Easy and Regioselective Synthesis of Highly Functionalized *o*-Quinodimethide Precursors from Fischer Carbene Complexes and Isocyanides

José Barluenga,* Fernando Aznar, and M. Angel Palomero[a]

Abstract: Highly functionalized *cis*- and *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutene derivatives have been synthesized in a completely regioselective fashion from easily available Fischer alkenylcyclobutenyl(alkoxy)carbene complexes and isocyanides. This methodology can be viewed as an alternative to existing methods of synthesis of this kind of compounds and overcomes the main problem of introducing functionality in the aromatic ring. Both *cis* and *trans* derivatives underwent the expected fragmentation to generate *o*-quinodimethide intermediates upon thermal treatment, affording complex polycyclic structures in a stereoselective manner when heating was carried out in the presence of a range of electron deficient dienophiles.

Keywords: carbene · cycloaddition · isocyanides · *o*-quinodimethide intermediates

Introduction

o-Quinodimethide intermediates have gained increasing interest for synthetic chemists since their early discovery in 1956.[1] Due to their remarkable reactivity in Diels–Alder cycloadditions, these substrates have been successfully applied to the synthesis of a broad range of complex polycyclic systems, including natural products such as alkaloids, steroids, anthracyclines or terpenes.[2] The most commonly used method to obtain *o*-quinodimethides involves the thermally promoted fragmentation of benzocyclobutenes.[3] The main drawback of this protocol is that the isomerization sometimes requires very high temperatures and, therefore, it is not compatible with certain dienophiles that are unstable in the harsh reaction conditions.[4] In order to perform intermolecular Diels–Alder processes of *o*-quinodimethides in conditions that allow the general use of various different dienophiles, Danishefsky and co-workers have recently synthesized several *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutenes; these generated the corresponding *o*-quinodimethide intermediates at unusually low temperatures, even 40 °C in some cases.[5]

Although there are several methods available for the preparation of benzocyclobutene derivatives, most of the described approaches employ pre-formed aromatic rings as starting materials.[3] This imposes a limitation on the introduction of functionality in the benzene moiety. Specifically, *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutene derivatives have been prepared by means of a seven-step synthetic sequence starting from anthranilic acid.[5a, 6] Consequently, it is not straightforward to extend this procedure to highly functionalized systems.

Fischer carbene complexes have proven to be very useful starting materials for the preparation of differentially substituted aromatic rings by benzannulation processes.[7] Thus, the well-known Dötz reaction involving aryl or alkenyl complexes and alkynes yields *p*-alkoxyphenol derivatives,[8] becoming one of the most widely synthetically applied reaction of Fischer complexes. On the other hand, the photochemically or thermally driven cyclization of alkenylcarbene complexes with a pendant additional double bond (1,3,5-metallahexatrienes)[9] leads to *o*-alkoxy- or *o*-aminophenol derivatives.[10] The tandem isocyanide metathesis[11]–electrocyclization process of metallahexatrienes allows the synthesis of 1-alkoxy-2-amino-,[12] 1-amino-4-phospho-[13] or 1,4-diamino-2-alkoxybenzene[14] derivatives in a regioselective fashion starting from appropriate substituted substrates (Scheme 1).

In our research group we have recently synthesized alkenylcyclobutenyl(alkoxy)carbene complexes by means of a [2 + 2] cycloaddition of alkenylethynyl(alkoxy)carbene complexes and enol ethers.[10d, 15] These novel *cis*-metallahexatrienes, in contrast to most reported analogous substrates, were stable at room temperature; this enabled their isolation and the performance of further studies of their reactivity, such

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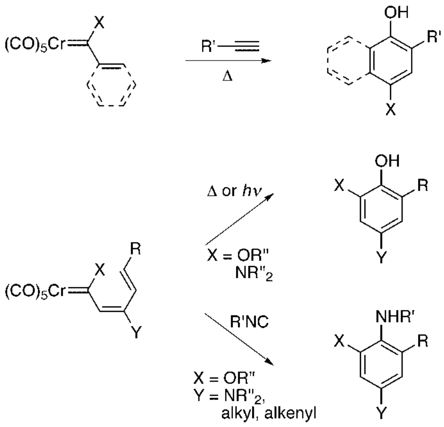
[a] Prof. Dr. J. Barluenga, Prof. Dr. F. Aznar, Dr. M. A. Palomero
Instituto Universitario de Química
Organometálica "Enrique Moles"
Unidad Asociada al C.S.I.C., Julián Clavería 8
33071 Oviedo (Spain)
Fax: (+34) 98 510 34 46
E-mail: barluenga@sauron.quimica.uniovi.es



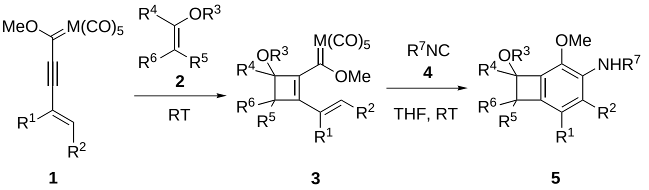
Scheme 1. Benzannulation reactions of Fischer carbene complexes.

as their thermal behavior towards alkynes.[16] The availability of stable dienyl complexes encouraged us to explore their reaction towards isocyanides. We envisaged that, given that the starting materials contained a cyclobutene moiety in their structure, if the expected benzannulation process took place, it would provide an easy and convenient method for the preparation of substituted benzocyclobutene derivatives in a regioselective manner.

Herein we report the reaction of alkenylcyclobutenyl(alkoxy)carbene complexes and isocyanides, the chemical modifications carried out on the resulting benzocyclobutenes to reach *cis*- and *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutene derivatives and their Diels–Alder cycloaddition with a range of electronically deficient dienophiles. We also report the thermal behavior towards methanol of several substituted benzocyclobutenedione derivatives which have been prepared as precursors of *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutenes.

Results and Discussion

Preparation of alkenylcyclobutenyl(alkoxy)carbene complexes: According to the general procedure described in the literature for [2+2] cycloadditions of Fischer alkynyl complexes and enol ethers or ketene acetals,[17] reactions involving 2,3-dihydrofurane, 2-methoxypropene, 1-methoxy-2-methyl-1-trimethylsilyloxypropene, 2,2-dimethyl-1,3-dioxole and 1,1,2,2-tetramethoxyethene were carried out by stirring carbene complex **1** in an excess of the corresponding alkene under nitrogen atmosphere until the reaction was complete; typically within 2 to 24 hours. However, the reaction of carbene complex **1d** with 1,1-dimethoxyethene had to be performed in a solution of dichloromethane because it was too exothermic to be carried out neat. All cycloadducts were isolated in moderate to high yields by flash chromatography and were found to be stable at room temperature (Scheme 2, Table 1); except for **3i**, which resulted from the reaction of **1d** with 1,1-dimethoxyethene and decomposed under the standard purification conditions so **3i** had to be used directly in the next reaction step (Table 1, entry 9). Complexes **3j** and **3k** also underwent partial decomposition upon column chromatography, possibly due to the trimethylsilyl moiety cleavage, but they could be isolated in reasonable yields (Table 1, entries 10, 11). The best results were obtained when 1,1,2,2-tetramethoxyethene was used (Table 1, entries 12–16). This result is in agreement with the previously reported behavior of this alkene in [2+2] cycloaddition reactions with Fischer alkynyl complexes.[18]



Scheme 2. Synthesis and reactivity towards isocyanides of Fischer (alkenylcyclobutenyl)(alkoxy)carbene complexes.

Table 1. Preparation of (alkenylcyclobutenyl) complexes **3**.

	1	M	R^1	R^2	R^3	R^5	$R^{4[a]}$	R^6	**3**	Yield [%]
1	**1a**	W	Me	Ph	$-CH_2CH_2-$		H	H	**3a**	64
2	**1b**	Cr	Me	Ph	$-CH_2CH_2-$		H	H	**3b**	83
3	**1c**	W	$-CH_2CH_2CH_2-$		$-CH_2CH_2-$		H	H	**3c**	85
4	**1d**	Cr	$-CH_2CH_2CH_2-$		$-CH_2CH_2-$		H	H	**3d**	93
5	**1d**	Cr	$-CH_2CH_2CH_2-$		$-C(CH_3)_2O-$		H	H	**3e**	78
6	**1e**	Cr	$-CH_2CH_2CH_2CH_2-$		$-C(CH_3)_2O-$		H	H	**3f**	79
7	**1f**	Cr	H	Ph	$-C(CH_3)_2O-$		H	H	**3g**	89
8	**1d**	Cr	$-CH_2CH_2CH_2-$		Me	H	Me	H	**3h**	68
9	**1d**	Cr	$-CH_2CH_2CH_2-$		Me	H	OMe	H	**3i**	[b]
10	**1b**	Cr	Me	Ph	Me	Me	OTMS	Me	**3j**	56
11	**1d**	Cr	$-CH_2CH_2CH_2-$		Me	Me	OTMS	Me	**3k**	64
12	**1d**	Cr	$-CH_2CH_2CH_2-$		MeO	MeO	MeO	MeO	**3l**	98
13	**1e**	Cr	$-CH_2CH_2CH_2CH_2-$		MeO	MeO	MeO	MeO	**3m**	87
14	**1g**	Cr	$-CH_2OC(CH_3)_2OCH_2-$		MeO	MeO	MeO	MeO	**3n**	71
15	**1f**	Cr	H	Ph	MeO	MeO	MeO	MeO	**3o**	88
16	**1h**	Cr	$-OCH_2CH_2CH_2-$		MeO	MeO	MeO	MeO	**3p**	91

[a] TMS = trimethylsilyl. [b] Not isolable.

