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Access to Tri- and Tetracyclic Structures by Thermally Promoted and High-Pressure-Promoted [4+2] Cycloadditions of 2-, 3- or 4-Vinyl-Substituted Binuclear Heterocycles

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A set of 3-(2-alkoxyvinyl)benzofurans, -furopyridines and -indoles **5**–**8** have been tested in [4+2] cycloaddition reactions. The results indicate that they all behave as good dienes, even with only moderately activated dienophiles such as acrylates or MVK. The *endo*/*exo* selectivity observed in the adducts depends on the activation conditions: in general, thermal conditions tend to favour the *exo* isomers, while high pressures preferentially provide the *endo* isomers. Only the (*E*) isomers of these dienes proved reactive, the (*Z*) isomers generally being recovered unaltered. The [4.4.0] binuclear heterocycles such as the isochromene compound **13** and the isoquinolinones **14**–**16** tested here proved to be significantly less reactive. Finally, the resulting tricyclic adducts **19** were engaged in ene reactions with NPM. Additions involving solely the *endo* isomers of these adducts took place, stereoselectively affording the succinimide derivatives **29**, although in low yields.

Introduction

Functionalised heterocycles in general, and polynuclear ones in particular, are a cornerstone of the development and practice of modern medicinal chemistry.[1] Because it is simple and generally efficient, the Diels–Alder cycloaddition reaction is frequently used to construct the nonaromatic six-membered rings that may be fused to the heterocyclic cores.[2] Dienes with one double bond embedded in an aromatic heterocycle (vinyl-substituted heterocycles) have been studied extensively for this purpose. Polycyclic structures have thus been prepared from vinylbenzofurans,[3] vinylindoles[4] and vinylisoquinolinones[5] through cycloadditions with activated dienophiles such as dimethyl acetylenedicarboxylate,[4b,6] tetracyanoethylene,[3a] arynes,[7] quinones[6,8] and maleimides.[3a,3c,4a] Comparable intramolecular strategies have also been used in the synthesis of indole alkaloids.[9] Note that these reactions have in most cases been performed under thermal conditions, although high pressures were preferred in at least one case.[3e] In this paper we present a series of results that we have obtained through the use of various vinyl-substituted heterocycles in Diels–Alder cycloadditions with dienophiles such as acrylates or maleic acid derivatives. In some cases the influence of the mode of activation on the yields and selectivities was also studied.

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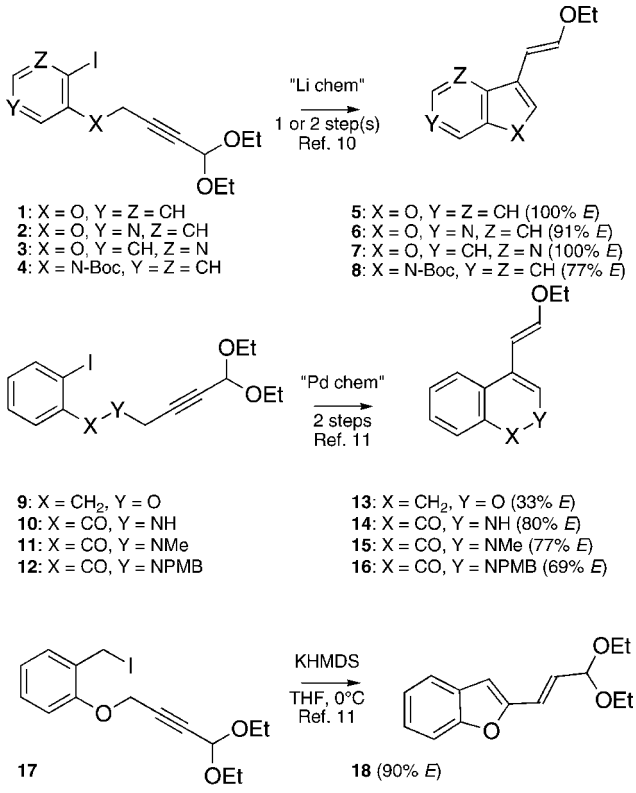
Results and Discussion

In previous papers we have described several routes to bicyclic heterocycles, mainly based on intramolecular carbometallation of propargylic acetals. Several [4.3.0] (**5**–**8**) and [4.4.0] (**13**–**16**) systems could thus be prepared either through an anionic cascade triggered by an aryllithium substrate[10] or by a palladium-catalysed tandem cyclisation/hydride capture process,[11] respectively (Scheme 1). In the second case, an extra elimination step to transform the resulting unsaturated acetal into the corresponding diene was required. A route to 2-vinylbenzofuran compound **18** from the benzylic iodide **17** was also discovered during these studies. We thus decided to examine, in a next stage, the synthetic potential of this relatively large set of compounds by treating them with electron-deficient dienophiles. The results are presented in this paper.

Cycloadditions Involving [4.3.0] Heterocycles

We first considered the cases of the benzofuran **5**, the furopyridines **6** and **7** and the indole **8**. These dienes were treated with a set of moderately activated dienophiles, such as acrylates and related electron-deficient olefins. Two types of conditions were employed: thermal (heating at reflux in toluene; cond. A) or hyperbaric (12 kbar in THF, cond. B)



1: X = O, Y = Z = CH
2: X = O, Y = N, Z = CH
3: X = O, Y = CH, Z = N
4: X = N-Boc, Y = Z = CH

5: X = O, Y = Z = CH (100% *E*)
6: X = O, Y = N, Z = CH (91% *E*)
7: X = O, Y = CH, Z = N (100% *E*)
8: X = N-Boc, Y = Z = CH (77% *E*)

9: X = CH_2, Y = O
10: X = CO, Y = NH
11: X = CO, Y = NMe
12: X = CO, Y = NPMB

13: X = CH_2, Y = O (33% *E*)
14: X = CO, Y = NH (80% *E*)
15: X = CO, Y = NMe (77% *E*)
16: X = CO, Y = NPMB (69% *E*)

17

18 (90% *E*)

Scheme 1. Routes to binuclear heterocyclic dienes.[10,11]

activation. All experiments were run in the presence of trace amounts of hydroquinone. The results are gathered in Table 1.

Let us first discuss the results obtained with diene **5** (Entries 1–13). Despite the aromatic character of one of its double bonds, this diene affords the expected cycloadducts in reasonable yields (31–63%), under both thermal and high-pressure conditions. If the regioselectivity is strictly controlled by the terminal ethoxy group, the endoselectivity depends mainly on the mode of activation. Thermal cycloadditions are generally in favour of the *exo* isomers, while the hyperbaric conditions tend to promote the *endo* compounds (compare Entries 2 and 3, 4 and 5, 9 and 10). Two dienophiles that do not seem to follow this "rule" are methyl acrylate (which favours the *endo* isomer **19a** even thermally; Entry 1) and phenyl acrylate, which exhibits no selectivity at reflux in toluene and the highest *endo* selectivity for **19d** under 12 to 16 kbar (70%, Entry 7, not increased under higher pressure, Entry 8). These results are difficult to interpret. One might suppose that the Alder *endo* rule would be followed by the small methyl acrylate under thermal conditions, while its bulkier analogues would prefer *exo* approaches.[12] Under pressure, the more compact *endo* transition state tends to be always favoured.[13] In the case of phenyl acrylate, a π-stacking interaction taking place between the phenyl rings of the ester and of the benzofuran can be invoked, but this is not observed with benzyl acrylate (see *de* for **19e**; Entries 9 and 10). Methyl vinyl ketone (MVK) reacts similarly to the acrylates and gives a slightly better yield of **19f** (Entry 11). We think it worth underlining that the double bond resulting from the cycloaddition remains, in all the above cases, in its original *exo* position with respect to the five-membered ring and therefore does not restore the aromaticity of the benzofuran. Advantage can be taken of this phenomenon (vide infra).

1-Cyanovinyl acetate (Entry 12) and 1,1-bis(phenylsulfonyl)ethylene (Entry 13) provide **20** and **21** in mediocre yields, probably due to the steric hindrance of these two *gem*-disubstituted dienophiles. The selectivity obtained with 1-cyanovinyl acetate is comparable to that measured with the acrylates, but we were unable to determine whether the *endo* or the *exo* isomer was the major one. It is worth noting that the double bond in the resulting adduct **21** had migrated from the exocyclic to the aromatic (benzofuranic) position. An AM1 semiempirical optimisation of **21** and its dearomatised exocyclic isomer suggested the latter form to be more stable by ≈ 0.3 kcal mol^{-1}. This negligible difference does not shed any light on the driving force behind this isomerisation.

The furo[2,3-*c*]pyridine **6** and the furo[3,2-*b*]pyridine **7** provided results comparable to those seen with **5** in this reaction. At 110 °C or under 12 kbar, they reacted with ethyl acrylate to give the expected cycloadducts in better yields (attributable to their better stabilities) and with comparable selectivities. The indole **8** behaved comparably but appeared to be slightly more reactive than the previous dienes.[10] The pure (*E*) isomer was used in the thermal experiment while the (*E*/*Z*) mixture (77:23) was employed under pressure. In this latter case, the (*E*) isomer reacted selectively while its (*Z*) counterpart was recovered unchanged. X-ray analysis of the *endo* isomers of adducts **19b** and **23** confirmed the stereochemistry of the adducts (Figure 1).

