+Na]^+$), 538.1 (39, $[M+1+Na]^+$), 537.1 (100, $[M+Na]^+$).

4.2.7. 11-Carbomethoxy-11-(4′,4′-dimethyl-3′,6′-dioxa-2′-oxobicyclo[3.1.0]hex-1′-yl)-9,10-dihydro-9,10-ethanoanthracene (12h). 45.32 mg (83%), white solid, mp 188–190°C; [Found: C, 73.73; H, 5.67. $C_{24}H_{22}O_5$ requires C, 73.83; H, 5.68%]; ν_{max} (KBr) 3074, 3029, 3013, 2955, 1777, 1720, 1459, 1389, 1373, 1254, 1091 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.31–7.07 (8H, m, Ph), 4.74 (1H, s, C*H*Ph), 4.35 (1H, t, *J*=2.7 Hz, CHHC*H*), 3.55 (3H, s, OMe), 3.50 (1H, s, OCH), 2.60 (1H, dd, *J*=13.5, 2.7 Hz, C*H*HCH), 1.89 (1H, dd, *J*=13.5, 2.7 Hz, CH*H*CH), 1.31 (3H, s, CH_3CCH_3), 1.20 (3H, s, CH_3CCH_3); δ_C (75 MHz, $CDCl_3$) 172.3, 169.8, 143.8, 140.1, 139.7, 126.7, 126.5, 126.0, 125.8, 125.2, 124.8, 123.6, 123.3, 81.0, 65.6, 64.9, 52.6, 50.0, 49.4, 43.6, 35.3, 24.1, 21.8; *m/z* (ES) 803.5 (35, $[2M+Na]^+$), 414.0 (25, $[M+1+Na]^+$), 413.0 (100, $[M+Na]^+$).

4.2.8. 11-Carbomethoxy-11-(4′-methyl-4′-phenyl-3′,6′-dioxa-2′-oxobicyclo[3.1.0]hex-1′-yl)-9,10-dihydro-9,10-ethanoanthracene (12i-I). 12i-I and **12i-II** were separated by PLC (20% EtOAc in hexane as eluent) followed by crystallization. 18.4 mg (29%), white solid, mp 126–128°C; [Found: C, 76.67; H, 5.64. $C_{29}H_{24}O_5$ requires 76.98; H, 5.35%]; ν_{max} (KBr) 3024, 2983, 2950, 1780, 1745, 1459, 1239, 1086, 764 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.50–6.44 (13H, m, Ph), 4.56 (1H, s, C*H*Ph), 4.30 (1H, dd, *J*=2.9, 2.5 Hz, CHHC*H*), 3.61 (1H, s, OCH), 3.49 (3H, s, OMe), 2.54 (1H, dd, *J*=12.5, 2.9 Hz, C*H*HCH), 1.94 (1H, dd, *J*=12.5, 2.5 Hz, CH*H*CH), 1.64 (3H, s, CH_3CPh); δ_C (75 MHz, $CDCl_3$) 171.8, 169.9, 143.6, 143.3, 140.4, 139.7, 138.9, 128.9, 128.4, 126.3, 126.2, 125.7, 125.5, 124.6, 124.4, 123.2, 122.9, 83.8, 64.9, 64.8, 52.5, 49.7, 48.9, 45.3, 35.2, 23.8; *m/z* (ES) 927.6 (34, $[2M+Na]^+$), 476.1 (33, $[M+1+Na]^+$), 475.1 (100, $[M+Na]^+$), 453.2 (11, $[M+1]^+$).

4.2.9. 11-Carbomethoxy-11-(4′-methyl-4′-phenyl-3′,6′-dioxa-2′-oxobicyclo[3.1.0]hex-1′-yl)-9,10-dihydro-9,10-ethanoanthracene (12i-II). 17.0 mg (27%), white solid, mp 215–217°C; ν_{max} (KBr) 3067, 3018, 2951, 1785, 1748, 1459, 1276, 1067, 766 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.38–7.10 (13H, m, Ph), 4.87 (1H, s, C*H*Ph), 4.38 (1H, dd, *J*=2.5, 2.4 Hz, CHHC*H*), 3.87 (1H, s, OCH), 3.58 (3H, s, OMe), 2.62 (1H, dd, *J*=13.6, 2.5 Hz, C*H*HCH), 1.92 (1H, dd, *J*=13.6, 2.4 Hz, CH*H*CH), 1.51 (3H, s, $PhCCH_3$); δ_C (75 MHz, $CDCl_3$) 172.2, 169.3, 143.8, 140.0, 139.6, 138.9, 128.5, 128.2, 126.8, 126.6, 126.1, 125.9, 125.3, 125.0, 124.9, 123.7, 123.3, 83.4, 65.6, 65.1, 52.7, 50.1, 49.4, 43.6, 35.4, 25.5; *m/z* (ES) 927.5 (22, $[2M+Na]^+$), 476.0 (27, $[M+1+Na]^+$), 475.1 (100, $[M+Na]^+$); HRMS (FAB^+): $[M+1]^+$, found: 453.1700. $C_{29}H_{24}O_5$ requires 453.1702.

4.2.10. 11-Carbomethoxy-11-{spiro[cyclohexane-1″,4′-(3′,6′)-dioxa-2′-oxobicyclo[3.1.0]hexan]-1′-yl}-9,10-dihydro-9,10-ethanoanthracene (12j). 37.3 mg (62%), white solid, mp 194–196°C; ν_{max} (KBr) 3074, 3028, 2945, 2865, 1773, 1720, 1459, 1287, 1095 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.00–7.27 (8H, m, Ph), 4.67 (1H, s, C*H*Ph), 4.25 (1H, dd, *J*=2.8, 2.7 Hz, CHHC*H*), 3.48 (3H, s, OMe), 3.34 (1H, s, OCH), 2.42 (1H, dd, *J*=13.6, 2.8 Hz, C*H*HCH), 1.80 (1H, dd, *J*=13.6, 2.7 Hz, CH*H*CH), 1.55–1.18 (10H, m, $(CH_2)_5$); δ_C (75 MHz, $CDCl_3$) 172.4, 169.9, 143.9, 143.8, 140.3, 139.8, 126.6, 126.4, 126.0, 125.8, 125.6, 125.0, 123.6, 123.2, 82.9, 64.5, 63.4, 52.6, 49.8, 49.2, 43.6, 35.3, 33.2, 31.0, 24.8, 22.2, 21.7; *m/z* (ES) 883.4 (7, $[2M+Na]^+$), 454.0 (29, $[M+1+Na]^+$), 453.0 (100, $[M+Na]^+$); HRMS (FAB^+): $[M+1]^+$, found: 431.1855. $C_{27}H_{26}O_5$ requires 431.1859.