Abstract in Spanish: *Se han sintetizado varios 1,2-bis(trialquilsililoxi)benzociclobutenos con configuración relativa* cis *o* trans *y con alta funcionalización en el anillo aromático a partir de complejos alcoxi(alquenilciclobutenil)carbeno de Fischer e isonitrilos. La metodología aquí desarrollada puede considerarse una alternativa interesante a los métodos de síntesis de este tipo de compuestos descritos hasta la fecha, ya que permite introducir regioselectivamente sustituyentes en el anillo aromático de los benzociclobutenos. Tanto los derivados con configuración* cis *como* trans *experimentaron la esperada fragmentación térmica para conducir diastereoselectivamente a los correspondientes* o*-quinodimetanos. La posterior cicloadición [4+2] con dienófilos electrónicamente deficientes presentes en el medio de reacción condujo a policiclos de estructura compleja de forma completamente diastereoselectiva.*

Preparation of *o*-alkoxyaniline derivatives by metathesis of (alkenylcyclobutenyl)alkoxycarbene complexes and isocya-

nides: Treatment of carbene complexes **3** with two equivalents of *tert*-butyl- or benzylisocyanide in tetrahydrofuran at room temperature regioselectively afforded the expected *o*-methoxyaniline derivatives **5** in short reaction times and with good to excellent yields (Scheme 2, Table 2). The behavior of systems **3** towards isocyanides has shown to be analogous to that described in the bibliography for other Fischer carbene complexes bearing an additional *cis*-double bond in their structure.[11, 12a]

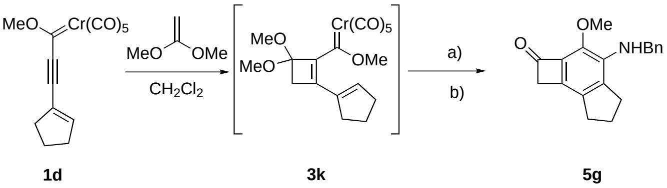
Table 2. Preparation of aniline derivatives **5**.

	3	R^{7}[a]	5	Yield [%][b]
1	**3a**	*t*Bu	**5a**	88[c]
2	**3b**	*t*Bu	**5a**	94
3	**3c**	Bn	**5b**	78[c]
4	**3d**	Bn	**5b**	86
5	**3e**	*t*Bu	**5c**	78
7	**3f**	Bn	**5d**	67
8	**3g**	*t*Bu	**5e**	98
9	**3h**	*t*Bu	**5f**	85
10	**3i**	Bn	**5g**	52[d]
11	**3j**	*t*Bu	**5h**	65
12	**3k**	Bn	**5i**	59
13	**3l**	*t*Bu	**5j**	85
14	**3m**	Bn	**5l**	76
15	**3n**	*t*Bu	**5m**	92
16	**3o**	Bn	**5n**	82
17	**3p**	*t*Bu	**5o**	97

[a] *t*Bu = *tert*-butyl, Bn = benzyl. [b] Reaction conditions: 2 equiv R^{7}NC, THF, room temperature, 15 min. [c] Reaction time: 1 h. [d] Yield of the *one-pot* reaction starting from alkynyl complex **1d**. **5g** was characterized after deprotection of the acetal group.

Reactions of complexes **3** and isocyanides proceeded in milder conditions (room temperature) and shorter reaction times than those of previously described substrates,[12–14] which could be easily rationalized since, in this case, none of the double bonds involved in the electrocyclization step belonged to an aromatic ring.

Benzannulations were not sensitive to changes in the solvent: Comparable results were observed when THF, diethyl ether, dichloromethane or toluene were used. THF was usually chosen and results displayed in Table 2 refer to reactions carried out in this solvent. The reaction exhibited high generality for differently substituted starting complexes and proceeded both with chromium and tungsten systems. However, chromium complexes were preferentially used because they led to higher yields of aniline derivatives in shorter reaction times (Table 2, entries 1/2, 3/4). Stoichiometrical amounts of complex R^{7}NC-M(CO)$_5$ were always obtained as side products, but they could be either oxidized by exposure to air and sunlight or separated from compounds **5** by column chromatography.

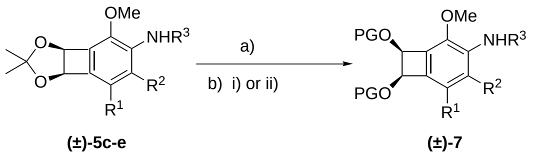


Scheme 3. Preparation of aniline derivative **5j** from unstable 1,3,5-metallahexatriene **3k**. a) BnNC, THF; b) silica gel.

The preparation of aniline derivative **5g** was accomplished by reaction of unstable metallahexatriene **3i** and benzylisocyanide (Scheme 3, Table 2, entry 10). Once [2 + 2] cycloaddition of carbene complex **1d** and 1,1-dimethoxyethene was completed, the solvent and the excess of olefin were removed in vacuo and replaced by THF, and the crude mixture was treated with two equivalents of benzylisocyanide at room temperature. The final aniline derivative **5g** was isolated after hydrolysis of the dimethylacetal protective group during chromatographic purification. Compounds **5h** and **5i** underwent only partial hydrolysis of the methyl(trimethylsilyl)acetal moiety in the column chromatography, the same as had been observed for their precursors **3j** and **3k**. The whole conversion of **5j** in the carbonyl derivative **6** was achieved by treatment with K_2CO_3 in a mixture of THF/H_2O at room temperature for 15 minutes (89 % yield).

Preparation of *cis*- and *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutene derivatives: Once a regioselective and high-yielding process had been developed for the preparation of substituted benzocyclobutene scaffolds, we carried out the conversion of the the initially obtained systems **5** in *o*-quinodimethide precursors bearing two trialkylsilyloxy functionalities in both sp^{3} carbons. Such compounds were adequate for our purposes since they were analogous to those described by Danishefsky and co-workers and, therefore, were expected to undergo electrocyclic ring-opening in mild conditions.[5] So far, only benzocyclobutenes with *trans*-disposed silyloxy groups have been tested in tandem fragmentation Diels–Alder processes. However, given that our methodology allowed the synthesis of *cis* and *trans* derivatives starting from compounds **5**, we decided to prepare both in order to compare their reactivity.

cis-1,2-Bis(trialkylsilyloxy)benzocyclobutene derivatives **7** were obtained from 1,3-dioxol-fused benzocyclobutenes **5c–e** by successive cleavage of the acetal functionality and protection of the resulting hydroxyl groups. Both transformations were accomplished by conventional procedures (Scheme 4, Table 3): The first step consisted of the treatment of aniline derivatives **5c–e** with trifluoroacetic acid (TFA) in a mixture THF/H_2O 10:1 at room temperature and afforded the corresponding 1,2-diols. These compounds were directly treated with either trimethylsilyl chloride (TMSCl)/triethyl-



Scheme 4. Preparation of *cis*-1,2-bis(trialkylsililoxy)benzocyclobutene derivatives **7**. a) TFA, THF, H_2O; b) i) for PG = TMS: THF, TMSCl, NEt_3, RT, 12 h; ii) for PG = TBS: MeCN, TBSCl, imidazole, RT, 12 h.

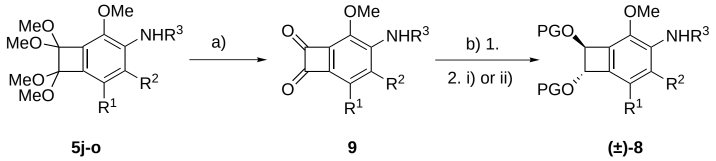
Table 3. Preparation of *cis*-benzocyclobutenes **7**.