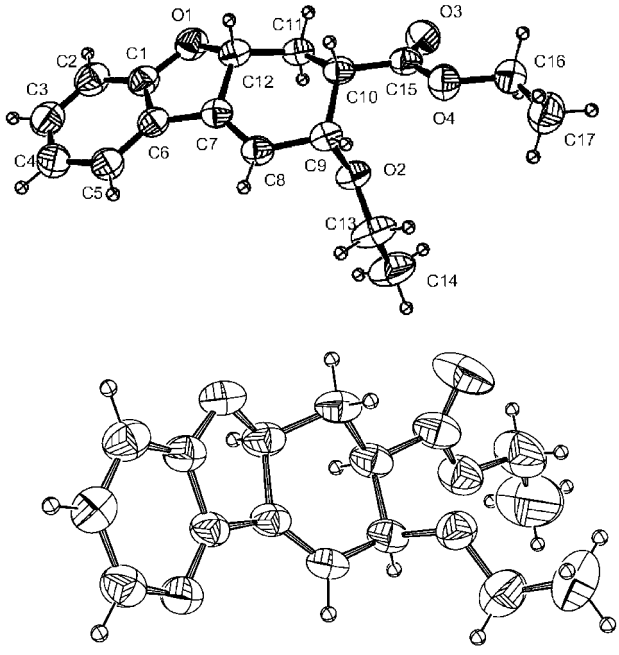
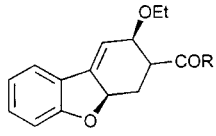
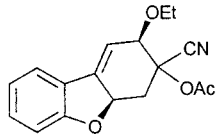
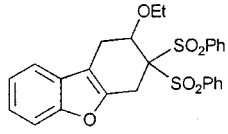
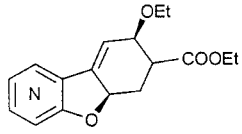
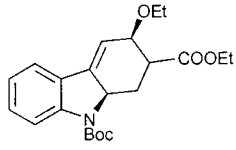
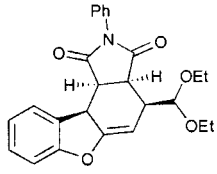


Figure 1. ORTEP representations of **19b** (top) and **23** (bottom).

Table 1. Cycloaddition involving dienes belonging to the class of [4.3.0] bicyclic heterocycles.

Entry	Diene	Dienophile	Conditions[a]	*t* (h)	Cycloadduct	#	Yield (%)[b]	*endo*/*exo*
1	**5**	methyl acrylate	A	96		**19a** (R = OMe)	46	63:37
2	**5**	ethyl acrylate	A	72		**19b** (R = OEt)	59	37:63
3	**5**	ethyl acrylate	B	18		**19b** (R = OEt)	53	72:28
4	**5**	*tert*-butyl acrylate	A	72		**19c** (R = O*t*Bu)	53	36:64
5	**5**	*tert*-butyl acrylate	B	24		**19c** (R = O*t*Bu)	54	70:30
6	**5**	phenyl acrylate	A	72		**19d** (R = OPh)	50	50:50
7	**5**	phenyl acrylate	B	18		**19d** (R = OPh)	53	85:15
8	**5**	phenyl acrylate	C	18		**19d** (R = OPh)	51	85:15
9	**5**	benzyl acrylate	A	72		**19e** (R = OBn)	51	39:61
10	**5**	benzyl acrylate	B	24		**19e** (R = OBn)	49	75:25
11	**5**	MVK	A	96		**19f** (R = Me)	63	40:60
12	**5**	1-cyanovinyl acetate	A	96		**20**	35	24:76[c]
13	**5**	1,1-bis(phenylsulfonyl)ethylene	A	96		**21**	31	–
14	**6**	ethyl acrylate	B	18		**22**	66	76:24
15	**7**	ethyl acrylate	A	168		**23**	65	32:68
16	**7**	ethyl acrylate	B	48		**23**	72	72:28
17	**8**	ethyl acrylate	A	18		**24**	61	27:73
18	**8**	ethyl acrylate	B	36		**24**	70	70:30
19	**18**	*N*-phenylmaleimide	A	16		**25**	0	–
20	**18**	*N*-phenylmaleimide	B	20		**25**	55[c]	100:0

[a] A: Toluene, reflux. B: 12 kbar, THF, room temp. C: 16 kbar, THF, room temp. [b] Calculated on the basis of the (*E*) isomer. [c] The *endo*/*exo* structures of the isomers have not been established.

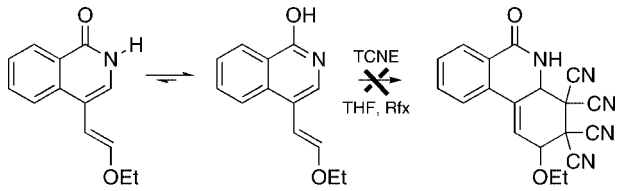
To conclude this section, we also considered the reactivity of the 2-vinylbenzofuran **18**. No reaction between this diene and phenyl or ethyl acrylate, nor with *N*-phenylmaleimide (NPM; Entry 19), couldbe observed under thermal conditions: only polymerisation of the diene was observed. In contrast, a single *endo* adduct **25** derived from the (*E*) isomer of **18** was recovered when it was treated with NPM under 12 kbar in THF (Entry 20). Here the minor (*Z*) isomer was again recovered unchanged.

Cycloadditions Involving [4.4.0] Heterocycles

The isochroman **13** and the isoquinolinones **14**–**16** were considered next. They were treated with a comparable set of dienophiles (acrylates, NPM and maleic anhydride), mainly under thermal conditions (Table 2). The reaction between **13** and ethyl acrylate provided an unexpected furoisochromene **26** in low yield (Entry 1).

This compound probably originated from reaction between **13** and small amounts of dioxygen in the solution. A comparable transformation of an exocyclic diene into a dihydrofuran through the action of O_2 in the presence of *meso*-tetraphenylporphine has been reported previously.[14] No trace of the expected adduct could be observed in this case. In contrast, the more activated maleic anhydride gave the pure *endo* adduct **27** in good yield (Entry 2) with respect to the minor (*E*) isomer of **13**. The (*Z*) isomer could not be recovered in this case.

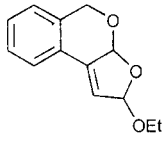
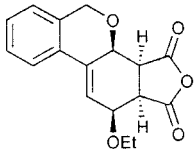
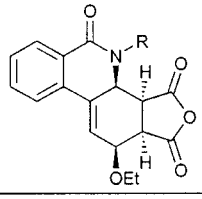
We then moved to the isoquinolinones **14**–**16**, first evaluating the reactivity of the secondary amide **14**. Cycloadditions with ethyl and methyl acrylates proved unsuccessful under both thermal and hyperbaric conditions. Switching to a highly activated dienophile such as tetracyanoethylene at reflux in toluene also did not provide the expected adduct. This inertia could be explained by the highly aromatic character of **14** induced by the prototropy of the NH proton (Scheme 2).



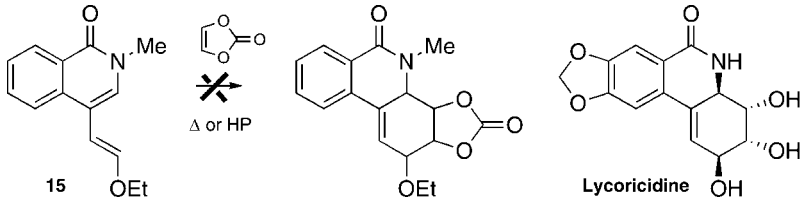
Scheme 2. Prototropy in isoquinolone **13**.

This hypothesis seems to be supported by the results obtained with the tertiary amide species. The isoquinolinone compound **15** was treated with maleic anhydride at reflux in toluene, and the expected adduct **28a** was recovered in fair yield and as a single *endo* isomer (Entry 3). Dienes such as **15** can be regarded as advanced precursors for the construction of the narciclasin or lycoricidin skeletons;[15] a cycloaddition between **15** and vinylene carbonate, for instance, could provide an analogue of lycoricidine. However, our attempts to induce a reaction between **15** and this dienophile failed (150 °C neat in a sealed tube or 12 kbar in THF, room temp., 24 h; Scheme 3).

Table 2. Thermal cycloaddition of dienes belonging to [4.4.0] bicyclic heterocycles.

Entry	Diene	Dienophile	Cycloadduct	#	Yield (%)	*endo*/*exo*
1	**13**	ethyl acrylate		**26**	33[a]	–
2	**13**	maleic anhydride		**27**	77[b]	100:0
3	**15**	maleic anhydride		**28a** (R = Me)	52[b]	100:0
4	**16**	maleic anhydride		**28b** (R = PMB)	17[b]	100:0

[a] Yield after 18 h at reflux in toluene, calculated on the basis of the (*E*) and (*Z*) isomers of the dienes. [b] Yield after 18 h at reflux in toluene, calculated on the basis of the (*E*) isomers of the dienes.

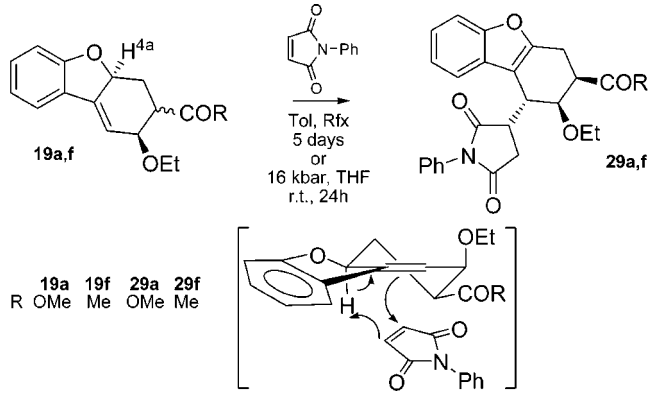


Scheme 3. Failed attempts to cyclise **13** and vinylene carbonate.

Neither ethyl acrylate nor NPM had reacted with diene **16** after 3 days at reflux in toluene. Maleic anhydride finally gave the expected tetracyclic adduct **28b** as a pure *endo* isomer, however, though in mediocre yield (Entry 4). This result is relatively encouraging in view of the synthesis of the Amaryllidaceae alkaloids mentioned above.

Further Reactivity of Cycloadducts 19

Finally, we tried to take advantage of the dearomatisation of the benzofuran moiety in **19** to trigger an ene reaction involving the angular proton H.[4a] NPM was employed as an highly activated enophile. Treatment of the *endo* + *exo* mixture of **19a** with 1.3 equiv. of NPM in toluene at reflux gave the condensation product **29a**, but in a meagre 16% yield. The NMR spectra suggest that a diastereoselective ene reaction had taken place, involving the allylic H[4a] of the *endo* isomer of **19a** and NPM (Scheme 4). The *exo* isomer of **19a** was recovered unaltered.



Scheme 4. Diastereoselective ene addition between **19a** and NPM.

A comparable experiment was repeated with the pure *endo* isomer of **19f** but this time under hyperbaric conditions. After 24 h at 16 kbar at room temp. this had provided the expected ene adduct **29f** in a comparably diastereoselective way.