4.2.11. 3′-Dihydrofuran-4′-one-1′,11-spiro-9,10-dihydro-9,10-ethanoanthracene (14). To a solution of the anhydride **13** (100.0 mg, 0.34 mmol) in 2-propanol (3.6 mL) and H_2O (0.6 mL) was slowly added $NaBH_4$ (26.0 mg, 0.69 mmol) at 0°C. The reaction mixture was left stirring at room temperature for 12 h and then evaporated to dryness. After addition of 20% aqueous HCl solution, the solution was extracted several times with CH_2Cl_2. The combined organic extract was washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel; 20% EtOAc in hexane as eluent) to afford the lactone **14** (61.2 mg, 64%) as a white solid, mp 135–137°C; ν_{max} ($CHCl_3$) 3026, 2935, 1776, 1468, 1170, 1017 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.26–7.03 (8H, m, Ph), 4.23 (1H, dd, *J*=3.0, 2.7 Hz, CHHC*H*), 3.94 (1H, s, C*H*Ph), 3.92 (1H, d, *J*=9.3 Hz, C*H*HO), 3.62 (1H, d, *J*=9.3 Hz, CH*H*O), 2.30 (1H, d, *J*=17.5 Hz, C*H*HCOO), 2.06 (1H, d, *J*=17.5 Hz, CH*H*COO), 1.80 (1H, dd, *J*=9.9, 3.0 Hz, C*H*HCH), 1.73 (1H, dd, *J*=9.9, 2.7 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 176.2, 143.0, 142.9, 140.3, 140.1, 126.7, 126.6, 126.1, 126.0, 125.5, 125.4, 123.6, 123.5, 77.7, 51.2, 44.8, 44.1, 42.1, 41.5; ESITOF: $[M+Na]^+$, found: 299.1049. $C_{19}H_{16}O_2$ requires 299.1048.

4.3. General method for the preparation of imide 15

A mixture of *n*-propylamine (28.5 mL, 345 mmol) and the anhydride **13** (10.0 g, 34.5 mmol) in toluene (250 mL) was heated to reflux for 48 h. The reaction mixture was then quenched with 10% aqueous HCl solution and extracted with CH_2Cl_2. The combined organic layer was washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel; 20% EtOAc in hexane as eluent) to afford the imide **15a** (9.2 g, 81%).

Imide **15b** (85%) was obtained when *n*-butylamine was employed in the above described method.

4.3.1. *N*-1-Propyl-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (15a). 9.2 g (81%), white solid, mp 157–158°C; ν_{max} ($CHCl_3$) 3027, 2965, 1774, 1701, 1401, 1138 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.40–7.10 (8H, m, Ph), 4.45 (1H, dd, *J*=2.8, 2.5 Hz, CHHC*H*), 4.02 (1H, s, C*H*Ph), 3.48 (2H, t, *J*=7.3 Hz, $NCH_2CH_2CH_3$), 2.70 (1H, d,

J=18.3 Hz, C*H*HC=O), 2.45 (1H, dd, J=12.5, 2.8 Hz, C*H*HCH), 2.22 (1H, d, J=18.3 Hz, CH*H*C=O), 1.75 (1H, dd, J=12.5, 2.5 Hz, CH*H*CH), 1.60 (2H, m, $NCH_2CH_2CH_3$), 0.90 (3H, t, J=7.3 Hz, $N(CH_2)_2CH_3$); δ_C (100 MHz, $CDCl_3$) 179.9, 175.3, 143.4, 142.6, 140.2, 139.4, 126.8, 126.5, 125.9, 125.8, 125.4, 125.2, 123.7, 123.0, 53.0, 47.8, 44.0, 41.0, 40.3, 21.0, 11.2; ESITOF: $[M+Na]^+$, found: 354.1351. $C_{22}H_{21}NO_2$ requires 354.1470.

4.3.2. *N*-1-Butyl-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (15b). 10.1 g (85%), white solid, mp 111–112°C; ν_{max} ($CHCl_3$) 3026, 2961, 1774, 1702, 1401, 1139, 924 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.20–6.90 (8H, m, Ph), 4.28 (1H, dd, J=3.0, 2.5 Hz, CHHC*H*), 3.85 (1H, s, C*H*Ph), 3.30 (2H, t, J=7.4 Hz, $NCH_2(CH_2)_2CH_3$), 2.50 (1H, d, J=18.3 Hz, C*H*HC=O), 2.28 (1H, dd, J=12.4, 3.0 Hz, C*H*HCH), 2.03 (1H, d, J=18.3 Hz, CH*H*C=O), 1.58 (1H, dd, J=12.4, 2.5 Hz, CH*H*CH), 1.40 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.15 (2H, m, $N(CH_2)_2CH_2CH_3$), 0.78 (3H, t, J=7.4 Hz, $N(CH_2)_3CH_3$); δ_C (100 MHz, $CDCl_3$) 179.9, 175.3, 143.4, 142.6, 140.2, 139.4, 126.8, 126.5, 125.9, 125.8, 125.3, 125.2, 123.8, 123.0, 53.0, 47.9, 44.2, 44.1, 41.2, 38.5, 29.7, 19.9, 13.6; ESITOF: $[M+Na]^+$, found: 368.1656. $C_{23}H_{23}NO_2$ requires 368.1626.

4.4. Methylation of the lactone 14 and imide 15

To a solution of LDA (58.4 mmol) in THF (50 mL) at −78°C was added a solution of the lactone **14** (13.4 g, 48.7 mmol) in THF (30 mL). The reaction mixture was left stirring at 0°C for 1 h after which CH_3I (9.1 mL, 146.2 mmol) was added at −78°C. The mixture was warmed up to 0°C and left stirring for 4 h. The solution was quenched with 10% aqueous HCl solution and extracted several times with CH_2Cl_2. The combined organic extract was washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was separated by column chromatography (silica gel; 20% EtOAc in hexane as eluent) to give the methylated products **16-i** and **16-ii** in a ratio of 6:1 (12.5 g, 88%).