	R^1	R^2	R^3	PG[a]	7	Yield [%][b]
1	$-CH_2CH_2CH_2-$		*t*Bu	TMS	**7a**	76
2	$-CH_2CH_2CH_2-$		*t*Bu	TBS	**7b**	62
3	$-CH_2CH_2CH_2CH_2-$		*t*Bu	TBS	**7c**	68
4	$-CH_2CH_2CH_2CH_2-$		Bn	TBS	**7d**	62
5	H	Ph	*t*Bu	TBS	**7e**	86

[a] TMS = trimethylsilyl, TBS = *tert*-butyldimethylsilyl. [b] Yield from starting complexes **5**.

amine or *tert*-butyldimethylsilyl chloride (TBSCl)/imidazole, depending on the protective group required in each case.

On the other hand, *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutene derivatives **8** were synthesized from compounds **5j**, **l**, **n**, **o** bearing two dimethylacetal functionalities in the cyclobutene ring. The experimental procedure involved hydrolysis of the acetal moieties with TFA, in a mixture THF/H_2O 10:1, to yield cyclobutenodione derivatives **9**, reduction of the carbonyl groups with $NaBH_4$ in methanol to afford almost exclusively the corresponding *trans*-1,2-diols[19] and silylation of the hydroxyl groups, which was carried out under the aforementioned conditions employed for compounds **7** (Scheme 5, Table 4).



Scheme 5. Preparation of benzocyclobutenedione derivatives **9** and *trans*-1,2-bis(trialkylsililoxy)benzocyclobutene derivatives **8**. a) TFA, THF, H_2O; b) 1. $NaBH_4$, MeOH; 2. i) for PG = TMS: THF, TMSCl, NEt_3, RT, 12 h; ii) for PG = TBS: MeCN, TBSCl, imidazole, RT, 12 h.

Table 4. Preparation of benzocyclobutenediones **9** and *trans*-benzocyclobutenes **8**.

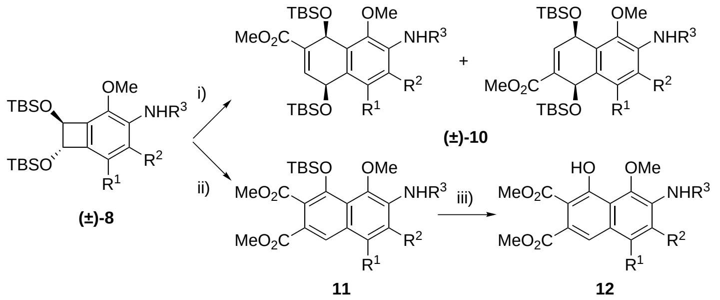
	R^1	R^2	$R^{3[a]}$	9	Yield [%]	PG[b]	8	Yield [%][c]
1	$-CH_2CH_2CH_2-$		*t*Bu	**9a**	85	TMS	**8a**	63
2	$-CH_2CH_2CH_2-$		*t*Bu	**9a**	85	TBS	**8b**	56
3	$-CH_2CH_2CH_2CH_2-$		Bn	**9b**	61	TMS	**8c**	64
4	$-CH_2CH_2CH_2CH_2-$		Bn	**9b**	61	TBS	**8d**	86
5	H	Ph	Bn	**9c**	84	TMS	**8e**	59
6	H	Ph	Bn	**9c**	84	TBS	**8f**	54
7	$-OCH_2CH_2CH_2-$		*t*Bu	**9d**	61	TBS	**8g**	33

[a] *t*Bu = *tert*-butyl, Bn = benzyl. [b] TMS = trimethylsilyl, TBS = *tert*-butyldimethylsilyl. [c] Yield from compounds **9**.

This methodology has enabled the preparation of highly substituted benzocyclobutene derivatives **7**, **8** and **9** by means of a synthetic route that involved no more than five steps starting from carbene complexes **1** and alkenes. Therefore, it can be considered as an alternative to previously reported routes to this kind of compounds, the main advantage of this method being that it regioselectively furnishes very highly functionalized *o*-quinodimethide precursors which would be difficult to prepare by conventional procedures.

Diels–Alder reactions of *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutene derivatives: The only difference between compounds **8** and those prepared by Danishefsky and co-workers is the substitution in the aromatic ring. Given that it has been established that a *peri*-methoxy group hinders the electrocyclic ring opening, thus increasing the temperature required for the tandem process electrocyclization-Diels–Alder reaction, we did not expect systems **8** to undergo the reaction at temperatures so low as Danishefsky's benzocyclobutenes did.

Thermal treatment of **8d** in benzene in the presence of three equivalents of methyl propiolate was carried out at different temperatures between 40 and 80 °C, recovering the starting material in all cases. We then attempted further heating using toluene as the solvent, and bicyclic compound **10** was finally obtained as a 1:1 mixture of regioisomers upon refluxing for 12 hours (Scheme 6, Table 5, entry 1). Reaction of benzocyclobutenes **8b**, **f** with dimethyl acetylendicarboxylate (DMAD) in the same conditions afforded compounds **11a**, **b** (Scheme 6, Table 5, entries 2 and 9). Their structure was elucidated on the basis of COSY, HMQC, HMBC and NOESY experiments. Aromatized compounds **11** were generated from the elimination of one of the two *tert*-butyldimethylsilyloxy groups. This regioselectivity should be rationalized by electronical effects and can not be attributed to steric reasons.[20] The remaining *tert*-butyldimethylsilyl moiety could be easily removed by using tetrabutylammonium fluoride (TBAF) in THF at room temperature, yielding naphthol derivative **12** (Scheme 6, Table 5, entry 2).



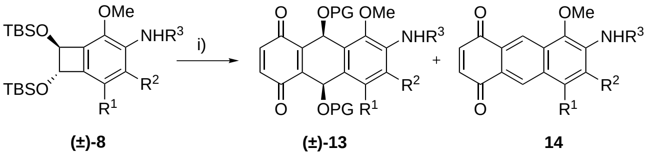
Scheme 6. Thermal reaction of compounds **8** and methyl propiolate or DMAD. i) $HCCCO_2Me$, toluene, reflux; ii) DMAD, toluene, reflux; iii) TBAF, THF/H_2O, RT.

Table 5. Thermal treatment of *trans*-benzocyclobutene derivatives **8**.[a]

	8	Dienophile	Product	Yield [%]
1	**8b**	$HCCCO_2Me$	**10**	62[b]
2	**8b**	DMAD	**11a**	82[c]
3	**8a**	*p*-benzoquinone	**14a**	67
4	**8b**	*p*-benzoquinone	**14a**	72
5	**8a**	*N*-phenylmaleimide	**15a**	86
6	**8b**	*N*-phenylmaleimide	**15b**	84
7	**8c**	*N*-phenylmaleimide	**15c**	73
8	**8d**	*N*-phenylmaleimide	**16**	49[d]
9	**8f**	DMAD	**11b**	85
10	**8f**	*p*-benzoquinone	**13**	40
			14b	45
11	**8e**	*N*-phenylmaleimide	**15d**	82
12	**8f**	*N*-phenylmaleimide	**15e**	82

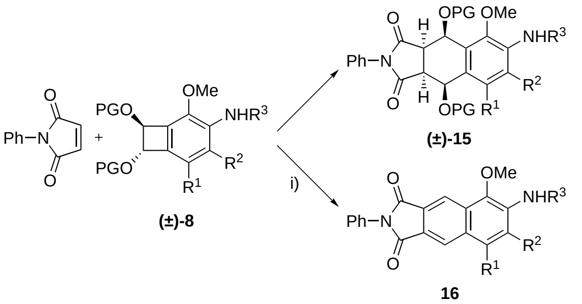
[a] Reaction conditions: 3–5 equivalents of dienophile, toluene, reflux, 12 h. [b] Equimolar inseparable 1:1 mixture of diastereomers. [c] **11a** was transformed in **12a** by treatment with TBAF in THF/H_2O (94%). [d] Reaction time = 72 h.

When *p*-benzoquinone was used as dienophile, the expected Diels–Alder cycloadduct of the initially formed *o*-quinodimethides was not observed. Instead, the reaction gave rise to two types of compounds derived from the mentioned intermediate adduct: the oxidation product **13**, as a single diastereoisomer, and the aromatized system **14** (Scheme 7, Table 5, entries 3, 4, 10).



Scheme 7. Thermal reaction of compounds **8** and *p*-benzoquinone. i) *p*-benzoquinone, toluene, reflux.