Note that these additions take place selectively on the less hindered faces of the *endo* substrates. The relative stereocontrol of the newly created asymmetric centre on the succinimide has not been determined. The aromatisation of the heterocycle is probably a significant driving force behind these ene additions.

Conclusions

The results collected in this paper suggest that 3-(2-alkoxyvinyl)benzofurans, -furopyridines and -indoles **5**–**8** behave as good dienes in [4+2] cycloaddition reactions, even with only moderately activated dienophiles such as acrylates or MVK. The *endo* selectivity observed in the adducts depends on the activation conditions. In general, thermal conditions tend to favour the *exo* isomers while high pressures preferentially provide the *endo* isomers. Only the (*E*) isomers of these dienes proved reactive, the (*Z*) isomers generally being recovered unaltered. In comparison, the only 2-vinylbenzofuran derivative used in this study (**18**) proved significantly less reactive.

A comparable conclusion can be applied to the [4.4.0] binuclear heterocycles tested here, such as the isochromene **13** and the isoquinolinones **14**–**16**. The secondary amide **14** turned out to be totally inert, probably because prototropy enhances the aromatic character of the heterocycle. Compounds **13**, **15** and **16** required an activated dienophile such as maleic anhydride for cyclisation to occur. The inertness of isoquinolinone **15** toward vinylene carbonate, even under harsh conditions, is worth underlining since this reaction could have opened a shortcut to the skeletons of interesting synthetic targets such as lycoricidine.

Finally, the resulting tricyclic adducts **19** were engaged in ene reactions with NPM under both thermal and hyperbaric conditions. Additions involving solely the *endo* isomers of these adducts occurred and stereoselectively afforded the succinimide derivatives **29**, though in low yields.

Experimental Section

General Aspects: ^{1}H NMR spectra were recorded at 200, 300 or 500 MHz and ^{13}C NMR spectra at 75 MHz; chemical shifts (δ) are given in parts per million (ppm) and the coupling constants (J) in Hertz. The solvent was deuterochloroform or [D_6]DMSO. IR spectra were recorded on a Perkin–Elmer 16 PC FT-IR. The mass spectra under electron impact conditions (EI) were recorded at 70 eV ionising potential; methane (CH_4) or isobutane (*i*BuH) were used for chemical ionisation (CI). The FAB MS spectrum of **28a** was recorded with a glycerol matrix under Xe bombardment (4 kV; threshold currant: 10 mA). The silica gel used for flash chromatography was 230–400 mesh. All reagents were of reagent grade and were used as such or distilled prior to use.

General Procedure for Cycloadditions Under Thermal Conditions (Conditions A): A mixture of diene and dienophile in toluene containing a small amount of hydroquinone was heated at reflux and followed by TLC until consumption of the diene. The solvent was then evaporated under vacuum and the residue was purified by column chromatography.

General Procedure for Cycloadditions Under Hyperbaric Conditions (Conditions B): A mixture of diene and dienophile in THF containing a small amount of hydroquinone was placed under high pressure (12 kbar) at room temperature. The solvent was then evaporated under vacuum and the residue was purified by column chromatography.

Methyl 2-Ethoxy-2,3,4,4a-tetrahydrodibenzofuran-3-carboxylate (19a): Conditions A were applied, with diene **5** (270 mg, 1.43 mmol) and methyl acrylate (2 mL, 22.2 mmol) in acetonitrile (2 mL) for 84 h. Column chromatography (5% ethyl acetate in heptane) of the crude product provided **19a** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (*endo*/*exo* = 63:37, total mass: 180 mg, 0.656 mmol, 46%).

endo Isomer: Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (d, J = 7.2 Hz, 1 H, aromatic C*H*), 7.19 (t, J = 7.7 Hz, 1 H, aromatic C*H*), 6.90 (t, J = 7.5 Hz, 1 H, aromatic C*H*), 6.85 (d, J = 8.7 Hz, 1 H, aromatic C*H*), 5.97 (dd, J = 3.0, 3.0 Hz, 1 H, 1-H), 4.85 (dm, J = 12.5 Hz, 1 H, axial 4a-H), 4.33 (m, 1 H, equatorial 2-H), 3.74 (s, 3 H, CO_2CH_3), 3.67 (m, 1 H, one of OCH_2CH_3), 3.48 (m, 1 H,

one of OCH_2CH_3), 2.77 (dm, J = 14.0 Hz, 1 H, axial 3-H), 2.50 (dm, J = 14.0 Hz, 1 H, equatorial 4-H), 2.07 (dt, J = 11.9, 11.9 Hz, 1 H, axial 4-H), 1.14 (t, J = 6.6 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.5 (*C*=O), 163.1 (aromatic *C*–O), 142.8, 131.1, 125.4, 121.8 and 121.5 (all aromatic or vinylic *C*H or *C*), 114.3 (C-1), 111.1 (aromatic *C*H), 83.1 (C-4a), 72.7 (C-2), 66.1 (OCH_2CH_3), 52.2 (CO_2CH_3), 44.4 (C-3), 25.7 (C-4), 16.0 (OCH_2CH_3) ppm. IR (film): $\tilde{\nu}_{max}$ = 2926, 1720 cm^{-1}. *m*/*z* (EI): 274 [*M*]$^+$ (11%), 228 (41), 188 (34), 169(100).

exo Isomer: Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, J = 7.5 Hz, 1 H, aromatic C*H*), 7.17 (t, J = 7.8 Hz, 1 H, aromatic C*H*), 6.87 (t, J = 7.3 Hz, 1 H, aromatic C*H*), 6.82 (d, J = 8.3 Hz, 1 H, aromatic C*H*), 5.90 (dd, J = 3.2 Hz, 3.2, 1 H, 1-H), 4.92 (m, 1 H, axial 4a-H), 4.36 (dd, J = 2.6, 2.6 Hz, 1 H, equatorial 2-H), 3.73 (s, 3 H, CO_2CH_3), 3.62 (dq, J = 1.5, 7.0 Hz, 2 H, OCH_2CH_3), 3.01 (m, 1 H, equatorial 3-H), 2.62 (ddd, J = 3.4, 5.6, 12.4 Hz, 1 H, equatorial 4-H), 1.98 (dt, J = 6.0, 12.0 Hz, 1 H, axial 4-H), 1.21 (t, J = 7.0 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.9 (*C*=O), 163.8 (aromatic *C*–O), 142.2, 131.1, 125.9, 122.0 and 121.6 (all aromatic or vinylic *C*H or *C*), 115.7 (C-1), 111.4 (aromatic *C*H), 80.5 (C-4a), 73.9 (C-2), 65.3 (OCH_2CH_3), 51.9 (CO_2CH_3), 43.1 (C-3), 27.2 (C-4), 16.1 (OCH_2CH_3) ppm. IR (film): $\tilde{\nu}_{max}$ = 2925, 1734 cm^{-1}. *m*/*z* (EI): 274 [*M*]$^+$ (32%), 228 (32), 188 (39), 169 (100).

Ethyl 2-Ethoxy-2,3,4,4a-tetrahydrodibenzofuran-3-carboxylate (19b): Conditions A were applied, with diene **5** (120 mg, 0.64 mmol) and ethyl acrylate (0.14 mL, 1.28 mmol) in toluene (5 mL) for 72 h. Column chromatography (10% ethyl acetate in heptane) of the crude product provided **19b** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (*endo*/*exo* = 37:63, total mass: 110 mg, 0.38 mmol, 59%).

Conditions B were also applied, with diene **5** (501 mg, 2.66 mmol) and ethyl acrylate (0.35 mL, 3.2 mmol) in THF (5 mL) for 18 h. Column chromatography (10% ethyl acetate in heptane) of the crude product provided **19b** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (*endo*/*exo* = 72:28, total mass: 400 mg, 1.39 mmol, 53%).

endo Isomer: White solid m.p. 89–91 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.34 (d, J = 7.6 Hz, 1 H, aromatic C*H*), 7.18 (t, J = 7.3 Hz, 1 H, aromatic C*H*), 6.90 (t, J = 7.3 Hz, 1 H, aromatic C*H*), 6.86 (d, J = 7.6 Hz, 1 H, aromatic C*H*), 5.98 (dd, J = 2.9, 3.7 Hz, 1 H, 1-H), 4.85 (dddd, J = 1.4, 2.9, 4.7, 11.3 Hz, 1 H, axial 4a-H), 4.33 (ddd, J = 1.4, 3.7, 4.7 Hz, 1 H, equatorial 2-H), 4.20 (q, J = 7.0 Hz, 2 H, $CO_2CH_2CH_3$), 3.66 (dq, J = 9.1, 7.0 Hz, 1 H, one of OCH_2CH_3), 3.47 (dq, J = 9.1, 7.0 Hz, 1 H, one of OCH_2CH_3), 2.75 (ddd, J = 2.5, 4.7, 13.1 Hz, 1 H, axial 3-H), 2.50 (ddd, J = 2.6, 4.7, 12.0 Hz, 1 H, equatorial 4-H), 2.01 (dt, J = 13.1, 12.0 Hz, 1 H, axial 4-H), 1.28 (t, J = 7.0 Hz, 3 H, $CO_2CH_2CH_3$), 1.11 (t, J = 7.0 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.5 (*C*=O), 162.6 (aromatic *C*–O), 142.3, 130.6, 125.0, 121.3, 121.0 (all aromatic or vinylic *C*H or *C*), 113.9 (C-1), 110.7 (aromatic *C*H), 82.7 (C-4a), 72.2 (C-2), 65.6 (OCH_2CH_3), 60.6 ($CO_2CH_2CH_3$), 43.0 (C-3), 25.2 (C-4), 15.5 (OCH_2CH_3), 13.2 ($CO_2CH_2CH_3$) ppm. IR (film): $\tilde{\nu}_{max}$ = 2979, 1727, 1608, 1256 cm^{-1}. *m*/*z* (EI): 288 [*M*]$^+$ (16%), 243 (10), 188 (100). $C_{17}H_{20}O_4$ (288.35): calcd. C 70.81, H 6.99; found C 70.79, H 7.08.