Methylation of imides **15a** and **15b** by the above method provided **17a** (98%) and **17b** (94%), respectively.

4.4.1. 5′-Methyl-3′-dihydrofuran-4′-one-1′,11-spiro-9,10-dihydro-9,10-ethanoanthracene (16-i). 10.7 g (75%), white solid, mp 155–157°C; ν_{max} ($CHCl_3$) 3026, 2956, 1771, 1468, 1172 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.30–7.09 (8H, m, Ph), 4.32 (1H, dd, J=2.9, 2.8 Hz, CHHC*H*), 4.02 (1H, s, C*H*Ph), 3.92 (1H, d, J=9.2 Hz, C*H*HO), 3.49 (1H, d, J=9.2 Hz, CH*H*O), 2.46 (1H, q, J=7.4 Hz, C*H*CH_3), 1.97 (1H, dd, J=10.1, 2.9 Hz, C*H*HCH), 1.52 (1H, dd, J=10.1, 2.8 Hz, CH*H*CH), 0.62 (3H, d, J=7.4 Hz, CHC*H*$_3$); δ_C (75 MHz, $CDCl_3$) 179.6, 143.3, 143.0, 140.3, 139.9, 126.6, 126.4, 125.9, 125.1, 125.0, 123.7, 123.5, 123.4, 77.5, 52.9, 47.5, 46.3, 43.9, 35.0, 10.9; ESITOF: $[M+Na]^+$, found: 313.1217. $C_{20}H_{18}O_2$ requires 313.1204.

4.4.2. 5′-Methyl-3′-dihydrofuran-4′-one-1′,11-spiro-9,10-dihydro-9,10-ethanoanthracene (16-ii). 1.8 g (13%), white solid, mp 145–146°C; ν_{max} ($CHCl_3$) 3012, 2957, 1771, 1459, 1172 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.30–7.09 (8H, m, Ph), 4.32 (1H, dd, J=2.5, 2.4 Hz, CHHC*H*), 4.17 (1H, s, C*H*Ph), 4.04 (1H, d, J=9.1 Hz, C*H*HO), 3.32 (1H, d, J=9.1 Hz, CH*H*O), 2.04 (1H, q, J=7.5 Hz, C*H*CH_3), 1.99 (1H, dd, J=10.0, 2.5 Hz, C*H*HCH), 1.77 (1H, dd, J=10.0, 2.4 Hz, CH*H*CH), 1.22 (3H, d, J=7.5 Hz, CHC*H*$_3$); δ_C (75 MHz, $CDCl_3$) 179.6, 143.8, 143.0, 140.3, 140.0, 126.6, 126.0, 125.9, 125.8, 124.7, 124.4, 123.4, 77.4, 52.9, 47.6, 47.4, 44.0, 35.1, 11.5; ESITOF: $[M+Na]^+$, found: 313.1214. $C_{20}H_{18}O_2$ requires 313.1204.

4.4.3. *N*-1-Propyl-3-methyl-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (17a). 16.5 g (98%), white solid, mp 127–128°C; ν_{max} ($CHCl_3$) 3014, 2968, 1770, 1698, 1403, 1150 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.40–7.10 (8H, m, Ph), 4.48 (1H, dd, J=3.2, 2.0 Hz, CHHC*H*), 4.10 (1H, s, C*H*Ph), 3.50 (2H, t, J=7.4 Hz, $NCH_2CH_2CH_3$), 2.70 (1H, q, J=7.4 Hz, C*H*CH_3), 2.10 (1H, dd, J=12.8, 3.2 Hz, C*H*HCH), 2.00 (1H, dd, J=12.8, 2.0 Hz, CH*H*CH), 1.60 (2H, m, $NCH_2CH_2CH_3$), 0.90 (3H, t, J=7.4 Hz, $N(CH_2)_2CH_3$), 0.70 (3H, d, J=7.4 Hz, CHC*H*$_3$); δ_C (100 MHz, $CDCl_3$) 180.0, 179.6, 144.3, 143.5, 139.9, 139.3, 126.7, 126.5, 126.0, 125.8, 125.4, 124.9, 123.6, 122.8, 54.6, 51.6, 45.7, 43.9, 40.2, 33.7, 21.0, 14.2, 11.2; ESITOF: $[M+Na]^+$, found: 368.1638. $C_{23}H_{23}NO_2$ requires 368.1626.

4.4.4. *N*-1-Butyl-3-methyl-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (17b). 16.4 g (94%), white solid, mp 105–106°C; ν_{max} ($CHCl_3$) 3021, 2961, 1771, 1698, 1402, 1149 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.50–7.10 (8H, m, Ph), 4.46 (1H, dd, J=3.0, 2.3 Hz, CHHC*H*), 4.07 (1H, s, C*H*Ph), 3.50 (2H, t, J=7.3 Hz, $NCH_2(CH_2)_2CH_3$), 2.68 (1H, q, J=7.5 Hz, C*H*CH_3), 2.10 (1H, dd, J=12.8, 3.0 Hz, C*H*HCH), 2.00 (1H, dd, J=12.8, 2.3 Hz, CH*H*CH), 1.60 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.38 (2H, m, $N(CH_2)_2CH_2CH_3$), 1.00 (3H, t, J=7.3 Hz, $N(CH_2)_3CH_3$), 0.70 (3H, d, J=7.5 Hz, CHC*H*$_3$); δ_C (100 MHz, $CDCl_3$) 180.5, 180.0, 144.0, 141.0, 140.0, 139.9, 127.2, 127.0, 126.5, 126.4, 125.8, 125.7, 124.0, 123.2, 55.0, 52.0, 46.0, 44.5, 39.0, 34.0, 30.0, 20.0, 15.0, 14.0; ESITOF: $[M+Na]^+$, found: 382.1778. $C_{24}H_{25}NO_2$ requires 382.1783.