The last dienophile to be tested was *N*-phenylmaleimide. From its reaction with **8** in refluxing toluene two different products could be obtained (Scheme 8, Table 5, entries 5–8, 11, 12): cycloadducts **15** are directly originated by [4+2] cycloaddition of *o*-quinodimethide intermediates with *N*-phenylmaleimide, but **16** has undergone aromatization by means of an elimination process in the reaction conditions. The tendency to suffer aromatization was smaller for products derived from *N*-phenylmaleimide than it had been for those arising from reactions with *p*-benzoquinone. Indeed, only in one case has compound **16** been observed (Table 5, entry 8).



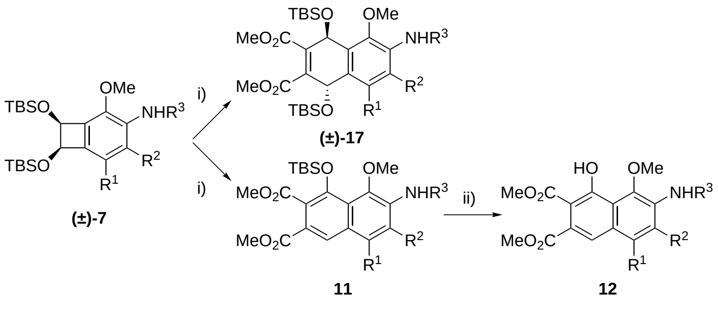
Scheme 8. Thermal reaction of compounds **8** and *N*-phenylmaleimide. Reaction conditions: toluene, reflux; i) $R^1R^2 = (CH_2)_3$, PG = TBS.

In all the cases in which aromatization did not take place, cycloadducts were obtained as single diastereoisomers. The geometry of the prepared compounds did not allow us to infer the relative configuration of the newly created stereocenters from their spectroscopical data; thus it was necessary to perform monocrystal X-ray analysis of tricyclic system **15a** to ensure that the spatial disposition of the substituents in that substrate was that depicted in Scheme 8.[21] We assumed that the relative stereochemistry experimentally found for **15a** was the same as of that of the remaining cycloadducts arising from the thermal treatment of *trans*-benzocyclobutene derivatives **8** in the presence of suitable dienophiles. One proof was the fact that the ^1H NMR spectra of all polycycles showed similar chemical shifts, multiplicity and coupling constants values for analogous protons. This suggested that chemical environment and dihedral angles were also similar in different structures, thus supporting our proposition.

Once the relative stereochemistry of compounds **13** and **15** had been unraveled, it was possible to ascertain the stereochemical course of the reactions from which they arose. Initially, a conrotatory ring-opening of the cyclobutene moiety afforded the corresponding (*E*,*E*)-quinone dimethide in which presumably, the two bulky substituents have torquoselectively rotated outwards.[22] Then, this intermediate underwent diastereoselectively *endo* Diels–Alder cycloaddition to furnish the final products as single diastereoisomers. Both results are in agreement with those previously obtained by Danishefsky and co-workers, concerning both the electrocyclic ring-opening and the [4+2] cycloaddition processes.[5]

Diels–Alder reactions of *cis*-1,2-bis(trialkylsilyloxy)benzocyclobutene derivatives: *cis*-Benzocyclobutenes **7** were expected to be much less reactive towards electrocyclic ring opening than their *trans*-analogues given that, assuming a selective conrotatory ring opening, they would give rise to (*E*,*Z*)-quinodimethides. The presence of a *cis*-trialkylsilyloxy moiety would impose serious steric hindrance in the transition state of the electrocyclic ring-opening reaction and would imply a higher temperature for the process to take place.

In order to find the optimal conditions for the tandem electrocyclic ring opening-Diels–Alder cycloaddition of *o*-quinodimethide precursors **7** and suitable dienophiles, we heated a solution of **7b** and DMAD in toluene in a sealed tube at temperatures in the range of 110–160 °C, reaching the best results at 160 °C. The product **11a** obtained in this case was identical to the one previously prepared by reaction of *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutene (**8b**) and DMAD (Scheme 9, Table 6, entry 1). Again, it was observed that the aromatization proceeded through regioselective elimination of the *tert*-butyldimethylsilyloxy moiety which was closer to the methoxy group. The lower yield achieved from **7b** compared with that obtained from **8b** can be explained by the higher temperatures and longer reaction times required in this case. The alcohol protective group of compounds **11** was readily removed by reaction with TBAF in THF. This strategy enabled the purification of **12b** which precursor **11b** was not easily separable from the impurities of the reaction by column chromatography (Scheme 9, Table 6, entry 6). Treatment of



Scheme 9. Thermal reaction of compounds **7** and DMAD. i) Methyl propiolate, toluene, reflux; ii) DMAD, toluene, reflux; iii) TBAF, THF/H_2O, RT.

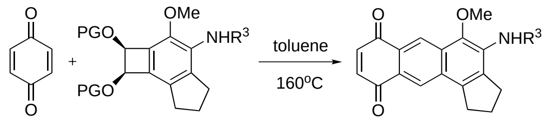
Table 6. Thermal treatment of *cis*-benzocyclobutene derivatives **7**.

	7	Dienophile	Product	Yield [%]
1	**7b**	DMAD	**11a**	52[a]
2	**7a**	*p*-benzoquinone	**14a**	55
3	**7b**	*p*-benzoquinone	**14a**	58
4	**7a**	*N*-phenylmaleimide	**18a**	66[b]
5	**7b**	*N*-phenylmaleimide	**18b**	61
6	**7c**	DMAD	**12b**	53[c]
7	**7e**	DMAD	**17**	85
8	**7e**	*N*-phenylmaleimide	**18c**	23
			19	34

[a] Reaction conditions: 3–5 equivalents of dienophile, toluene, 160 °C, 24 h. [a] **11a** was transformed in **12a** by treatment with TBAF in THF/H_2O (94 %). [b] Conversion = 63 % after 48 h. [c] Crude mixture was treated with TBAF in THF/H_2O in order to purify compound **12b**.

benzocyclobutene **7e** with DMAD in the same experimental conditions afforded non-aromatized system **17** instead, in good yield (Scheme 9, Table 6, entry 7).

Thermal treatment of compounds **7a, b** in the same conditions in the presence of an excess of *p*-benzoquinone directly led to system **14a**, which has undergone aromatization through elimination reaction of both trialkylsilyloxy groups (Scheme 10, Table 6, entries 2,3). Once again, yields were lower than those obtained when *trans*-benzocyclobutenes **8a**,**b** were used as starting materials.

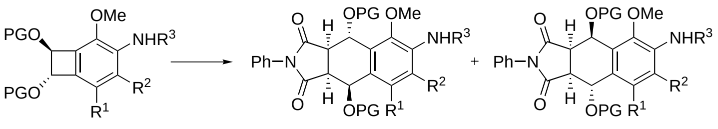


(±)-7a , b **14a**

Scheme 10. Thermal reaction of compounds **7** and *p*-benzoquinone. PG = TMS, TBS.

When *N*-phenylmaleimide was used, different results were observed depending on the susbtitution pattern of the starting *o*-quinodimethide precursor **7**. Thus, while systems **7a** and **7b**, bearing a cyclopentane ring fused to the benzene moiety, afforded products **18a** and **18b**; compound **7e** (with $R^1 = H$) gave rise to the mixture of diastereoisomers **18c** and **19** (Scheme 11, Table 6, entries 4, 5, 8).

Once more, it was necessary to perform monocrystal X-ray experiments to elucidate the relative stereochemistry of those cycloadducts derived from *cis*-benzocyclobutenes **7** that had not undergone aromatization upon thermal treatment (Table 7). X-ray analyses of compounds **18c** and **19** showed that the spatial disposition of the substituents was that of the structure shown in Scheme 11. The stereochemistry of the remaining compounds **18** was assigned by analogy of the spectroscopic data. Given the reasonable assumption that similarities in the ^{1}H NMR spectra of analogous species are due to the same spatial disposition of their substituents, we have inferred that compounds **18a**,**b**, arising from the reaction of **7a**,**b** and *N*-phenylmaleimide, were stereochemically related to **18c** and not to **19**.



(±)-7 **(±)-18** **(±)-19**

Scheme 11. Thermal reaction of compounds **7** and *N*-phenylmaleimide. Reaction conditions: *N*-Phenylmaleimide, toluene, 160 °C, PG = TMS, TBS.

Table 7. Preparation of benzo[*c*]furane derivatives **20**.[a]

	9	**20**	*t* [h]	Yield [%]
1	**9a**	**20a**	48	92
2	**9c**	**20b**	72	88
3	**9d**	**20c**	48	90

[a] Reaction conditions: methanol, 100 °C.