exo Isomer: Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.33 (d, J = 7.3 Hz, 1 H, aromatic C*H*), 7.17 (t, J = 7.7 Hz, 1 H, aromatic C*H*), 6.87 (t, J = 7.3 Hz, 1 H, aromatic C*H*), 6.82 (d, J = 7.7 Hz, 1 H, aromatic C*H*), 5.90 (dd, J = 3.3, 4.0 Hz, 1 H, 1-H), 4.93 (ddd, J = 3.3, 5.5, 11.3 Hz, , 1 H axial 4a-H), 4.36 (dd, J = 2.5, 4.0 Hz, 1 H, equatorial 2-H), 4.18 (q, J = 7.0 Hz, 2 H, $CO_2CH_2CH_3$), 3.62 (q, J = 7.0 Hz, 2 H, OCH_2CH_3), 2.99 (ddd, J = 2.5, 3.3, 6.2 Hz, 1 H, equatorial 3-H), 2.63 (ddd, J = 3.3, 5.5, 12.0 Hz, 1 H, equatorial 4-H), 1.98 (dt, J = 6.2, 11.6 Hz, 1 H, axial 4-H), 1.27 (t, J = 7.0 Hz, 3 H, $CO_2CH_2CH_3$), 1.21 (t, J = 7.0 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.8 (*C*=O), 163.0 (aromatic *C*–O), 142.1, 130.8 (2 C), 121.8 and 121.5 (all aromatic or vinylic *C*H or *C*), 115.1 (C-1), 110.9 (aromatic *C*H), 80.1 (C-4a), 73.4 (C-2), 65.5 (OCH_2CH_3), 61.5 ($CO_2CH_2CH_3$), 42.8 (C-3), 26.7 (C-4), 15.9 (OCH_2CH_3), 14.6 ($CO_2CH_2CH_3$) ppm. IR (film): $\tilde{\nu}_{max}$ = 2976, 1729, 1610, 1183 cm^{-1}. *m*/*z* (EI): 288 [*M*]$^+$ (15%), 242 (20), 188 (29), 169 (100). $C_{17}H_{20}O_4$ (288.35): calcd. C 70.81, H 6.99; found C 70.24, H 7.18.

***tert*-Butyl 2-Ethoxy-2,3,4,4a-tetrahydrodibenzofuran-3-carboxylate (19c):** Conditions A were applied, with diene **5** (405 mg, 2.15 mmol) and *tert*-butyl acrylate (0.41 mL, 2.76 mmol) in toluene (15 mL) for 72 h. Column chromatography (5% ethyl acetate in heptane) of the crude product provided **19c** as a mixture of *endo* and *exo* cycloadducts, which were not separated (*endo*/*exo* = 36:64, total mass: 360 mg, 1.14 mmol, 53%).

Conditions B were also applied, with diene **5** (250 mg, 1.33 mmol) and *tert*-butyl acrylate (0.25 mL, 1.73 mmol) in THF (2.5 mL) for 24 h. Column chromatography (10% ethyl acetate in heptane) of the crude product provided **19c** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (*endo*/*exo* = 70:30, total mass: 227 mg, 0.72 mmol, 54%).

endo Isomer: White solid. m.p. 146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (d, J = 7.5 Hz, 1 H, aromatic C*H*), 7.18 (t, J = 7.5 Hz, 1 H, aromatic C*H*), 6.89 (t, J = 7.5 Hz, 1 H, aromatic C*H*), 6.84 (d, J = 8.3 Hz, 1 H, aromatic C*H*), 6.00 (t, J = 3.2 Hz, 1 H, 1-H), 4.84 (m, 1 H, 4a-H), 4.29 (m, 1 H, 2-H), 3.69 (dq, J = 8.7, 7.2 Hz, 1 H, one of OCH_2CH_3), 3.51 (dq, J = 8.7, 7.2 Hz, 1 H, one of OCH_2CH_3), 2.66 (ddd, J = 2.7, 4.9, 13.2 Hz, 1 H, 3-H), 2.46 (ddd, J = 2.7, 5.3, 11.7 Hz, 1 H, equatorial 4-H), 2.00 (dt, J = 13.2, 11.7 Hz, 1 H, axial 4-H), 1.48 [s, 9 H, $C(CH_3)_3$], 1.13 (t, J = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.1 (*C*=O), 163.0 (aromatic *C*–O), 142.7, 130.9, 125.5, 121.7 and 121.4 (all aromatic or vinylic *C*H or *C*), 114.5 (C-1), 111.1 (aromatic *C*H), 83.4 (C-4a), 81.1 (CMe_3), 72.8 (C-2), 65.8 (OCH_2CH_3), 45.1 (C-3), 28.5 [$C(CH_3)_3$], 25.7 (C-4), 15.9 (OCH_2CH_3) ppm IR (film): $\tilde{\nu}_{max}$ = 2968, 1732, 1650, 1176 cm^{-1}. *m*/*z* (CI, *t*BuH): 317 [*M* + H]$^+$ (3%), 316 (4), 271 (100), 215 (56). $C_{19}H_{24}O_4$ (316.40): calcd. C 72.13, H 7.65; found C 71.49, H 7.88.

exo Isomer (obtained as a mixture with *endo* isomer): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, J = 7.5 Hz, 1 H, aromatic C*H*), 7.21–6.81 (m, 3 H, aromatic C*H*), 5.89 (t, J = 2.8 Hz, 1 H, 1-H), 4.81 (m, 1 H, 4a-H), 4.31 (m, 1 H, 2-H), 3.61 (q, J = 7.2 Hz, 2 H, OCH_2CH_3), 2.91 (m, 1 H, 3-H), 2.59 (m, 1 H, equatorial 4-H), 1.95 (dt, J = 6.0, 11.8 Hz, 1 H, axial 4-H), 1.45 [s, 9 H, $C(CH_3)_3$], 1.21 (t, J = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.0 (*C*=O), 162.9 (aromatic *C*–O), 141.9, 130.7, 125.4, 121.8 and 121.4 (all aromatic or vinylic *C*H or *C*), 115.3 (C-1), 110.9 (aromatic *C*H), 81.8 (CMe_3), 80.2 (C-4a), 73.4 (C-2), 65.5 (OCH_2CH_3), 43.6 (C-3), 28.4 [$C(CH_3)_3$], 26.9 (C-4), 15.9 (OCH_2CH_3) ppm.

Phenyl 2-Ethoxy-2,3,4,4a-tetrahydrodibenzofuran-3-carboxylate (19d): Conditions A were applied, with diene **5** (160 mg, 0.85 mmol) and phenyl acrylate (200 mg, 1.35 mmol) in toluene (5 mL) for 72 h. Column chromatography (10% ethyl acetate in heptane) of the crude product provided **19d** as a mixture of *endo* and *exo* cycloadducts, which were not separated (*endo*/*exo* = 50:50, total mass: 142 mg, 0.42 mmol, 50%).

Conditions B were also applied, with diene **5** (502 mg, 2.66 mmol) and phenyl acrylate (0.48 g, 3.2 mmol) in THF (5 mL) for 16 h. Column chromatography (10% ethyl acetate in heptane) of the crude product provided **19d** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (*endo*/*exo* = 85:15, total mass: 470 mg, 1.40 mmol, 53%).

endo Isomer: White solid. m.p. 162 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40–6.85 (m, 9 H, all aromatic C*H*), 6.06 (dd, *J* = 2.5, 2.9 Hz, 1 H, 1-H), 4.93 (ddd, *J* = 2.5, 4.9, 11.9 Hz, 1 H, 4a-H), 4.52 (dd, *J* = 2.9, 4.7 Hz, 1 H, 2-H), 3.77 (dq, *J* = 9.3, 7.2 Hz, 1 H, one of OCH_2CH_3), 3.60 (dq, *J* = 9.3, 7.2 Hz, 1 H, one of OCH_2CH_3), 3.04 (ddd, *J* = 2.2, 4.7, 13.1 Hz, 1 H, 3-H), 2.62 (ddd, *J* = 2.2, 4.9, 11.9 Hz, 1 H, equatorial 4-H), 2.19 (dt, *J* = 13.1, 11.9 Hz, 1 H, axial 4-H), 1.19 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5 (*C*=O), 163.1 (aromatic *C*–O), 151.2, 143.1, 131.2, 129.8, 126.2, 125.3, 121.9, 121.8 and 121.6 (aromatic and vinylic carbons), 113.9 (C-1), 111.2 (aromatic carbon), 83.0 (C-4a), 72.5 (C-2), 65.8 (OCH_2CH_3), 44.6 (C-3), 25.7 (C-4), 16.1 (OCH_2CH_3) ppm. IR (film): $\tilde{\nu}_{max}$ = 2975, 1760, 1605, 1120 cm^{-1}. *m*/*z* (CI, *t*BuH): 337 $[M + H]^+$ (10%), 243 (6), 211 (100). $C_{21}H_{20}O_4$ (336.39): calcd. C 74.98, H 5.99; found C 75.05, H 6.15.

exo Isomer (obtained as a mixture with *endo* isomer): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–6.77 (m, 9 H, all aromatic C*H*), 5.90 (t, *J* = 3.0 Hz, 1 H, 1-H), 5.01 (ddd, *J* = 3.0, 5.6, 11.3 Hz, 1 H, 4a-H), 4.40 (dd, *J* = 2.6, 5.3 Hz, 1 H, 2-H), 3.62 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.19 (m, 1 H, 3-H), 2.74 (ddd, *J* = 3.4, 5.6, 12.0 Hz, 1 H, equatorial 4-H), 2.06 (dt, *J* = 6.4, 12.0 Hz, 1 H, axial 4-H), 1.18 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0 (*C*=O), 162.6 (aromatic *C*–O), 150.4, 141.7, 130.5, 129.4, 126.0, 124.7, 121.5, 121.4 and 121.3 (aromatic and vinylic carbons), 114.6 (C-1), 110.5 (aromatic carbon), 79.5 (C-4a), 73.1 (C-2), 65.4 (OCH_2CH_3), 42.6 (C-3), 26.4 (C-4), 15.6 (OCH_2CH_3).

Benzyl 2-Ethoxy-2,3,4,4a-tetrahydrodibenzofuran-3-carboxylate (19e): Conditions A were applied, with diene **5** (403 mg, 2.14 mmol) and benzyl acrylate (0.57 mL, 2.8 mmol) in toluene (15 mL) for 72 h. Column chromatography (10% ethyl acetate in heptane) of the crude product provided **19e** as a mixture of *endo* and *exo* cycloadducts, which were not separated (*endo*/*exo* = 39:61, total mass: 385 mg, 1.10 mmol, 51%).