4.5. One-pot selenoxide elimination of compounds 16 and 17: formation of the olefins 18 and 19

To a solution of LDA (43.0 mmol) in THF (60 mL) was added dropwise, under nitrogen atmosphere at −78°C, a solution of **16-i** (9.9 g, 34.1 mmol) in THF (20 mL) and the mixture was stirred at 0°C for 1 h. A solution of phenylselenyl bromide (10.5 g, 44.3 mmol) in THF (20 mL) was introduced dropwise to the mixture at −78°C and the reaction was left stirring at 0°C for 4 h. Glacial acetic acid (1.6 mL) was added followed by 30% aqueous hydrogen peroxide solution (7 mL). The reaction temperature was raised to 0°C and the reaction mixture was left stirring for 2 h, then it was poured into cold saturated aqueous sodium bicarbonate solution. The reaction mixture was extracted several times with CH_2Cl_2. The combined organic extract was washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by using column chromatography (silica gel; 20% EtOAc in hexane as eluent) to afford the olefin **18** (7.6 g, 77%).

Accordingly, products **19a** (90%) and **19b** (98%) were obtained from **17a** and **17b**, respectively.

4.5.1. 5′-Methylene-3′-dihydrofuran-4′-one-1′,11-spiro-9,10-dihydro-9,10-ethanoanthracene (18). 7.6 g (77%), white solid, mp 158–160°C; ν_{max} ($CHCl_3$) 3026, 3013, 1760, 1659, 1459, 1120, 1011 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.38–7.11 (8H, m, Ph), 5.97 (1H, s, C*H*HCOO), 4.41 (1H, dd, *J*=2.8, 2.6 Hz, CHHC*H*), 4.17 (1H, d, *J*=9.4 Hz, C*H*HO), 4.07 (1H, s, CH*H*COO), 3.99 (1H, s, C*H*Ph), 3.77 (1H, d, *J*=9.4 Hz, CH*H*O), 2.06 (1H, dd, *J*=10.3, 2.8 Hz, C*H*HCH), 1.86 (1H, dd, *J*=10.3, 2.6 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 170.5, 141.3, 143.6, 143.1, 139.7, 139.1, 127.0, 126.8, 126.7, 126.2, 126.0, 125.6, 123.5, 123.1, 122.9, 76.1, 52.3, 47.2, 44.2, 43.6; ESITOF: $[M+Na]^+$, found: 311.1047. $C_{20}H_{16}O_2$ requires 311.1048.

4.5.2. *N*-1-Propyl-3-methylene-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (19a). 10.5 g (90%), white solid, mp 181–182°C; ν_{max} ($CHCl_3$) 3022, 2966, 1769, 1705, 1655, 1071, 944 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.45–7.10 (8H, m, Ph), 5.98 (1H, s, C=C*H*H), 4.52 (1H, dd, *J*=2.8, 2.5 Hz, CHHC*H*), 4.02 (1H, s, C*H*Ph), 3.78 (1H, s, C=CH*H*), 3.55 (2H, t, *J*=7.4 Hz, $NCH_2CH_2CH_3$), 2.42 (1H, dd, *J*=12.5, 2.8 Hz, C*H*HCH), 1.85 (1H, dd, *J*=12.5, 2.5 Hz, CH*H*CH), 1.67 (2H, m, $NCH_2CH_2CH_3$), 0.95 (3H, t, *J*=7.4 Hz, $N(CH_2)_2CH_3$); δ_C (100 MHz, $CDCl_3$) 177.5, 168.6, 143.6, 142.8, 142.3, 139.3, 139.0, 126.8, 126.7, 126.6, 125.9, 125.4, 125.2, 123.2, 123.1, 120.4, 53.4, 50.5, 44.0, 40.2, 21.1, 11.2; ESITOF: $[M+Na]^+$, found: 366.1461. $C_{23}H_{21}NO_2$ requires 366.1470.

4.5.3. *N*-1-Butyl-3-methylene-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (19b). 11.9 g (98%), white solid, mp 124–125°C; ν_{max} ($CHCl_3$) 3027, 2961, 1769, 1705, 1656, 1095, 952 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.50–7.10 (8H, m, Ph), 5.98 (1H, s, C=C*H*H), 4.51 (1H, dd, *J*=2.8, 2.5 Hz, CHHC*H*), 4.00 (1H, s, C*H*Ph), 3.78 (1H, s, C=CH*H*), 3.59 (2H, t, *J*=7.3 Hz, $NCH_2(CH_2)_2CH_3$), 2.41 (1H, dd, *J*=12.5, 2.8 Hz, C*H*HCH), 1.82 (1H, dd, *J*=12.5, 2.5 Hz, CH*H*CH), 1.62 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.35 (2H, m, $N(CH_2)_2CH_2CH_3$), 0.95 (3H, t, *J*=7.3 Hz, $N(CH_2)_3CH_3$); δ_C (100 MHz, $CDCl_3$) 177.0, 168.6, 144.0, 143.4, 143.0, 140.0, 139.6, 127.4, 127.3, 127.1, 126.3, 126.0, 125.9, 123.8, 123.7, 120.0, 58.0, 50.0, 44.0, 40.0, 38.0, 29.0, 20.0, 13.6; ESITOF: $[M+Na]^+$, found: 380.1606. $C_{24}H_{23}NO_2$ requires 380.1626.

4.6. Hydrogen peroxide oxidation of the olefin 18: formation of the oxirane 20

To a solution of olefin **18** (50.0 mg, 0.17 mmol) in methanol (4 mL) was added 30% aqueous H_2O_2 solution (0.06 mL, 0.61 mmol), followed by 20% aqueous NaOH solution (0.04 mL, 0.17 mmol) at 0°C and the reaction mixture was left stirring at room temperature for 6 h. Saturated aqueous NH_4Cl solution was added and the crude material extracted with CH_2Cl_2. The combined organic extract was washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by PLC (silica gel; 20% EtOAc in hexane as eluent) to obtain the epoxylactone **20** (22.7 mg, 43%).

Epoxyimides **24a** (67%) and **24b** (69%) were obtained, respectively, from **19a** and **19b** according to the above described method.