The *trans* relative disposition of the *tert*-butyldimethylsilyloxy groups in cycloadducts **18** suggested that they all came from (*E*,*Z*)-dienes resulting from the expected conrotatory ring opening of the *cis*-benzocyclobutenes.[22] In this case, the two different dienes **A** and **B** can be formed in the electrocyclic ring-opening reaction (Figure 1). When assuming *endo*-selective Diels–Alder cycloaddition, the former would be responsible for the formation of compounds **18**, whereas the latter would furnish **19**. We found experimental evidence that when R^1, R^2 belong to a five-membered carbocycle, only products **18** are formed, and that $R^1 = H$ was necessary to obtain product **19** derived from intermediate **B**. This behavior could be rationalized in terms of electronic and steric effects: We believe that path (a) is usually favored over (b) for electronic reasons; however, when the steric hindrance in the position occupied by R^1 is reduced, the reaction can be partially directed through intermediate **B**, affording both diastereoisomeric systems **18c** and **19**.

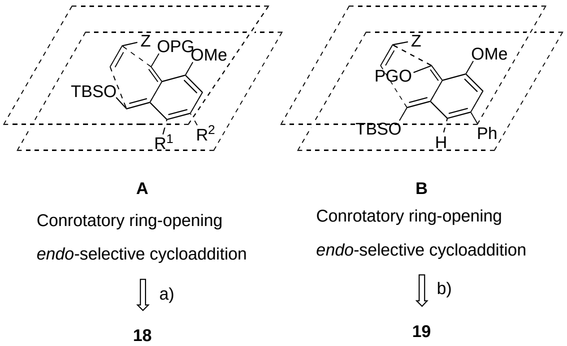


Figure 1. Transition states of the *endo*-selective Diels–Alder reaction of **7** leading to cycloadducts **18** and **19**.

Thermal treatment of benzocyclobutenedione derivatives: Benzocyclobutenedione derivatives are known to undergo thermal or photochemically driven cyclobutene ring opening to generate bisketene intermediates which in turn are capable of further transformations.[23] Then, we decided to test the reactivity of compounds **9**, which had been synthesized as intermediates in the preparation of *trans*-benzocyclobutenes **8**.

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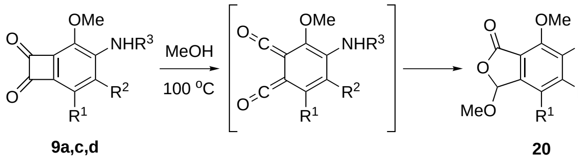
When a solution of compounds **9a**, **c**, **d** in methanol was heated at 100 °C in a sealed tube benzo[*c*]furane derivatives **20** were obtained as single regioisomers in high yields (Scheme 12, Table 3).



Scheme 12. Preparation of benzo[*c*]furane derivatives **20**.

This transformation implies electrocyclic ring opening of the cyclobutene moiety, nucleophilic addition of one molecule of methanol to the bisketene intermediate species and subsequent cyclization. There is a clear precedent of this behavior consisting of the photochemical reaction of the unsubstituted benzocyclobutenodione in methanol.[24] The introduction of several substituents in the structure of the starting materials has not caused regioselectivity problems. Actually, only one of the two possible regioisomers has been detected in the crude mixture. It is possible to rationalize this result by supposing that the ketene functionality conjugated to the nitrogen substituent exhibits greater electron density than the one conjugated to the oxygen atom, consequently displaying a smaller disposition for a potential nucleophilic attack of methanol.

Conclusion

In summary, the reaction of (alkenylcyclobutenyl)alkoxycarbene complexes and isocyanides has been investigated. We have concluded that the synthesis leads to *o*-alkoxyaniline derivatives in all the cases studied, in a regioselective fashion and with good yields. This process is analogous to a previously reported process involving alkoxy(dienyl)carbene complexes with *cis* configuration in the central double bond and two equivalents of isocyanide; however, it proceeds under milder conditions and shorter reaction times because none of the double bonds that take part in the electrocyclization belong to an aromatic ring. The chemical modification of the initially formed compounds led to highly functionalized *cis*- and *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutene derivatives, in an overall process of no more than five reaction steps. The key step is a completely regioselective benzannulation reaction. Therefore, we believe that the methodology described herein provides a convenient synthetic method of these highly substituted benzocyclobutene derivatives, overcoming the difficulties to introduce functionality in the aromatic ring shown by standard methodology.

Generation of *o*-quinodimethides upon thermal treatment of the compounds just prepared and subsequent Diels–Alder cycloaddition reactions to a range of electron-deficient dienophiles have also been tested, furnishing complex polycyclic systems. When aromatization did not take place in the reaction conditions, cycloadducts derived from the conrotatory ring opening of the cyclobutene moiety and the *endo*-selective [4 + 2] cycloaddition reaction.

The heating of highly functionalized benzocyclobutenediones in methanol afforded benzo[*c*]furane derivatives in a completely regioselective fashion and with good yields.

Experimental Section

General methods: For all reactions run under N_2 atmosphere, tetrahydrofuran, diethyl ether, dichloromethane, toluene and methanol were dried and distilled by standard procedures before use. Solvents used in column chromatography were distilled prior to use. All other reagents used in the reactions were of the best commercial grade available. Column chromatography was carried out on silica gel 60 (230–400 mesh). R_f values are referred to the mixture of solvents in which column chromatography was carried out. All melting points are uncorrected. NMR spectra were recorded at 300 or 200 MHz for ^{1}H and 75, or 50.3 MHz for ^{13}C, with tetramethylsilane as internal standard for ^{1}H and the residual solvent signals as standard for ^{13}C. Chemical shifts are given in ppm. The multiplicity of the signals is indicated as follows: s = singlet, d = doublet, t = triplet, q = quatriplet, quint. = quintuplet, m = multiplet. Mass spectra were obtained by EI (70 eV), FAB + or MALDI-TOF. IR spectra are given in cm^{-1}.

Preparation of alkynyl carbene complexes 1 and enol ethers and ketene acetals 2: Fischer carbene complexes **1** had already been synthesized in our research group by standard methodology from the corresponding acetylenes. Their analytical and spectroscopic data have been reported.[10c, 16, 25] 2,3-Dihydrofuran, 3,4-dihydro-2*H*-pyran, 2-methoxypropene and 1-methoxy-2-methyl-1-trimethylsilyloxypropene are commercially available reagents. The remaining enol ethers and ketene acetals **2** were prepared according to the following methods described in the literature: 2,2-dimethyl-1,3-dioxole,[26] 1,1-dimethoxyethene,[27] 1,1,2,2-tetramethoxyethene.[28]

General procedure for the preparation of Fischer dienyl complexes 3: All carbene complexes **3** were synthesized by the same experimental procedure previously described by Wulff:[29] 1 mmol of carbene neat with 10 mmol of the corresponding enol ether were stirred at room temperature, under nitrogen atmosphere until TLC analyses revealed that the starting complex had been consumed. Removal of the volatiles by vacuum (10 mm Hg) and flash chromatography afforded the title compounds. Exceptionally, when 1,1-dimethoxyethene was used, 3 mmol of the olefin and 1 mmol of complex **1d** were dissolved in 10 mL of dry dichloromethane and the mixture was stirred under nitrogen atmosphere at room temperature until total consumption of the starting carbene complex. The resulting adduct **3i** could not be isolated by column chromatography, so it was directly used in the next step after removal of solvents in vacuum. Data for compounds **3a**, **c**, **d**[10c] and **3n**[16] have already been reported.

Pentacarbonyl{[2,3,3a,5a-tetrahydro-4-(1-methyl-2-phenylethenyl)cyclobuta[*b*]furan-5-yl]methoxymethylen}tungsten(0) (3a): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/Et_2O/CH_2Cl_2 4:1:1, **3a** as a dark orange solid (64%). R_f = 0.44; m.p. 92–94 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.82-2.07$ (m, 2H), 1.93 (s, 3H), 3.54 (dd, $J = 7.7$, 3.8 Hz, 1H), 3.90 (td, $J = 8.9$, 5.6 Hz, 1H), 4.17 (t, $J = 7.9$ Hz, 1H), 4.62 (s, 3H), 5.57 (d, $J = 3.8$ Hz, 1H), 6.92 (br s, 1H), 7.32–7.41 (m, 5H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 16.6$ (CH_3), 27.4 (CH_2), 43.9 (CH), 66.6 (CH_2), 68.2 (CH_3), 79.1 (CH), 127.9 (CH), 128.3 (2CH), 129.4 (2CH), 131.2 (C), 136.2 (CH), 136.7 (C), 143.7 (C), 151.2 (C), 196.9 (4C), 203.4 (C), 310.7 (C); IR (CH_2Cl_2): $\tilde{\nu} = 2066$, 1937 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{18}O_7W$: C 45.67, H 3.14; found: C 45.42, H 3.28.