Conditions B were also applied, with diene **5** (250 mg, 1.33 mmol) and benzyl acrylate (0.33 mL, 1.73 mmol) in THF (2.5 mL) for 24 h. Column chromatography (10% ethyl acetate in heptane) of the crude product provided **19e** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (*endo*/*exo* = 75:25, total mass: 228 mg, 0.65 mmol, 49%).

endo Isomer: White solid m.p. 110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–6.77 (m, 9 H, all aromatic C*H*), 5.97 (t, *J* = 3.4 Hz, 1 H, 1-H), 5.19 (s, 2 H, CH_2Ph), 4.85 (m, 1 H, 4a-H), 4.34 (m, 1 H, 2-H), 3.61 (dq, *J* = 9.0, 7.2 Hz, 1 H, one of OCH_2CH_3), 3.37 (dq, *J* = 9.0, 7.2 Hz, 1 H, one of OCH_2CH_3), 2.82 (ddd, *J* = 2.6, 4.9, 13.2 Hz, 1 H, 3-H), 2.54 (ddd, *J* = 2.6, 5.3, 11.7 Hz, 1 H, equatorial 4-H), 2.11 (dt, *J* = 13.2, 11.7 Hz, 1 H, axial 4-H), 1.02 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.8 (*C*=O), 163.1 (aromatic *C*–O), 142.8, 136.3, 131.1, 129.0, 128.8, 128.7, 125.4, 121.8 and 121.5 (aromatic and vinylic carbons), 114.3 (C-1), 111.1 (aromatic carbon), 83.1 (C-4a), 72.6 (C-2), 66.9 (CH_2Ph), 66.0 (OCH_2CH_3), 44.6 (C-3), 25.7 (C-4), 15.9 (OCH_2CH_3) ppm. IR (film): $\tilde{\nu}_{max}$ = 2969, 1732, 1602, 1182, 1075 cm^{-1}. *m*/*z* (CI, *t*BuH): 351 $[M + H]^+$ (36%), 305 (100), 243 (33). $C_{22}H_{22}O_4$ (350.42): calcd. C 75.41, H 6.33; found C 75.26, H 6.52.

exo Isomer (obtained as a mixture with *endo* isomer): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–6.77 (m, 9 H, all aromatic C*H*), 5.90 (t, *J* = 3.4 Hz, 1 H, 1-H), 5.20 (s, 2 H, CH_2Ph), 4.95 (m, 1 H, 4a-H), 4.38 (m, 1 H, 2-H), 3.62 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.04 (m, 1 H, 3-H), 2.65 (m, 1 H, equatorial 4-H), 2.00 (dt, *J* = 5.7, 11.7 Hz, 1 H, axial 4-H), 1.19 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.7 (*C*=O), 163.0 (aromatic *C*–O), 142.1, 136.3, 130.8, 129.0, 128.8, 128.4, 125.2, 121.8 and 121.5 (aromatic and vinylic carbons), 115.1 (C-1), 110.9 (aromatic carbon), 80.1 (C-4a), 73.5 (C-2), 67.2 (CH_2Ph), 65.6 (OCH_2CH_3), 42.8 (C-3), 26.8 (C-4), 15.9 (OCH_2CH_3).

1-(2-Ethoxy-2,3,4,4a-tetrahydrodibenzofuran-3-yl)ethanone (19f): Conditions A were applied, with diene **5** (500 mg, 2.66 mmol) and methyl vinyl ketone (0.87 mL, 10.6 mmol) in toluene (15 mL) for 51 h. Column chromatography (10% ethyl acetate in heptane) of the crude product provided **19f** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (*endo*/*exo* = 40:60, total mass: 430 mg, 1.66 mmol, 63%).

endo Isomer: Beige solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.3 Hz, 1 H, aromatic C*H*), 7.19 (t, *J* = 7.3 Hz, 1 H, aromatic C*H*), 6.88 (t, *J* = 7.3 Hz, 1 H, aromatic C*H*), 6.84 (d, *J* = 7.6 Hz, 1 H, aromatic C*H*), 6.03 (dd, *J* = 3.3, 3.3 Hz, 1 H, 1-H), 4.84 (dm, *J* = 11.7 Hz, 1 H, axial 4a-H), 4.45 (m, 1 H, equatorial 2-H), 3.67 (dq, *J* = 6.9, 9.1 Hz, 1 H, one of OCH_2CH_3), 3.42 (dq, *J* = 6.9, 8.8 Hz, 1 H, one of OCH_2CH_3), 2.75 (ddd, *J* = 2.9, 5.1, 13.2 Hz, 1 H, axial 3-H), 2.49 (ddd, *J* = 2.9, 5.1, 11.7 Hz, 1 H, equatorial 4-H), 2.24 (s, 3 H, $COCH_3$), 2.00 (dt, *J* = 12.8, 11.7 Hz, 1 H, axial 4-H), 1.10 (t, *J* = 6.9 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.8 (*C*=O), 163.2 (aromatic *C*–O), 143.5, 131.2, 125.3, 121.8 and 121.5 (all aromatic or vinylic *C*H or *C*), 113.8 (C-1), 111.2 (aromatic *C*H), 83.5 (C-4a), 72.6 (C-2), 65.0 (OCH_2CH_3), 51.4 (C-3), 28.4 ($COCH_3$)25.5 (C-4), 15.9 (OCH_2CH_3) ppm. IR (film): $\tilde{\nu}_{max}$ = 2923, 1715 cm^{-1}. *m*/*z* (EI): 258 $[M]^+$ (25%), 188 (100), 169 (29), 131 (29).

exo Isomer: Beige solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 7.5 Hz, 1 H, aromatic C*H*), 7.09 (t, *J* = 6.6 Hz, 1 H, aromatic C*H*), 6.84 (t, *J* = 7.3 Hz, 1 H, aromatic C*H*), 6.77 (d, *J* = 7.7 Hz, 1 H, aromatic C*H*), 5.91 (dd, *J* = 3.0, 3.0 Hz, 1 H, 1-H), 4.74 (m, 1 H, axial 4a-H), 4.20 (dd, *J* = 3.1, 5.6 Hz, 1 H, equatorial 2-H), 3.60 (dq, *J* = 7.0, 10.2 Hz, 1 H, one of OCH_2CH_3), 3.48 (dq, *J* = 7.1, 9.4 Hz, 1 H, one of OCH_2CH_3), 2.99 (m, 1 H, equatorial 3-H), 2.50 (ddd, *J* = 3.0, 5.6, 12.4 Hz, 1 H, equatorial 4-H), 2.25 (s, 3 H, $COCH_3$), 1.91 (dt, *J* = 7.4, 11.3 Hz, 1 H, axial 4-H), 1.16 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.9 (*C*=O), 163.0 (aromatic *C*–O), 141.4, 130.8, 125.0, 121.8 and 121.5 (all aromatic or vinylic *C*H or *C*), 115.5 (C-1), 110.9 (aromatic *C*H), 80.0 (C-4a), 73.4 (C-2), 65.4 (OCH_2CH_3), 50.3 (C-3), 29.7 ($COCH_3$), 26.9 (C-4), 15.9 (OCH_2CH_3) ppm. IR (film): $\tilde{\nu}_{max}$ = 2970, 1703 cm^{-1}. *m*/*z* (EI): 258 $[M]^+$ (66%), 188 (58), 169 (100), 131 (53)

3-Acetoxy-2-ethoxy-2,3,4,4a-tetrahydrodibenzofuran-3-carbonitrile (20): Conditions A were applied, with diene **5** (199 mg, 1.06 mmol) and 1-cyanovinyl acetate (0.37 mL, 3.18 mmol) in toluene (5 mL) for 120 h. Column chromatography (2% ethyl acetate in heptane) of the crude product provided **20** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (24:76, total mass: 110 mg, 0.37 mmol, 35%).

Minor isomer: Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.1 Hz, 1 H, aromatic C*H*), 7.33 (m, 1 H, aromatic C*H*), 6.89 (t, *J* = 7.5 Hz, 1 H, aromatic C*H*), 6.83 (d, *J* = 6.9 Hz, 1 H, aromatic C*H*), 5.87 (dd, *J* = 3.4, 3.4 Hz, 1 H, 1-H), 5.18 (dm, *J* = 11.5 Hz, 1 H, axial 4a-H), 4.61 (dd, *J* = 1.7, 3.8 Hz, 1 H, equatorial

2-H), 3.69 (s, 3 H, COCH_3), 3.67 (dq, J = 6.8, 9.0 Hz, 1 H, one of OCH_2CH$_3$), 3.55 (dq, J = 6.8, 7.1 Hz, 1 H, one of OCH_2CH$_3$), 2.81 (dd, J = 5.4, 11.5 Hz, 1 H, equatorial 4-H), 2.25 (dd, J = 11.5, 11.5 Hz, 1 H, axial 4-H), 1.12 (t, J = 7.0 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.2 (*C*=O), 162.9 (aromatic *C*–O), 142.7, 131.6, 128.5, 126.4 and 124.6 (all aromatic or vinylic *C*H or *C*), 117.3 (*C*N), 112.2 (C-1), 111.5 (aromatic *C*H), 79.8 (C-4a), 74.3 (C-2), 71.4 (C-3), 67.2 (O*C*H$_2$CH$_3$), 26.7 (C-4), 21.3 (CO*C*H$_3$), 16.0 (OCH$_2$*C*H$_3$) ppm. *m*/*z* (EI): 188 (100%), 131 (24).