4.6.1. 1′,5′-Dioxaspiro[2,4]heptane-4′-one-7′,11-spiro-9,10-dihydro-9,10-ethanoanthracene (20). 22.7 mg (43%), white solid, mp 163–165°C; ν_{max} ($CHCl_3$) 3027, 2958, 1789, 1460, 1281, 1001 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.36–7.11 (8H, m, Ph), 4.30 (1H, dd, *J*=2.7, 2.5 Hz, CHHC*H*), 4.22 (1H, s, C*H*Ph), 4.15 (1H, d, *J*=9.3 Hz, COOC*H*H), 3.89 (1H, d, *J*=9.3 Hz, COOCH*H*), 2.98 (1H, d, *J*=4.9 Hz, OC*H*H), 1.81 (1H, dd, *J*=11.4, 2.7 Hz, C*H*HCH), 1.61 (d, *J*=4.9 Hz, OCH*H*), 1.53 (1H, dd, *J*=11.4, 2.5 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 173.5, 144.0, 143.4, 139.7, 127.0, 126.9, 126.3, 126.2, 125.6, 125.0, 123.7, 76.6, 76.1, 60.0, 49.3, 46.7, 43.5, 34.5; ESITOF $[M+1]^+$, found: 305.1167. $C_{20}H_{16}O_3$ requires 305.1177.

4.6.2. *N*-1-Propyl-3-oxirane-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (24a). 40.9 mg (67%), white solid, mp 164–165°C; ν_{max} ($CHCl_3$) 3027, 2967, 1770, 1718, 1404, 1076 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.40–7.10 (8H, m, Ph), 4.40 (1H, dd, *J*=2.8, 2.6 Hz, CHHC*H*), 4.20 (1H, s, C*H*Ph), 3.50 (2H, t, *J*=7.4 Hz, $NCH_2CH_2CH_3$), 3.20 (1H, d, *J*=4.9 Hz, OC*H*H), 2.10 (1H, dd, *J*=13.2, 2.8 Hz, C*H*HCH), 1.75 (1H, dd, *J*=13.2, 2.8 Hz, CH*H*CH), 1.60 (2H, m, $NCH_2CH_2CH_3$), 1.46 (1H, d, *J*=4.9 Hz, OCH*H*), 0.97 (3H, t, *J*=7.4 Hz, $N(CH_2)_2CH_3$); δ_C (100 MHz, $CDCl_3$) 177.6, 172.8, 143.9, 143.5, 139.6, 139.0, 127.0, 126.8, 126.0, 125.9, 125.1, 125.0, 123.9, 123.3, 60.9, 52.1, 49.6, 46.0, 43.4, 40.7, 31.4, 21.0, 11.2; ESITOF: $[M+Na]^+$, found: 382.1426. $C_{23}H_{21}NO_3$ requires 382.1419.

4.6.3. *N*-1-Butyl-3-oxirane-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (24b). 43.8 mg (69%), white solid, mp 128–129°C; ν_{max} ($CHCl_3$) 3021, 2961, 1756, 1718, 1404, 1339 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.50–7.10 (8H, m, Ph), 4.41 (1H, dd, *J*=2.8, 2.5 Hz, CHHC*H*), 4.20 (1H, s, C*H*Ph), 3.59 (2H, t, *J*=4.9 Hz, $NCH_2(CH_2)_2CH_3$), 3.20 (1H, d, *J*=4.9 Hz, OC*H*H), 2.29 (1H, dd, *J*=13.0, 2.8 Hz, C*H*HCH), 1.79 (1H, dd, *J*=13.0, 2.5 Hz, CH*H*CH), 1.60 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.50 (1H, d, *J*=4.9 Hz, OCH*H*), 1.40 (2H, m, $N(CH_2)_2CH_2CH_3$), 1.00 (3H, t, *J*=7.3 Hz, $N(CH_2)_3CH_3$); δ_C (100 MHz, $CDCl_3$) 178.0, 173.0, 144.0, 143.5, 139.7, 139.0, 127.1, 126.8, 126.0, 125.9, 125.2, 125.0, 124.0, 123.4, 61.0, 52.1, 46.0, 44.1, 38.9, 31.4, 30.0, 29.7, 19.9, 13.6; ESITOF: $[M+Na]^+$, found: 396.1568. $C_{24}H_{23}NO_3$ requires 396.1576.

4.7. Generation of oxiranyl anions 21 and 25 and their reactions with electrophiles

To a solution of LTMP (0.82 mmol) in THF (1 mL) was added dropwise a solution of epoxylactone **20** (50.0 mg, 0.16 mmol) in the presence of dimethyl carbonate (0.28 mL, 1.64 mmol) in THF (2 mL) under nitrogen atmosphere at −78°C. The reaction mixture was stirred at −78°C for 4 h and then quenched by saturated aqueous NH_4Cl solution. The crude material was extracted several times with CH_2Cl_2, and the combined organic extract was washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by PLC

(silica gel; 20% EtOAc in hexane as eluent) to afford product **22** (17.9 mg, 30%). Chlorotrimethylsilane was also used as electrophile to provide product **23** (42%).

Generation and in situ trapping of anions **25a** and **25b** were performed as described above to finally yield products **26a** (82%), **26b** (62%), **27a** (69%) and **27b** (65%).

4.7.1. 2′-Carbomethoxy-1′,5′-dioxaspiro[2,4]heptane-4′-one-7′,11-spiro-9,10-dihydro-9,10-ethanoanthracene (22). 17.9 mg (30%), white solid, mp 173–174°C; ν_{max} ($CHCl_3$) 3028, 2957, 1794, 1760, 1459, 1096, 1013 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.34–7.08 (8H, m, Ph), 4.23 (1H, s, C*H*Ph), 4.23 (1H, dd, *J*=2.8, 2.6 Hz, CHHC*H*), 4.07 (1H, d, *J*=9.3 Hz, OC*H*H), 3.82 (1H, d, *J*=9.3 Hz, OCH*H*), 3.73 (3H, s, OMe), 2.28 (1H, s, MeOCOC*H*), 1.74 (1H, dd, *J*=10.8, 2.8 Hz, C*H*HCH), 1.45 (1H, dd, *J*=10.8, 2.6 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 170.5, 165.6, 143.7, 143.2, 139.4, 138.7, 127.1, 127.0, 126.4, 126.3, 126.2, 125.7, 123.8, 123.4, 75.8, 63.5, 53.4, 52.6, 48.8, 45.3, 43.3, 34.4; ESITOF: $[M+Na]^+$, found: 385.1052. $C_{22}H_{18}O_5$ requires 385.1052.