Pentacarbonyl{[2,3,3a,5a-tetrahydro-4-(1-methyl-2-phenylethenyl)cyclobuta[*b*]furan-5-yl]methoxymethylen}chromium(0) (3b): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/Et_2O/CH_2Cl_2 4:1:1, **3b** as a dark orange solid (83%). R_f = 0.47; m.p. 95–97 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.83-2.02$ (m, 2H), 1.90 (s, 3H), 3.59–3.60 (m, 1H), 3.90–3.99 (m, 1H), 4.19 (t, $J = 8.3$ Hz, 1H), 4.69 (s, 3H), 5.62 (d, $J = 2.9$ Hz, 1H), 6.82 (s, 1H), 7.26–7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 16.2$ (CH_2), 27.3 (CH_2), 43.7

(CH), 65.7 (CH_3), 67.0 (CH_2), 79.5 (CH), 127.8 (CH), 128.2 (2 CH), 129.3 (2 CH), 130.5 (C), 135.6 (CH), 136.2 (C), 139.6 (C), 148.0 (C), 216.0 (4 C), 223.8 (C), 340.5 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 2064, 1935 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{18}CrO_7$: C 59.20, H 4.06; found: C 59.45, H 3.88.

Pentacarbonyl{[4-(1-cyclopentenyl)-2,3,3a,5a-tetrahydrocyclobuta[*b*]furan-5-yl]methoxymethylen}tungsten(0) (3c): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/Et_2O/CH_2Cl_2 4:1:1, **3c** as a dark orange solid (85%). R_f = 0.50; m.p. 113–115 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.70–2.04 (m, 4H), 2.28–2.53 (m, 4H), 3.31 (dd, J = 7.9, 3.6 Hz, 1H), 3.77–3.90 (m, 1H), 4.11 (t, J = 7.4 Hz, 1H), 4.56 (s, 3H), 5.54 (d, J = 3.6 Hz, 1H), 6.51 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6 (CH_2), 26.9 (CH_2), 33.3 (CH_2), 33.4 (CH_2), 44.5 (CH), 66.2 (CH_2), 68.0 (CH_3), 80.0 (CH), 139.1 (C), 141.3 (C), 144.4 (CH), 148.4 (C), 197.2 (4 C), 203.2 (C), 305.6 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 2060, 1939 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{16}O_7W$: C 40.93, H 3.05; found: C 41.12, H 3.33.

Pentacarbonyl{[4-(1-cyclopentenyl)-2,3,3a,5a-tetrahydrocyclobuta[*b*]furan-5-yl]methoxymethylen}chromium(0) (3d): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/Et_2O/CH_2Cl_2 4:1:1, **3d** as a dark orange solid (93%). R_f = 0.56; m.p. 113–115 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.72–2.03 (m, 4H), 2.19–2.49 (m, 4H), 3.40 (dd, J = 7.9, 3.3 Hz, 1H), 3.75–3.91 (m, 1H), 4.13 (t, J = 8.2 Hz, 1H), 4.73 (s, 3H), 5.61 (d, J = 3.3 Hz, 1H), 6.37 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6 (CH_2), 27.1 (CH_2), 33.1 (CH_2), 33.2 (CH_2), 44.1 (CH), 65.5 (CH_3), 66.5 (CH_2), 80.1 (CH), 136.9 (C), 138.4 (C), 142.9 (CH), 146.1 (C), 216.2 (4 C), 223.8 (C), 334.3 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 2057, 1942 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{16}CrO_7$: C 54.55, H 4.07; found: C 54.16, H 4.29.

Pentacarbonyl{[4-(1-cyclopentenyl)-3a,5a-dihydro-2,2-dimethylcyclobuta[*d*]dioxol-5-yl]methoxymethylen}chromium(0) (3e): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/CH_2Cl_2 5:1, **3e** as a dark orange solid (78%). R_f = 0.30; m.p. 95–97 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.43 (s, 3H), 1.86–2.03 (m, 2H), 2.15–2.26 (m, 1H), 2.33–2.39 (m, 1H), 2.39–2.51 (m, 2H), 4.75 (s, 3H), 5.08 (d, J = 3.7 Hz, 1H), 5.84 (d, J = 3.7 Hz, 1H), 6.47–6.48 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.5 (CH_2), 28.4 (CH_3), 29.0 (CH_3), 33.0 (CH_2), 33.4 (CH_2), 66.0 (CH_3), 75.9 (CH), 81.0 (CH), 137.0 (C), 137.4 (C), 143.3 (CH), 150.3 (C), 215.9 (4 C), 223.6 (C), 336.5 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 2057, 1938 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{18}CrO_8$: C 53.53, H 4.26; found: C 53.81, H 4.50.

Pentacarbonyl{[4-(1-cyclohexenyl)-3a,5a-dihydro-2,2-dimethylcyclobuta[*d*]dioxol-5-yl]methoxymethylen}chromium(0) (3f): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/dichloromethane 5:1, **3f** as a dark orange solid (79%). R_f = 0.38; m.p. 89–91 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.41 (s, 3H), 1.45 (s, 3H), 1.58–1.93 (m, 6H), 1.21–1.23 (m, 2H), 4.69 (s, 3H), 5.13 (d, J = 3.6 Hz, 1H), 5.75 (d, J = 3.6 Hz, 1H), 6.33–6.34 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_2), 22.0 (CH_2), 25.9 (CH_2), 26.2 (CH_2), 28.3 (CH_3), 28.8 (CH_3), 66.2 (CH_3), 75.4 (CH), 80.2 (CH), 116.5 (C), 131.2 (C), 137.1 (CH), 140.0 (C), 149.8 (C), 215.8 (4 C), 223.6 (C), 340.2 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 2053, 1938 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{20}CrO_8$: C 54.55, H 4.58; found: C 54.67, H 4.40.

Pentacarbonyl{[3a,5a-dihydro-2,2-dimethyl-4-(2-phenylethenyl)cyclobuta[*d*]dioxol-5-yl]methoxymethylen}chromium(0) (3g): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/CH_2Cl_2 5:1, **3g** as a dark orange solid (89%). R_f = 0.32; m.p. 97–99 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.47 (s, 3H), 1.50 (s, 3H), 4.88 (s, 3H), 5.27 (brs, 1H), 5.84 (brs, 1H), 7.16 (d, J = 15.9 Hz, 1H), 7.31–7.55 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.6 (CH_3), 28.8 (CH_3), 66.0 (CH_3), 75.1 (CH), 80.5 (CH), 116.5 (C), 120.6 (CH), 127.8 (2 CH), 128.9 (2 CH), 130.1 (CH), 135.6 (C), 144.1 (CH), 144.9 (C), 149.7 (C), 216.2 (4 C), 224.1 (C), 332.8 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 2055, 1944 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{18}CrO_8$: C 57.15, H 3.92; found: C 56.98, H 3.61.

Pentacarbonyl{[2-(1-cyclopentenyl)-4-methoxy-4-methylcyclobut-1-enyl]methoxymethylen}chromium(0) (3h): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/CH_2Cl_2 5:1, **3j** as a dark orange solid (68%). R_f = 0.32; m.p. 79–81 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.80 (s, 3H), 1.98 (s, 3H), 2.56 (d, J = 12.8 Hz, 1H), 2.79 (d, J = 12.8 Hz, 1H), 3.34 (s, 3H), 4.57 (s, 3H), 6.58 (s, 1H), 7.20–7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.1 (CH_3), 22.4 (CH_3), 38.5 (CH_2), 51.8 (CH_3), 65.9 (CH_3), 82.3 (C), 127.4 (CH), 128.2 (2 CH), 129.2 (2 CH), 129.2 (C), 131.3 (C), 132.8 (CH), 136.5 (C), 152.5 (C), 216.3 (4 C), 224.3 (C), 347.5 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 2065, 1943 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{20}CrO_7$: C 58.93, H 4.50; found: C 59.09, H 4.24.

Pentacarbonyl{[3,3-dimethyl-2-(1-methyl-2-phenylethenyl)-4-trimethylsilyloxy-4-methoxycyclobut-1-enyl]methoxymethylen}chromium(0) (3j): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **3j** as an orange oil (56%). R_f = 0.22; ^1H NMR (200 MHz, $CDCl_3$): δ = 0.31 (s, 9H), 1.45 (s, 3H), 1.49 (s, 3H), 1.92 (s, 3H), 3.30 (s, 3H), 4.47 (brs, 3H), 6.73 (s, 1H), 7.28–7.43 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 1.6 (3 CH_3), 16.7 (CH_3), 22.0 (CH_3), 23.0 (CH_3), 52.8 (CH_3), 54.3 (C), 65.4 (CH_3), 127.4 (CH), 128.2 (2 CH), 129.3 (2 CH), 129.8 (C), 133.5 (CH), 136.5 (C), 216.4 (4 C), 224.8 (C), the signal corresponding to the carbene carbon has not been detected; LRMS (MALDI-TOF): calcd for $C_{26}H_{30}CrO_8Si$: 550; found: 550; IR (CH_2Cl_2): $\tilde{\nu}$ = 2053, 1939 cm^{-1}.