Major isomer: Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.6 Hz, 1 H, aromatic C*H*), 7.17 (m, 1 H, aromatic C*H*), 6.85 (t, J = 7.5 Hz, 1 H, aromatic C*H*), 6.82 (d, J = 8.3 Hz, 1 H, aromatic C*H*), 5.73 (dd, J = 3.1, 3.1 Hz, 1 H, 1-H), 4.90 (m, 1 H, axial 4a-H), 4.23 (m, 1 H, equatorial 2-H), 3.91 (dq, J = 7.2, 9.1 Hz, 1 H, one of OCH_2CH$_3$), 3.76 (dq, J = 7.1, 9.0 Hz, 1 H, one of OCH_2CH$_3$), 3.70 (s, 3 H, COCH_3), 3.03 (dd, J = 5.3, 12.8 Hz, 1 H, equatorial 4-H), 2.33 (dd, J = 12.4, 12.4 Hz, 1 H, axial 4-H), 1.17 (t, J = 3.8 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.5 (*C*=O), 161.5 (aromatic *C*–O), 141.2, 130.2, 127.0, 125.0 and 123.4 (all aromatic or vinylic *C*H or *C*), 116.0 (*C*N), 110.8 (C-1), 109.9 (aromatic *C*H), 76.4 (C-4a), 72.8 (C-2), 72.6 (C-3), 67.0 (O*C*H$_2$CH$_3$), 31.5 (C-4), 19.9 (CO*C*H$_3$), 14.3 (OCH$_2$*C*H$_3$) ppm. *m*/*z* (EI): 188 (100%), 131 (32).

3,3-Bis(phenylsulfonyl)-2-ethoxy-1,2,3,4-tetrahydrodibenzofuran (21): Conditions A were applied, with diene **5** (188 mg, 1 mmol) and 1,1-bis(phenylsulfonyl)ethylene (463 mg, 1.5 mmol) in toluene (5 mL) for 72 h. Column chromatography (40% ethyl acetate in heptane) of the crude product provided **21** (total mass: 152 mg, 0.31 mmol, 31%).

Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.0 Hz, 2 H, aromatic C*H*), 8.02 (d, J = 8.0 Hz, 2 H, aromatic C*H*), 7.40 (m, 10 H, aromatic C–*H*), 4.74 (dd, J = 6.2, 8.9 Hz, 1 H, 2-H), 3.47 (m, 4 H, 4-H and OCH_2CH$_3$), 3.24 (dd, J = 6.0, 15.4 Hz, 1 H, equatorial 1-H), 3.01 (dd, J = 9.0, 15.1 Hz, 1 H, axial 1-H), 0.76 (t, J = 7.0 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6 (C-4a), 147.4 (aromatic *C*–O), 140.8, 138.2, 134.8, 134.3, 132.2, 131.7, 128.9 and 128.3 (*C* Ar IV), 127.8, 124.4, 123.1, 119.1, 111.6 and 111.2 (all aromatic or vinylic *C*H or *C*), 92.6 (C-3), 75.7 (C-2), 65.4 (O*C*H$_2$CH$_3$), 28.5 (C-4), 25.1 (C-1), 15.1 (OCH$_2$*C*H$_3$) ppm. *m*/*z* (CI, CH_4) 497 [*M*]$^+$ (43%), 355 (35), 143 (100).

Ethyl 6-Ethoxy-6,7,8,8a-tetrahydrobenzofuro[2,3-*c*]pyridine-7-carboxylate (22): Conditions B were applied, with diene **6** (48 mg, 0.25 mmol, (*E*/*Z*) = 91:9) and ethyl acrylate (0.40 mL, 0.38 mmol) in THF (2 mL) for 24 h. Column chromatography (60% diethyl ether in heptane) of the crude product provided **22** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (*endo*/*exo* = 76:24, total mass: 44 mg, 0.15 mmol, 66% from *E* isomer).

endo Isomer: Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (s, 1 H, 1-H), 8.20 (d, J = 4.5 Hz, 1 H, 3-H), 7.24 (d, J = 4.5 Hz, 1 H, 4-H), 6.20 (t, J = 3.4 Hz, 1 H, 5-H), 4.89 (m, 1 H, 8a-H), 4.34 (m, 1 H, 6-H), 4.21 (q, J = 7.1 Hz, 2 H, CO$_2$CH_2CH$_3$), 3.70 (dq, J = 9.0, 7.1 Hz, 1 H, one of OCH_2CH$_3$), 3.51 (dq, J = 9.0, 7.1 Hz, 1 H, one of OCH_2CH$_3$), 2.75 (ddd, J = 2.6, 4.9, 13.2 Hz, 1 H, 7-H), 2.55 (ddd, J = 2.8, 5.3, 12.0 Hz, 1 H, equatorial 8-H), 2.06 (dt, J = 13.2, 12.0 Hz, 1 H, axial 8-H), 1.29 (t, J = 7.1 Hz, 3 H, CO$_2$CH$_2$CH_3), 1.12 (t, J = 7.1 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.5 (*C*=O), 159.2 (C-9a), 142.9, 140.7, 133.9, 132.8, 119.7 and 115.9 (aromatic and vinylic carbons), 83.4 (C-8a), 72.3 (C-6), 66.5 (O*C*H$_2$CH$_3$), 61.1 (CO$_2$*C*H$_2$CH$_3$), 44.1 (C-7), 25.5 (C-8), 15.9 (OCH$_2$*C*H$_3$), 14.6 (CO$_2$CH$_2$*C*H$_3$) ppm. IR (film): $\tilde{\nu}_{max}$ = 2969, 1729, 1599, 1074 cm^{-1}. *m*/*z* (CI, CH_4) 290 [*M* + H]$^+$ (27%), 244 (100), 149 (45).

exo Isomer (obtained as a mixture with *endo* isomer): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (s, 1 H, 1-H), 8.17 (d, J = 4.9 Hz, 1 H, 3-H), 7.23 (d, 1 H, J = 4.9 Hz, 4-H), 6.12 (t, 1 H, J = 3.0 Hz, 5-H), 4.96 (m, 1 H, 8a-H), 4.35 (m, 1 H, 6-H), 4.19 (q, J = 7.0 Hz, 2 H, CO$_2$CH_2CH$_3$), 3.63 (q, J = 7.0 Hz, 2 H, OCH_2CH$_3$), 3.01 (m, 1 H, 7-H), 2.66 (ddd, J = 3.2, 5.3, 12.0 Hz, 1 H, equatorial 8-H), 1.97 (dt, J = 6.0, 12.0 Hz, 1 H, axial 8-H), 1.27 (t, J = 7.0 Hz, 3 H, CO$_2$CH$_2$CH_3), 1.21 (t, J = 7.1 Hz, 3 H, OCH$_2$CH_3).

Ethyl 8-Ethoxy-5a,6,7,8-tetrahydrobenzo[4,5]furo[3,2-*b*]pyridine-7-carboxylate (23): Conditions A were applied, with diene **7** (96 mg, 0.51 mmol) and ethyl acrylate (0.10 mL, 0.92 mmol) in toluene (5 mL) for 7 days. Column chromatography (60% diethyl ether in heptane) of the crude product provided **23** as a mixture of *endo* and *exo* cycloadducts, which were separated (*endo*/*exo* = 32:68, total mass: 96 mg, 0.33 mmol, 65%).

Conditions B were also applied, with diene **7** (182 mg, 0.96 mmol) and ethyl acrylate (0.21 mL, 2.0 mmol) in THF (3 mL) for 48 h. Column chromatography (60% diethyl ether in heptane) of the crude product provided **23** as a mixture of *endo* and *exo* cycloadducts, which were separated (*endo*/*exo* = 72:28, total mass: 201 mg, 0.69 mmol, 72%).

endo Isomer: Yellow solid. m.p. 110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (dd, J = 1.7, 4.1 Hz, 1 H, 2-H), 7.08 (m, 2 H, 3-H and 4-H), 6.42 (t, J = 3.2 Hz, 1 H, 9-H), 4.96 (m, 1 H, 5a-H), 4.37 (m, 1 H, 8-H), 4.28 (q, J = 7.2 Hz, 2 H, CO$_2$CH_2CH$_3$), 3.71 (dq, J = 9.0, 7.2 Hz, 1 H, one of OCH_2CH$_3$), 3.51 (dq, J = 9.0, 7.2 Hz, 1 H, one of OCH_2CH$_3$), 2.77 (ddd, J = 2.6, 4.9, 13.2 Hz, 1 H, 7-H), 2.52 (ddd, J = 2.6, 5.3 11.7 Hz, 1 H, equatorial 6-H), 2.08 (dt, J = 13.2, 11.7 Hz, 1 H, axial 6-H), 1.28 (t, J = 7.2 Hz, 3 H, CO$_2$CH$_2$CH_3), 1.11 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.6 (*C*=O), 157.7 (aromatic C-4a), 146.4, 143.2, 140.9, 124.7, 117.7 (2 C) (aromatic and vinylic carbons), 83.0 (C-5a), 72.3 (C-8), 66.3 (O*C*H$_2$CH$_3$), 61.1 (CO$_2$*C*H$_2$CH$_3$), 44.2 (C-7), 25.7 (C-6), 15.9 (OCH$_2$*C*H$_3$), 14.7 (CO$_2$CH$_2$*C*H$_3$) ppm. IR (film): $\tilde{\nu}_{max}$ = 2971, 1737, 1258, 1073 cm^{-1}. *m*/*z* (EI): 289 [*M*]$^+$ (16%), 244 (33), 216 (36), 189 (77), 170 (100). $C_{16}H_{19}NO_4$ (289.33): calcd. C 66.42, H 6.62, N 4.84; found C 66.82, H 6.93, N 4.81.

exo Isomer: Brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (dd, J = 1.7, 4.5 Hz, 1 H, 2-H), 7.06 (m, 2 H, 3-H and 4-H), 6.35 (t, J = 3.2 Hz, 1 H, 9-H), 5.06 (m, 1 H, 5a-H), 4.38 (m, 1 H, 8-H), 4.18 (q, J = 7.2 Hz, 2 H, CO$_2$CH_2CH$_3$), 3.64 (m, 2 H, OCH_2CH$_3$), 3.00 (m, 1 H, 7-H), 2.64 (ddd, J = 3.0, 5.6 12.0 Hz, 1 H, equatorial 6-H), 1.98 (dt, J = 6.4, 11.7 Hz, 1 H, axial 6-H), 1.27 (t, J = 7.2 Hz, 3 H, CO$_2$CH$_2$CH_3), 1.20 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.5 (*C*=O), 157.7 (C-4a), 146.2, 143.1, 140.1 and 124.5 (aromatic and vinylic carbons), 118.7 (C-9), 117.5 (aromatic *C*H), 80.1 (C-5a), 73.3 (C-8), 65.7 (O*C*H$_2$CH$_3$), 61.6 (CO$_2$*C*H$_2$CH$_3$), 42.9 (C-7), 26.7 (C-6), 15.9 (OCH$_2$*C*H$_3$), 14.6 (CO$_2$CH$_2$*C*H$_3$) ppm. IR (film): $\tilde{\nu}_{max}$ = 2974, 1727, 1229, 1073 cm^{-1}. *m*/*z* (EI): 289 [*M*]$^+$ (7%), 260 (9), 243 (25), 216 (29), 170 (100).