4.7.2. 2′-Trimethylsilyl-1′,5′-dioxaspiro[2,4]heptane-4′-one-7′,11-spiro-9,10-dihydro-9,10-ethanoanthracene (23). 24.7 mg (42%), white solid, mp 140–142°C; ν_{max} ($CHCl_3$) 3027, 2958, 1789, 1459, 1249, 1008, 846 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.29–7.05 (8H, m, Ph), 4.19 (1H, dd, *J*=2.8, 2.7 Hz, CHHC*H*), 4.15 (1H, s, C*H*Ph), 4.00 (1H, d, *J*=9.1 Hz, OC*H*H), 3.86 (1H, d, *J*=9.1 Hz, OCH*H*), 1.52 (1H, dd, *J*=10.9, 2.8 Hz, C*H*HCH), 1.31 (1H, dd, *J*=10.9, 2.7 Hz, CH*H*CH), 0.71 (1H, s, Me_3SiCH), 0.00 (9H, s, Me_3Si); δ_C (75 MHz, $CDCl_3$) 173.8, 144.2, 143.4, 140.1, 140.0, 126.8, 126.7, 126.1, 125.9, 125.8, 125.5, 123.8, 123.6, 75.6, 63.4, 51.7, 49.1, 46.3, 43.5, 32.9, −1.8; ESITOF: $[M+Na]^+$, found: 399.1392. $C_{23}H_{24}SiO_3$ requires 399.1392.

4.7.3. *N*-1-Propyl-3-(carbomethoxy)-oxirane-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (26a). 54.7 mg (82%), white solid, mp 182–183°C; ν_{max} ($CHCl_3$) 3029, 2957, 1790, 1759, 1721, 1398, 1081, 971 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.50–7.00 (8H, m, Ph), 4.36 (1H, dd, *J*=2.7, 2.6 Hz, CHHC*H*), 4.28 (1H, s, C*H*Ph), 3.76 (3H, s, OMe), 3.44 (2H, t, *J*=7.4 Hz, $NCH_2CH_2CH_3$), 2.15 (1H, s, MeOCOC*H*), 2.12 (1H, dd, *J*=13.3, 2.7 Hz, C*H*HCH), 1.68 (1H, dd, *J*=13.3, 2.6 Hz, CH*H*CH), 1.56 (2H, m, $NCH_2CH_2CH_3$), 0.88 (3H, t, *J*=7.4 Hz, $NCH_2CH_2CH_3$); δ_C (100 MHz, $CDCl_3$) 176.7, 170.4, 165.4, 144.0, 143.4, 138.9, 127.4, 127.0, 126.5, 126.3, 126.1, 125.1, 123.8, 123.5, 64.3, 53.5, 52.5, 52.0, 50.2, 43.3, 41.0, 31.4, 21.0, 11.2; ESITOF: $[M+Na]^+$, found: 440.1486. $C_{25}H_{23}NO_5$ requires 440.1477.

4.7.4. *N*-1-Butyl-3-(carbomethoxy)-oxirane-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (26b). 42.8 mg (62%), colorless liquid; ν_{max} ($CHCl_3$) 3029, 2959, 1790, 1759, 1721, 1398, 1085, 971 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.80–7.00 (8H, m, Ph), 4.30 (1H, dd, *J*=2.8, 2.5 Hz, CHHC*H*), 4.25 (1H, s, C*H*Ph), 3.78 (3H, s, OMe), 3.45 (2H, t, *J*=7.3 Hz, $NCH_2(CH_2)_2CH_3$), 2.12 (1H, s, MeOCOC*H*), 2.05 (1H, dd, *J*=13.3, 2.8 Hz, C*H*HCH), 1.65 (1H, dd, *J*=13.3, 2.5 Hz, CH*H*CH), 1.50 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.25 (2H, m, $N(CH_2)_2CH_2CH_3$), 0.85 (3H, t, *J*=7.3 Hz, $N(CH_2)_3CH_3$); δ_C (100 MHz, $CDCl_3$) 176.6, 170.3, 165.3, 143.8, 143.3, 138.8, 127.4, 126.9, 126.4, 126.2, 125.9, 124.9, 123.6, 123.4, 64.2, 53.4, 52.5, 51.8, 50.0, 43.2, 39.1, 31.2, 29.6, 19.9, 13.5; ESITOF: $[M+Na]^+$, found: 454.1631. $C_{26}H_{25}NO_5$ requires 454.1630.

4.7.5. *N*-1-Propyl-3-(trimethylsilyl)-oxirane-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (27a). 47.6 mg (69%), white solid, mp 131–132°C; ν_{max} ($CHCl_3$) 3027, 2936, 1784, 1717, 1249, 1076, 847 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.30–7.00 (8H, m, Ph), 4.29 (1H, dd, *J*=2.7, 2.5 Hz, CHHC*H*), 4.05 (1H, s, C*H*Ph), 3.40 (2H, t, *J*=7.4 Hz, $NCH_2CH_2CH_3$), 2.00 (1H, dd, *J*=13.3, 2.7 Hz, C*H*HCH), 1.55 (2H, m, $NCH_2CH_2CH_3$), 1.40 (1H, dd, *J*=13.3, 2.5 Hz, CH*H*CH), 0.89 (3H, t, *J*=7.4 Hz, $N(CH_2)_2CH_3$), 0.63 (1H, s, Me_3SiCH), 0.00 (9H, s, Me_3Si); δ_C (100 MHz, $CDCl_3$) 179.7, 175.2, 145.7, 145.3, 141.6, 140.9, 128.8, 128.5, 127.6, 127.0, 126.6, 125.7, 125.0, 66.5, 54.5, 54.1, 53.3, 45.2, 42.2, 31.4, 22.9, 13.0, 0.0; ESITOF: $[M+Na]^+$, found: 454.1864. $C_{26}H_{29}NSiO_3$ requires 454.1874.