Pentacarbonyl{[2-(1-cyclopentenyl)-3,3-dimethyl-4-trimethylsilyloxy-4-methoxycyclobut-1-enyl]methoxymethylen}chromium(0) (3k): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **3k** as an orange oil (64%). R_f = 0.21; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.26 (s, 9H), 1.28 (s, 3H), 1.36 (s, 3H), 1.88 (quint., J = 7.3 Hz, 2H), 2.21–2.23 (m, 2H), 2.45–2,47 (m, 2H), 3.24 (s, 3H), 4.43 (brs, 3H), 6.02–6.03 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 1.5 (3 CH_3), 21.4 (CH_3), 22.7 (CH_3), 23.01 (CH_2), 33.3 (CH_2), 52.9 (CH_3), 54.3 (C), 65.2 (CH_3), 104.9 (C), 135.3 (C), 136.1 (CH), 167.3 (C), 216.3 (4 C), 224.8 (C), 345.4 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 2057, 1940 cm^{-1}.

Pentacarbonyl{[2-(1-cyclopentenyl)-3,3,4,4-tetramethoxycyclobut-1-enyl]methoxymethylen}chromium(0) (3l): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/CH_2Cl_2 5:1, **3l** as a dark orange solid (98%). R_f = 0.22; m.p. 80–82 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.86 (t, J = 6.8 Hz, 2H), 2.20–2.25 (m, 2H), 2.42–2.44 (m, 2H), 3.31 (brs, 6H), 3.48 (s, 6H), 4.37 (brs, 3H), 6.21–6.24 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.1 (CH_2), 32.9 (CH_2), 33.3 (CH_2), 51.2 (2 CH_3), 52.5 (2 CH_3), 65.8 (CH_3), 106.2 (C), 110.7 (C), 130.5 (C), 134.7 (C), 134.7 (C), 137.6 (C), 215.8 (4 C), 224.8 (C), 334.7 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 1950, 2063 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{22}CrO_{10}$: C 50.64, H 4.67; found: C 50.29, H 4.32.

Pentacarbonyl{[2-(1-cyclohexenyl)-3,3,4,4-tetramethoxycyclobut-1-enyl]methoxymethylen}chromium(0) (3m): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/CH_2Cl_2 5:1, **3m** as an orange solid (87%). R_f = 0.25; m.p. 75–77 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.86 (t, J = 6.8 Hz, 2H), 2.20–2.25 (m, 2H), 2.42–2.44 (m, 2H), 3.31 (brs, 6H), 3.48 (s, 6H), 4.37 (brs, 3H), 6.21–6.24 (m, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6 (CH_2), 22.2 (CH_2), 22.6 (CH_3), 25.8 (CH_2), 26.1 (CH_2), 38.3 (CH_2), 51.7 (CH_3), 65.8 (CH_3), 82.6 (C), 132.7 (CH), 136.3 (C), 150.5 (C), 170.0 (C), 216.4 (4 C), 224.3 (C), 347.3 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 1947, 2048 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{20}CrO_7$: C 55.34, H 4.89; found: C 55.67, H 5.02.

Pentacarbonyl{[2-(4,7-dihydro-2,2-dimethyl-1,3-dioxepin-5-yl)-3,3,4,4-tetramethoxycyclobut-1-enyl]methoxymethylen}chromium(0) (3n): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **3n** as an orange oil (71%). R_f = 0.29; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.39 (s, 6H), 3.33 (brs, 6H), 3.50 (s, 6H), 4.19 (brs, 3H), 4.32–4.39 (m, 4H), 6.11 (t, J = 3.9 Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 23.5 (2 CH_3), 51.3 (2 CH_3), 52.5 (2 CH_3), 60.9 (CH_2), 61.1 (CH_2), 66.1 (CH_3), 102.1 (C), 106.3 (C), 110.4 (C), 131.8 (C), 133.9 (C), 134.5 (C), 215.8 (4 C), 224.7 (C), 343.4 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 1957, 2039 cm^{-1}.

Pentacarbonyl{[3,3,4,4-tetramethoxy-2-(2-phenylethenyl)cyclobut-1-enyl]methoxymethylen}chromium(0) (3o): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/CH_2Cl_2 5:1, **3o** as an orange solid (88%). R_f = 0.28; m.p. 83–85 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 3.41 (s, 6H), 3.59 (s, 6H), 4.48 (s, 3H), 6.71 (d, J = 15.7 Hz, 1H9, 6.98 (d, J = 15.7 Hz, 1H), 7.35–7.45 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.5 (2 CH_3), 52.3 (2 CH_3), 66.0 (CH_3), 106.2 (C), 110.4 (C), 117.6 (CH), 126.9 (2 CH), 128.6 (2 CH), 129.0 (CH), 133.2 (C), 135.8 (C), 138.1 (CH), 151.0 (C), 215.7 (4 C), 225.0 (C), 342.8 (C); IR (CH_2Cl_2): $\tilde{\nu}$ = 1952, 2040 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{22}CrO_{10}$: C 54.12, H 4.34; found: C 54.35, H 4.21.

Pentacarbonyl{[2-(3,4-dihydro-2*H*-pyran-3-yl)-3,3,4,4-tetramethoxycyclobut-1-enyl]methoxymethylen}chromium(0) (3p): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **3p** as an orange oil (91%). $R_f = 0.21$; ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 1.71 - 1.82$ (m, 2H), 2.03 – 2.20 (m, 2H), 3.29 (brs, 6H), 3.52 (s, 6H), 3.92 – 4.05 (m, 2H), 4.23 (s, 3H), 5.21 – 5.44 (m, 1H); ^{13}C NMR (50.3 MHz, CDCl$_3$): $\delta = 20.5$ (CH$_2$), 21.8 (CH$_2$), 51.2 (2CH$_3$), 52.6 (2CH$_3$), 65.7 (CH$_3$), 66.0 (CH$_2$), 106.1 (C), 107.7 (CH), 110.7 (C), 128.6 (C), 145.9 (C), 145.9 (C), 215.9 (4C), 225.6 (C), 343.0 (C); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 1952$, 2039 cm^{-1}.

General procedure for the preparation of aniline derivatives 5: A solution of complex **3** (1 mmol) and isocyanide **4** (2 mmol) in dry THF (20 mL) was stirred under nitrogen atmosphere until TLC analyses revealed the consumption of the starting material and the formation of a new compound. Typically, chromium complexes **3** immediately underwent the transformation, but the reacting mixtures were stirred for 15 minutes; for tungsten complexes **3a** and **3c**, the reaction was completed after one hour. For reactions arising from chromium complexes, removal of THF by vacuum, addition of hexane (50 mL) and exposure to sun light and air for 12 h, followed by flash chromatography afforded the title compounds **5**. For tungsten complexes, the residue was loaded directly onto a silica gel column without previous exposure to light and air.

6-*tert*-Butylamino-2,3,3a,7b-tetrahydro-7-methoxy-4-methyl-5-phenylbenzo[3,4]cyclobuta[1,2-*b*]furane (5a): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **5a** as a white solid (88% from complex **3a**, or 94% from complex **3b**). $R_f = 0.29$; m.p. 106 – 108 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.93$ (s, 9H), 1.79 (s, 3H), 1.80 – 1.95 (m, 2H), 3.67 – 3.75 (m, 1H), 4.00 (dd, $J = 7.4$, 3.5 Hz, 1H), 4.04 (s, 3H), 4.11 (t, $J = 8.1$ Hz, 1H), 5.65 (d, $J = 3.5$ Hz, 1H), 7.12 – 7.19 (m, 2H), 7.31 – 7.46 (m, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 14.8$ (CH$_3$), 28.5 (CH$_2$), 30.2 (3CH$_3$), 42.2 (CH), 53.5 (C), 57.0 (CH$_3$), 66.5 (CH$_2$), 80.3 (CH), 122.4 (C), 124.6 (C), 126.9 (CH), 128.4 (2CH), 129.8 (CH), 130.0 (CH), 132.3 (C), 137.7 (C), 139.0 (C), 139.4 (C), 147.2 (C); elemental analysis calcd (%) for $C_{22}H_{27}NO_2$: C 78.30, H 8.06, N 4.15; found: C 78.56, H 8.33, N 3.97.