9-*tert*-Butyl 2-Ethyl 3-Ethoxy-2,3-dihydro-1*H*-carbazole-2,9(9a*H*)-dicarboxylate (24): Conditions A were applied, with diene **8** (268 mg, 0.93 mmol, pure (*E*) isomer) and ethyl acrylate (0.2 mL, 1.87 mmol) in toluene (5 mL) for 18 h. Column chromatography (10% ethyl acetate in heptane) of the crude product provided **24** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (*endo*/*exo* = 27:73, total mass: 221 mg, 0.57 mmol, 61%).

Conditions B were also applied, with diene **8** (340 mg, 1.2 mmol, (*E*/*Z*) = 77:23) and ethyl acrylate (0.26 mL, 2.4 mmol) in THF (2 mL) for 36 h. Column chromatography (10% ethyl acetate in heptane) of the crude product provided **24** as a mixture of *endo* and *exo* cycloadducts, which were partly separated (*endo*/*exo* = 70:30, total mass: 248 mg, 0.64 mmol, 70% from (*E*) isomer).

endo Isomer: White solid m.p. 100 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (br. s, 1 H, aromatic C*H*), 7.28 (d, *J* = 7.5 Hz, 1 H, aromatic C*H*), 7.12 (t, *J* = 7.5 Hz, 1 H, aromatic C*H*), 6.87 (t, *J* = 7.5 Hz, 1 H, aromatic C*H*), 5.93 (t, *J* = 3.2 Hz, 1 H, 4-H), 4.28 (m, 1 H, 9a-H), 4.21 (m, 1 H, 3-H), 4.12 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 3.60 (dq, *J* = 9.1, 7.2 Hz, 1 H, one of OCH_2CH_3), 3.41 (dq, *J* = 9.1, 7.2 Hz, 1 H, one of OCH_2CH_3), 2.83 (m, 1 H, 2-H), 2.72 (m, 1 H, equatorial 1-H), 1.72 (q, *J* = 12.0 Hz, 1 H, axial 1-H), 1.48 [s, 9 H, $C(CH_3)_3$], 1.20 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.03 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.2 (ester *C*=O), 153.0 (carbamate *C*=O), 145.6, 140.2, 130.3, 127.7, 123.0, 120.7, 115.9 and 115.0 (aromatic and vinylic carbons), 82.0 (CMe_3), 72.6 (C-3), 65.9 (OCH_2CH_3), 62.3 (C-9a), 60.7 ($CO_2CH_2CH_3$), 45.0 (C-2), 28.7 [$C(CH_3)_3$], 26.1 (C-1), 15.9 (OCH_2CH_3), 14.7 ($CO_2CH_2CH_3$) ppm. IR (film): $\tilde{\nu}_{max}$ = 2976, 1739, 1705, 1602 cm^{-1}. *m*/*z* (EI): 387 [*M*]$^+$ (5%), 231 (72), 168 (100), 58 (63). $C_{22}H_{29}NO_5$ (387.48): calcd. C 68.20, H 7.54, N, 3.61; found C 68.14, H 7.69, N 3.65.

exo Isomer: Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (br. s, 1 H, aromatic C*H*), 7.35 (d, *J* = 7.5 Hz, 1 H, aromatic C*H*), 7.19 (t, *J* = 7.5 Hz, 1 H, aromatic C*H*), 6.94 (t, *J* = 7.5 Hz, 1 H, aromatic C*H*), 5.99 (t, *J* = 3.0 Hz, 1 H, 4-H), 4.43 (m, 1 H, 9a-H), 4.33 (m, 1 H, 3-H), 4.19 (m, 2 H, $CO_2CH_2CH_3$), 3.62 (m, 2 H, OCH_2CH_3), 2.93 (m, 1 H, equatorial 1-H), 2.81 (dt, *J* = 3.4, 7.5 Hz, 1 H, 2-H), 1.68 (dt, *J* = 7.5, 12.0 Hz, 1 H, axial 1-H), 1.54 [s, 9 H, $C(CH_3)_3$], 1.28 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.20 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7 (ester *C*=O), 152.7 (carbamate *C*=O), 145.5, 139.6, 130.2, 127.4, 123.1, 120.8, 116.1 and 115.9 (aromatic and vinylic carbons), 81.7 (CMe_3), 74.2 (C-3), 65.5 (OCH_2CH_3), 61.3 (C-9a), 58.9 ($CO_2CH_2CH_3$), 43.2 (C-2), 28.7 [$C(CH_3)_3$], 28.2 (C-1), 15.9 (OCH_2CH_3), 14.7 ($CO_2CH_2CH_3$) ppm. IR (film): $\tilde{\nu}_{max}$ = 2975, 1728, 1709, 1602 cm^{-1}. *m*/*z* (EI): 387 [*M*]$^+$ (2%), 287 (5), 168 (100) 143 (65), 58 (86).

4-Diethoxymethyl-2-phenyl-3a,4,10b,10c-tetrahydro-6-oxa-2-aza-cyclopenta[*c*]fluorene-1,3-dione (25): Conditions B were applied, with diene **18** (26 mg, 0.105 mmol, (*E*/*Z*) = 9:1) and *N*-phenylmaleimide (43 mg, 0.248 mmol) in THF (2 mL) for 20 h. Column chromatography (20% ethyl acetate in heptane) of the crude product provided cycloadduct **25** (22 mg, 0.52 mmol, 55% from (*E*) isomer) as a yellow solid. m.p. 180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–6.80 (m, 9 H, aromatic C*H*), 5.54 [m, 2 H, 5-H and C*H*$(OEt)_2$], 3.83 (q, *J* = 7.0 Hz, 2 H, two of OCH_2CH_3), 3.59 (dq, *J* = 9.0, 7.0 Hz, 1 H, one of OCH_2CH_3), 3.44 (dq, *J* = 9.0, 7.0 Hz, 1 H, one of OCH_2CH_3), 3.31 (m, 1 H, 10b-H), 3.14 (dd, *J* = 4.9, 8.7 Hz, 1 H, 3a-H), 2.84 (dd, *J* = 5.6, 8.7 Hz, 1 H, 10c-H), 2.40 (m, 1 H, 4-H), 1.29 (t, *J* = 7.0 Hz, 3 H, one of OCH_2CH_3), 1.12 (t, *J* = 7.0 Hz, 3 H, one of OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.4 and 173.9 (*C*=O), 159.3 and 157.3 (*C*=CH and aromatic *C*–O), 132.8, 129.4, 129.1, 127.7, 127.1, 125.7, 122.6, 116.7, 110.7 (aromatic carbons), 103.2 (C-5), 95.7 [*C*H$(OEt)_2$], 64.7 and 61.9 (OCH_2CH_3), 43.3, 42.5, 42.3 and 41.8 (C-10b, C-10c, C-3a and C-4), 16.2 (OCH_2CH_3) ppm. *m*/*z* (CI, CH_4): 420 [*M* + H]$^+$ (4%), 402 (22), 374 (100), 59 (33).

2-Ethoxy-3a,5-dihydro-2*H*-furo[2,3-*c*]isochromene (26): Conditions A were applied, with diene **13** (67 mg, 0.34 mmol, (*E*/*Z*) = 1:2) and ethyl acrylate (75 μL, 0.68 mmol) in toluene (5 mL) for 18 h. Column chromatography (10% ethyl acetate in heptane) provided **26** (25 mg, 0.11 mmol, 33%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.06 (m, 4 H, aromatic C*H*), 6.01, 5.87 and 5.64 (3 H, three s, 1-H, 2-H and 3a-H), 5.04 (d, *J* = 15.8 Hz, 1 H, one 5-H), 4.96 (d, *J* = 15.8 Hz, 1 H, one 5-H), 3.78 (dq, *J* = 9.4, 7.1 Hz, 1 H, one of OCH_2CH_3), 3.66 (dq, *J* = 9.4, 7.1 Hz, 1 H, one of OCH_2CH_3), 1.22 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6, 135.2 and 127.7 (C-5a, 9a and 9b), 129.4, 127.6, 126.0, and 124.6 (C-6, 7, 8 and 9), 119.4 (C-1), 109.2 and 104.3 (C-2 and 3a), 67.3 (C-5), 62.7 (OCH_2CH_3), 15.6 (OCH_2CH_3) ppm. *m*/*z* (EI): 218 [*M*]$^+$ (20%), 172 (48), 115 (100).

12-Ethoxy-8,12,13,14-tetrahydro-6*H*-7,16-dioxacyclopenta[*a*]phenanthrene-15,17-dione (27): Conditions A were applied; a solution of diene **13** (360 mg, 1.78 mmol, (*E*/*Z*) = 1:2) in toluene (5 mL) was added to a solution of maleic anhydride (294 mg, 3 mmol) in toluene (8 mL). The mixture was heated at reflux for 18 h. The solvent was evaporated under vacuum. Diethyl ether (5 mL) was then added and the precipitate was filtered. The sequence was repeated with pentane (5 mL) to provide cycloadduct **27** (140 mg, 0.46 mmol, 77% from (*E*) isomer) as a grey solid. m.p. 180 °C. ^{1}H NMR (500 MHz; $[D_6]$DMSO): δ = 7.71 (d, *J* = 8.9 Hz, 1 H, aromatic C*H*), 7.28–7.25 (m, 2 H, aromatic C*H*), 7.19 (d, *J* = 8.7 Hz, 1 H, aromatic C*H*), 6.43 (t, *J* = 2.5 Hz, 1 H, 11-H), 4.79 (d, *J* = 14.3 Hz, 1 H, one of 6-H), 4.61 (m, 2 H, one of 6-H and 8-H), 4.40 (d, *J* = 7.8 Hz, 1 H, 12-H), 4.02 (dd, *J* = 7.8, 8.9 Hz, 1 H, 13-H), 3.90 (dd, *J* = 6.9, 8.9 Hz, 1 H, 14-H), 3.80 (dq, *J* = 9.1, 7.0 Hz, 1 H, one of OCH_2CH_3), 3.61 (dq, *J* = 9.1, 7.0 Hz, 1 H, one of OCH_2CH_3), 1.21 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.6 and 169.5 (*C*=O), 134.8, 130.0, 129.2, 128.2, 128.0, 125.4, 123.2 and 122.0 (aromatic and vinylic carbons), 71.8 and 70.7 (C-8 and C-12), 67.2 (C-6), 64.6 (OCH_2CH_3), 44.7 and 43.9 (C-13 and C-14), 15.4 (OCH_2CH_3) ppm. IR (film): $\tilde{\nu}_{max}$ = 2984, 1848, 1780, 1636, 1195 cm^{-1}. *m*/*z* (CI, CH_4): 257 [*M* + H – $CO]_2^+$ (29%), 183 (59), 167 (100). HRMS (EI): Calcd. for $C_{17}H_{16}O_5$: 300.0998; found [*M*]$^+$ 300.0998.