4.7.6. *N*-1-Butyl-3-(trimethylsilyl)-oxirane-11′,2-spiro(9′,10′-dihydro-9′,10′-ethanoanthracene)-succinimide (27b). 46.3 mg (65%), white solid, mp 113–114°C; ν_{max} ($CHCl_3$) 3028, 2960, 1784, 1718, 1259, 1249, 863, 846 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.30–7.00 (8H, m, Ph), 4.26 (1H, dd, *J*=2.7, 2.6 Hz, CHHC*H*), 4.10 (1H, s, C*H*Ph), 3.41 (2H, t, *J*=7.0 Hz, $NCH_2(CH_2)_2CH_3$), 2.00 (1H, dd, *J*=13.2, 2.7 Hz, C*H*HCH), 1.45 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.40 (1H, dd, *J*=13.2, 2.6 Hz, CH*H*CH), 1.25 (2H, m, $N(CH_2)_2CH_2CH_3$), 0.89 (3H, t, *J*=7.0 Hz, $N(CH_2)_3CH_3$), 0.60 (1H, s, Me_3SiCH), 0.00 (9H, s, Me_3Si); δ_C (100 MHz, $CDCl_3$) 177.9, 173.4, 144.0, 143.6, 139.9, 139.2, 127.0, 126.8, 125.9, 125.3, 124.9, 124.0, 123.4, 64.8, 52.7, 52.4, 51.5, 43.5, 38.8, 29.9, 29.8, 20.0, 13.6, −1.7; ESITOF: $[M+Na]^+$, found: 468.1959. $C_{27}H_{31}NSiO_3$ requires 468.1971.

4.8. Hydrogen peroxide oxidation of α-methylene cyclopentenone 28

To a solution of cyclopentenone **28** (100.0 mg, 0.59 mmol) in THF (2 mL) and H_2O (0.2 mL) was added 30% aqueous H_2O_2 solution (0.18 mL, 1.76 mmol), followed by 20% aqueous NaOH solution (0.12 mL, 0.59 mmol) at 0°C. The reaction mixture was left stirring at 0°C for 2 h, saturated aqueous NH_4Cl solution was added and the crude material was extracted several times with CH_2Cl_2. The combined organic layer was washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was separated by PLC (silica gel; 20% EtOAc in hexane as eluent) to afford diepoxyspirocyclopentanones **29** (53.5 mg, 45%) and **30** (47.5 mg, 40%).

4.8.1. 1-Phenyl-2*H*-spiro[6-oxabicyclo[3.1.0]hexane-3,2′-oxiran]-2-one (29). 53.5 mg (45%), white solid, mp 84–85°C; ν_{max} ($CHCl_3$) 3027, 2936, 1763, 1502, 1434, 1200, 1002 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.52–7.48 (5H, m, Ph), 4.13 (1H, d, *J*=0.8 Hz, CHHC*H*), 3.13 (1H, d, *J*=6.2 Hz, C*H*H), 2.95 (1H, d, *J*=6.2 Hz, CH*H*), 2.66 (1H, d, *J*=15.2 Hz, C*H*HCH), 2.55 (1H, dd, *J*=15.2, 0.8 Hz, CH*H*CH);

δ_C (100 MHz, $CDCl_3$) 203.3, 129.3, 128.9, 128.5, 127.0, 65.3, 61.8, 58.8, 53.8, 28.5; ESITOF $[M+Na]^+$, found: 225.0529. $C_{12}H_{10}O_3$ requires 225.0528.

4.8.2. 1-Phenyl-2*H*-spiro[6-oxabicyclo[3.1.0]hexane-3,2′-oxiran]-2-one (30). 47.5 mg (40%), white solid, mp 92–93°C; ν_{max} ($CHCl_3$) 3028, 2990, 1758, 1503, 1468, 993 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.50–7.30 (5H, m, Ph), 4.11 (1H, d, J=1.3 Hz, CHHC*H*), 3.29 (1H, d, J=6.3 Hz, C*H*H), 3.03 (1H, d, J=6.3 Hz, CH*H*), 2.66 (1H, dd, J=15.7, 1.3 Hz, C*H*HCH), 2.43 (1H, d, J=15.7 Hz, CH*H*CH); δ_C (100 MHz, $CDCl_3$) 202.8, 129.4, 129.0, 128.5, 127.0, 63.8, 63.1, 57.0, 51.4, 29.3; ESITOF: $[M+1]^+$, found: 203.0709. $C_{12}H_{10}O_3$ requires 203.0708.

4.9. LDA-induced Meerwein–Ponndorf–Verley hydride transfer reaction of ketoepoxides 29 and 30

A solution of diepoxycyclopentanone **29** (50.0 mg, 0.25 mmol) in THF (1 mL) was introduced to the solution of LDA (0.49 mmol) in THF (1 mL) under nitrogen atmosphere at −78°C and the reaction was left stirring at that temperature for 3 h. Saturated aqueous NH_4Cl solution was added at 0°C and the mixture was extracted several times with CH_2Cl_2. The combined organic layer was washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by PLC (silica gel; 20% EtOAc in hexane as eluent) to afford the product **33** (19.7 mg, 39%).

Identical reaction of the diepoxide **30** afforded, after separation by PLC (silica gel; 20% EtOAc in hexane as eluent), alcohols **34** (24%), **35** (12%) and **36** (3%).

4.9.1. 1-Phenylspiro[6-oxabicyclo[3.1.0]hexane-3,2′-oxiran]-2-ol (33). 19.7 mg (39%), white solid, mp 129–130°C; ν_{max} ($CHCl_3$) $_{max}$ 3462, 3025, 2959, 1713, 1450, 1390, 1262, 1091 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.40–7.20 (5H, m, Ph), 4.76 (1H, s, C*H*(OH)), 3.61 (1H, s, CHHC*H*), 3.04 (1H, d, J=5.1 Hz, C*H*H), 2.54 (1H, d, J=5.1 Hz, CH*H*), 2.28 (1H, d, J=15.0 Hz, C*H*HCH), 2.19 (1H, d, J=15.0 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 134.0, 128.5, 128.3, 126.1, 73.9, 66.4, 63.7, 63.0, 51.1, 32.1; ESITOF: $[M+Na]^+$, found: 227.0682. $C_{12}H_{12}O_3$ requires 227.0684.

4.9.2. 1-Phenylspiro[6-oxabicyclo[3.1.0]hexane-3,2′-oxiran]-2-ol (34). 12.2 mg (24%), white solid, mp 81–82°C; ν_{max} ($CHCl_3$) 3529, 3017, 2925, 1430, 1266, 1085, 873 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.50–7.32 (5H, m, Ph), 4.88 (1H, s, C*H*(OH)), 3.69 (1H, d, J=1.0 Hz, CHHC*H*), 2.83 (1H, d, J=4.0 Hz, C*H*H), 2.78 (1H, d, J=4.0 Hz, CH*H*), 2.53 (1H, dd, J=15.6, 1.0 Hz, C*H*HCH), 2.08 (1H, d, J=15.6 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 134.3, 128.4, 128.1, 126.4, 71.2, 66.7, 62.5, 59.5, 44.6, 33.0; ESITOF: $[M+Na]^+$, found: 227.0689. $C_{12}H_{12}O_3$ requires 227.0684.

4.9.3. 5-Phenylspiro[6-oxabicyclo[3.1.0]hexane-2,2′-oxiran]-4-ol (35). 6.1 mg (12%), white solid, mp 75–77°C; ν_{max} ($CHCl_3$) 3428, 2923, 1736, 1462, 1264, 1062 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.57–7.39 (5H, m, Ph), 4.01 (1H, s, C*H*(OH)), 3.52 (1H, d, J=0.8 Hz, CHHC*H*(OH)), 2.98 (1H, d, J=4.3 Hz, C*H*H), 2.82 (1H, d, J=4.3 Hz, CH*H*), 2.68 (1H, dd, J=15.3, 0.8 Hz, C*H*HCH(OH)), 1.90 (1H, d, J=15.3 Hz, CH*H*CH(OH)); δ_C (75 MHz, $CDCl_3$) 133.0, 128.9, 128.6, 128.3, 78.7, 68.0, 64.7, 62.3, 45.3, 33.8; ESITOF: $[M+1]^+$, found: 205.0864. $C_{12}H_{12}O_3$ requires 205.0864.

4.9.4. (1-Phenyl-3,7-dioxatricyclo[4.1.0.0^{2,4}]hept-4-tyl)-methanol (36). 1.5 mg (3%), white solid; ν_{max} ($CHCl_3$) 3418, 3061, 2926, 1713, 1448, 1306, 1076 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.57–7.39 (5H, m, Ph), 4.62 (1H, s, OC*H*CPh), 3.70 (1H, d, J=1.0 Hz, CHHC*H*), 3.50 (2H, s, CH_2OH), 2.34 (1H, dd, J=15.4, 1.0 Hz, C*H*HCH), 2.24 (1H, d, J=15.4 Hz, CH*H*CH); δ_C (75 MHz, $CDCl_3$) 133.5, 128.6, 128.5, 126.4, 77.2, 73.4, 68.8, 63.6, 46.9, 36.2; ESITOF: $[M+Na]^+$, found: 227.0682. $C_{12}H_{12}O_3$ requires 227.0684.

4.10. Generation of oxiranyl anions 39 and 40 and their reactions with electrophiles

To a solution of LTMP (1.30 mmol) in THF (5 mL) was added dropwise a solution of oxirane **38**[12] (53.4 mg, 0.26 mmol) and freshly distilled TMSCl (0.33 mL, 2.60 mmol) in THF (10 mL) at −78°C under nitrogen atmosphere. The reaction mixture was left stirring at that temperature for 5 h and then quenched with saturated aqueous $NaHCO_3$ solution. The crude mixture was extracted several times with CH_2Cl_2 and the combined organic layer was washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was separated by PLC (silica gel; 10% EtOAc in hexane as eluent) to obtain products **41** (49.7 mg, 69%) and **42** (5.0 mg, 7%).

Compound **43** (38%) was obtained as the only product isolated when methyl iodide was used as electrophile.

4.10.1. Methyl 2-benzoyl-3-(trimethylsilyl)-oxirane-2-carboxylate (41). 49.7 mg (69%), colorless liquid; [Found: C, 60.24; H, 6.58. $C_{14}H_{18}SiO_4$ requires C, 60.41; H, 6.47%]; ν_{max} ($CHCl_3$) 3029, 2957, 1753, 1690, 1599, 1450, 1253, 847 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.88 (2H, d, J=8.0 Hz, Ph), 7.60 (1H, t, J=8.0 Hz, Ph), 7.47 (2H, t, J=8.0 Hz, Ph), 3.75 (3H, s, OMe), 2.78 (1H, s, CH), 0.20 (9H, s, Me_3Si); δ_C (125 MHz, $CDCl_3$) 192.2, 167.9, 134.2, 134.0, 128.7, 128.4, 64.8, 57.4, 52.9, −2.6; ESITOF: $[M+Na]^+$, found: 301.0877. $C_{14}H_{18}SiO_4$ requires 301.0872.

4.10.2. Methyl 2-benzoyl-3-(trimethylsilyl)-oxirane-2-carboxylate (42). 5.0 mg (7%), colorless liquid; ν_{max} ($CHCl_3$) 3029, 2957, 1753, 1690, 1599, 1450, 1438, 847 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 8.03 (2H, d, J=9.0 Hz, Ph), 7.61 (1H, t, J=9.0 Hz, Ph), 7.49 (2H, t, J=9.0 Hz, Ph), 3.76 (3H, s, OMe), 2.94 (1H, s, CH), 0.03 (9H, s, Me_3Si); δ_C (125 MHz, $CDCl_3$) 191.7, 169.1, 134.7, 134.2, 129.2, 128.7, 63.5, 58.8, 53.4, −2.9; ESITOF: $[M+Na]^+$, found: 301.0872. $C_{14}H_{18}SiO_4$ requires 301.0872.

4.10.3. Methyl 2-benzoyl-3-methyl-oxirane-2-carboxylate (43). 21.7 mg (38%), colorless liquid; ν_{max} ($CHCl_3$) 3029, 2929, 1754, 1689, 1599, 1450, 1438, 1273 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 8.02 (2H, d, J=8.0 Hz, Ph), 7.64 (1H, t, J=8.0 Hz, Ph), 7.51 (2H, t, J=8.0 Hz, Ph), 3.79 (3H, s, OMe), 3.63 (1H, q, J=5.0 Hz, C*H*CH_3), 1.55 (3H, d, J=5.0 Hz, CHCH_3); δ_C (125 MHz, $CDCl_3$) 190.8, 166.8,

134.2, 134.1, 129.2, 128.8, 64.7, 58.7, 53.2, 13.2; ESITOF: $[M+Na]^+$, found: 243.0633. $C_{12}H_{12}O_4$ requires 243.0634.

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