12-Ethoxy-7-methyl-8,12,13,14-tetrahydro-7*H*-16-oxa-7-azacyclopenta[*a*]phenanthrene-6,15,17-trione (28a): Conditions A were applied; a mixture of diene **15** (190 mg, 0.83 mmol, (*E*/*Z*) = 77:23) and maleic anhydride (148 mg, 1.5 mmol) was heated at reflux in toluene (10 mL) containing a small amount of hydroquinone for 18 h. The mixture was then filtered to provide cycloadduct **Y** (110 mg, 0.33 mmol, 52% from (*E*) isomer) as a grey solid m.p. > 250 °C. ^{1}H NMR (300 MHz; $[D_6]$DMSO): δ = 8.02 (dd, *J* = 1.5, 7.5 Hz, 1 H, aromatic C*H*), 7.96 (d, *J* = 7.5 Hz, 1 H, aromatic C*H*), 7.53 (dt, *J* = 1.5, 7.5 Hz, 1 H, aromatic C*H*), 7.43 (t, *J* = 7.5 Hz, 1 H, aromatic C*H*), 6.85 (t, *J* = 3.0 Hz, 1 H, 11-H), 4.63 (m, 1 H, 8-H), 4.40 (m, 1 H, 12-H), 4.15 (dd, *J* = 4.9, 9.0 Hz, 1 H, 14-H), 3.98 (t, *J* = 8.7 Hz, 1 H, 13-H), 3.87 (dq, *J* = 9.0, 7.1 Hz, 1 H, one of OCH_2CH_3), 3.64 (dq, *J* = 9.0, 7.1 Hz, 1 H, one of OCH_2CH_3), 3.13 (s, 3 H, NCH_3), 1.26 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9 and 169.2 (anhydride *C*=O), 161.4 (amide *C*=O), 132.5, 131.3, 129.4, 129.1, 128.1, 125.8, 124.8 and 122.5 (aromatic and vinylic carbons), 73.0 (C-12), 64.6 (OCH_2CH_3), 55.9 (C-8), 43.3 and 41.6 (C-13 and C-14), 32.5 (NCH_3), 15.4 (OCH_2CH_3) ppm. IR (film): $\tilde{\nu}_{max}$ = 2984, 1870, 1844, 1774, 1651, 1224 cm^{-1}. *m*/*z* (FAB+): 328 [*M* + H]$^+$ (26%), 283 (24), 195 (100). Elemental analysis: $C_{18}H_{17}NO_5$ calcd: C 66.05, H 5.23, N 4.28; found C 65.21, H 5.14, N 4.33. HRMS (EI): Retro Diels–Alder, calcd. for dienic fragment $C_{14}H_{15}NO_2$: 229.1103; found [*M*]$^+$ 229.1107.

12-Ethoxy-7-(4-methoxybenzyl)-8,12,13,14-tetrahydro-7*H*-16-oxa-7-azacyclopenta[*a*]phenanthrene-6,15,17-trione (28b): Conditions A were applied; a mixture of diene **16** (88.5 mg, 0.26 mmol, (*E*/*Z*) = 69:31) and maleic anhydride (31.6 mg, 0.32 mmol) was heated at reflux in toluene (5 mL) containing a small amount of hydroquinone for 18 h. The mixture was then concentrated under vacuum, and ethyl acetate (5 mL) was added to the residue. The mixture was then filtered to provide cycloadduct **28b** (13.5 mg, 0.031 mmol, 17% from (*E*) isomer) as a grey solid m.p. 212–214 °C. ^{1}H NMR (300 MHz; [D$_6$]DMSO): δ = 8.06 (d, *J* = 7.5 Hz, 1 H, aromatic C*H*), 7.96 (d, *J* = 7.5 Hz, 1 H, aromatic C*H*), 7.53 (t, *J* = 7.5 Hz, 1 H, aromatic C*H*), 7.44 (t, *J* = 7.5 Hz, 1 H, aromatic C*H*), 7.30 (d, *J* = 8.4 Hz, 2 H, PMB aromatic C*H*), 6.87 (m, 3 H, PMB aromatic C*H* and 11-H), 5.24 [d, *J* = 15.3 Hz, 1 H, one of NCH_2(C$_6$H$_4$OMe)], 4.52 (m, 1 H, 8-H), 4.37 [m, 2 H, one of NCH_2(C$_6$H$_4$OMe) and 12-H], 4.20 (dd, *J* = 4.7, 9.0 Hz, 1 H, 14-H), 3.96 (t, *J* = 8.7 Hz, 1 H, 13-H), 3.83 (dq, *J* = 9.0, 7.1 Hz, 1 H, one of OCH_2CH$_3$), 3.72 (s, 3 H, OCH_3), 3.62 (dq, *J* = 9.0, 7.1 Hz, 1 H, one of OCH_2CH$_3$), 1.22 (t, *J* = 7.1 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 171.0 and 169.0 (anhydride *C*=O), 161.8 and 158.9 (amide *C*=O and *C*–OMe), 132.7, 131.4, 129.4, 129.3, 129.2, 128.5, 125.7, 125.3, 122.5 and 114.1 (aromatic and vinylic carbons), 72.9 (C-12), 64.6 (O*C*H$_2$CH$_3$), 55.4 and 54.3 (C-8 and O*C*H$_3$)), 46.8 [N*C*H$_2$(C$_6$H$_4$OMe)], 43.6 and 41.8 (C-13 and C-14), 15.4 (OCH$_2$*C*H$_3$) ppm. IR (film): $\tilde{\nu}_{max}$ = 2985, 1864, 1772, 1649, 1248 cm^{-1}. *m*/*z* (EI): 433 [*M*]$^+$ (18%), 387 (7), 121 (100).

3-(3-Acetyl-2-ethoxy-1,2,3,4-tetrahydrodibenzofuran-1-yl)-1-phenylpyrrolidine-2,5-dione (29a): The *endo* and *exo* isomers of **19a** (90 mg, 0.328 mmol), NMP (74 mg, 0.427 mmol) and hydroquinone were dissolved in toluene (5 mL). The mixture was heated at reflux for 4 days. Column chromatography (30% ethyl acetate in heptane) of the crude mixture provided the succinimide **29a** (orange solid, 23 mg, 0.051 mmol, 16%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.38 (m, 4 H, aromatic C*H*), 7.16 (m, 2 H, aromatic C*H*), 7.03 (m, 3 H, aromatic C*H*), 4.19 (m, 1 H, 2-H), 4.11 (m, 1 H, 1-H), 3.75 (s, 3 H, CO$_2$CH_3), 3.68 (m, 1 H, one of OCH_2CH$_3$), 3.47 (m, 1 H, one of OCH_2CH$_3$), 3.25 (m, 1 H, one of CH_2 NMP), 3.21 (m, 1 H, 3-H), 2.96 (dd, *J* = 6.4, 17.3 Hz, 1 H, one of CH_2 NMP), 2.75 (m, 1 H, C*H* NMP), 2.70 (m, 1 H, axial 4-H), 2.45 (dd, *J* = 5.6, 17.7 Hz, 1 H, equatorial 4-H), 1.04 (t, *J* = 6.8 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 178.8, 175.2 and 172.6 (all carbonyl *C*=O), 155.5, 154.6, 132.1, 129.7, 129.3, 127.5, 127.0, 124.5, 123.3, 120.0, 116.5, 111.8 and 108.9 (all aromatic *C*H or *C*), 79.8 (C-2), 66.1 (O*C*H$_2$CH$_3$), 52.7 (CO$_2$*C*H$_3$), 43.6 (C-3 or *C*H NMP), 42.5 (*C*H NMP or C-3), 37.1 (C-1), 31.8 (*C*H$_2$ NMP), 21.9 (C-4), 15.7 (OCH$_2$*C*H$_3$) ppm. *m*/*z* (EI): 447 [*M*]$^+$ (41%), 401 (100), 342 (89), 169(93).

Methyl 1-(2-Dioxo-1-phenylpyrrolidin-3-yl)-2-ethoxy-1,2,3,4-tetrahydrodibenzofuran-3-carboxylate (29f): A mixture of *endo* isomer (45 mg, 0.174 mmol) and NMP (60 mg, 0.347 mmol) in THF (2 ml) was placed under high pressure (16 kbar) at room temperature for 24 h. The solvent was then evaporated under vacuum. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.29 (m, 9 H, aromatic C*H*), 4.24 (m, 1 H, 2-H), 4.12 (m, 1 H, 1-H), 3.70 (m, 1 H, one of OCH_2CH$_3$), 3.48 (m, 1 H, one of OCH_2CH$_3$), 3.26 (m, 2 H, one of CH_2 NMP and 3-H), 2.93 (dd, *J* = 6.2, 17.2 Hz, 1 H, one of CH_2 NMP), 2.72 (m, 2 H, C*H* NMP and axial 4-H), 2.48 (dd, *J* = 5.8, 17.9 Hz, 1 H, equatorial 4-H), 2.28 (s, 3 H, COCH_3), 1.06 (t, *J* = 6.9 Hz, 3 H, OCH$_2$CH_3).

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