4-Benzylamino-2,3,5b,7,8,8a-hexahydro-5-methoxy-1*H*-inden[4′,5′:3,4]cyclobuta[1,2-*b*]furane (5b): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **5b** as a light yellow oil (78% from complex **3c**, or 86% from complex **3d**). $R_f = 0.23$; ^{1}H NMR (200 MHz, CDCl$_3$): 1.84 – 2.00 (m, 2H), 2.11 (quint., $J = 7.4$ Hz, 2H), 2.74 (t, $J = 7.4$ Hz, 2H), 2.91 (t, $J = 7.4$ Hz, 2H), 3.66 – 3.79 (m, 1H), 3.98 (dd, $J = 7.7$, 3.3 Hz, 1H), 4.02 (s, 3H), 4.13 (t, $J = 8.0$ Hz, 1H), 4.34 (s, 2H), 5.66 (d, $J = 3.3$ Hz, 1H), 7.28 – 7.42 (m, 5H); ^{13}C NMR (50.3 MHz, CDCl$_3$): $\delta = 26.3$ (CH$_2$), 28.8 (CH$_2$), 28.9 (CH$_2$), 31.5 (CH$_2$), 47.5 (CH), 51.4 (CH$_2$), 57.7 (CH$_3$), 66.6 (CH$_2$), 81.1 (CH), 124.1 (C), 126.8 (CH), 127.5 (2CH), 127.9 (2CH), 131.2 (C), 131.3 (C), 133.3 (C), 136.4 (C), 140.5 (C), 143.3 (C).

4-*tert*-Butylamino-2,3,5b,8a-tetrahydro-5-methoxy-7,7-dimethyl-1*H*-inden[4′,5′:3,4]cyclobuta[1,2-*d*][1,3]dioxole (5c): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 3:1, **5c** as a light yellow solid (78%). $R_f = 0.22$; m.p. 106 – 108 °C; ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 1.03$ (s, 3H), 1.15 (s, 9H), 1.43 (s, 3H), 2.00 (quint., $J = 6.9$ Hz, 2H), 2.77 – 2.87 (m, 4H), 3.98 (s, 3H), 5.67 (d, $J = 3.6$ Hz, 1H), 5.86 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (50.3 MHz, CDCl$_3$): $\delta = 26.6$ (CH$_2$), 27.7 (CH$_3$), 28.7 (CH$_3$), 29.7 (CH$_3$), 30.3 (3CH$_3$), 32.8 (CH$_2$), 54.9 (C), 57.4 (CH$_3$), 80.8 (CH), 81.7 (CH), 115.0 (C), 127.5 (C), 132.0 (C), 132.8 (C), 136.6 (C), 145.3 (C), 147.8 (C); HRMS: calcd for $C_{19}H_{27}NO_3$: 317.1991; found: 317.1994; MS (70 eV): m/z (%): 317 (21), 259 (7), 244 (11), 188 (100); elemental analysis calcd (%) for $C_{19}H_{27}NO_3$: C 71.89, H 8.57, N 4.41; found: C 72.07, H 8.24, N 4.55.

5-Benzylamino-1,2,3,4,6b,9a-hexahydro-6-methoxy-8,8-dimethylnaphtho[1′,2′:3,4]cyclobuta[*d*][1,3]dioxole (5d): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 3:1, **5e** as a colorless oil (67%). $R_f = 0.25$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.07$ (s, 3H), 1.48 (s, 3H), 1.76 – 1.77 (m, 4H), 2.67 – 2.73 (m, 4H), 3.65 (brs, 1H), 3.98 (s, 3H), 4.12 (d, $J = 14.2$ Hz, 1H), 4.19 (d, $J = 14.2$ Hz, 1H), 5.70 (d, $J = 3.5$ Hz, 1H), 5.85 (d, $J = 3.5$ Hz, 1H), 7.24 – 7.35 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 22.0$ (CH$_2$), 23.0 (CH$_2$), 24.4 (CH$_2$), 26.1 (CH$_2$), 27.9 (CH$_3$), 28.7 (CH$_3$), 52.2 (CH$_2$), 57.6 (CH$_3$), 80.6 (CH), 80.9 (CH), 115.1 (C), 126.1 (C), 126.7 (C), 126.9 (CH), 127.8 (2CH), 128.2 (2CH), 132.4 (C), 136.5 (C), 138.1 (C), 140.3 (C), 144.0 (C).

5-*tert*-Butylamino-3a,7a-dihydro-4-methoxy-2,2-dimethyl-6-phenylbenzo[1′,2′:3,4]cyclobuta[1,2-*d*][1,3]dioxole (5e): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **5f** as a light yellow solid (98%). $R_f = 0.19$; m.p. 131 – 133 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.86$ (s, 9H), 1.13 (s, 3H), 1.47 (s, 3H), 4.07 (s, 3H), 5.73 (d, $J = 3.7$ Hz, 1H), 5.94 (d, $J = 3.7$ Hz, 1H), 6.78 (s, 1H), 7.26 – 7.40 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 27.9$ (CH$_3$), 28.8 (CH$_3$), 30.1 (3CH$_3$), 54.4 (C), 57.3 (CH$_3$), 81.4 (CH), 81.7 (CH), 115.4 (C), 117.5 (CH), 126.8 (CH), 128.0 (2CH), 128.7 (C), 129.6 (2CH), 134.3 (C), 141.3 (C), 141.4 (C), 142.0 (C), 149.4 (C); elemental analysis calcd (%) for $C_{22}H_{27}NO_3$: C 74.76, H 7.70, N 3.96; found: C 75.00, H 7.85, N 4.09.

4-*tert*-Butylamino-2,3,6,7-tetrahydro-5,6-dimethoxy-6-methyl-1*H*-cyclobuta[1,2-*e*]indene (5f): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **5i** as a light yellow solid (85%). $R_f = 0.34$; m.p. 94 – 96 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.17$ (s, 9H), 1.71 (s, 3H), 2.00 (quint., $J = 7.4$ Hz, 2H), 2.67 (t, $J = 7.4$ Hz, 1H), 2.88 (t, $J = 7.4$ Hz, 2H), 2.89 (d, $J = 14.4$ Hz, 1H), 3.27 (s, 3H), 3.36 (d, $J = 14.4$ Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 26.6$ (CH$_2$), 27.5 (CH$_3$), 29.8 (CH$_2$), 30.1 (3CH$_3$), 33.0 (CH$_2$), 38.6 (CH$_2$), 51.6 (CH$_3$), 55.5 (C), 57.3 (CH$_3$), 82.7 (C), 128.5 (C), 129.8 (C), 131.3 (C), 132.0 (C), 144.5 (C), 148.9 (C); elemental analysis calcd (%) for $C_{18}H_{27}NO_2$: C 74.70, H 9.40, N 4.84; found: C 74.86, H 9.03, N 5.04.

4-Benzylamino-2,3,6,7-tetrahydro-5-methoxy-1*H*-cyclobuta[1,2-*e*]inden-6-one (5g): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 10:1, **5j** as a light yellow oil (52%). $R_f = 0.22$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 2.14$ (quint., $J = 7.4$ Hz, 2H), 2.81 (t, $J = 7.4$ Hz, 2H), 2.94 (t, $J = 7.4$ Hz, 2H), 3.79 (s, 2H), 4.16 (s, 3H), 4.33 (s, 2H), 7.30 – 7.33 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 26.2$ (CH$_2$), 29.5 (CH$_2$), 32.4 (CH$_2$), 49.3 (CH$_2$), 51.1 (CH$_2$), 60.1 (CH$_3$), 127.0 (CH), 127.3 (2CH), 128.3 (2CH), 130.5 (C), 131.7 (C), 134.1 (C), 134.6 (C), 140.2 (C), 141.8 (C), 143.2 (C), 184.7 (C); HRMS: calcd for $C_{19}H_{19}NO_2$: 293.1416; found: 293.1414; MS (FAB +): m/z (%): 293 (58), 289 (61), 282 (16), 219 (15).

3-*tert*-Butylamino-2,8-dimethoxy-5,7,7-trimethyl-8-trimethylsilyloxy-4-phenylbicyclo[4.2.0]octa-1,3,5-triene (5h): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **5k** as a yellow oil (65%). $R_f = 0.21$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.21$ (s, 9H), 0.91 (s, 9H), 1.36 (s, 3H), 1.38 (s, 3H), 1.81 (s, 3H), 3.42 (s, 3H), 3.98 (s, 3·H), 7.14 – 7.16 (m, 2H), 7.26 – 7.44 (m, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 1.4$ (3CH$_3$), 15.4 (CH$_3$), 21.5 (CH$_3$), 24.1 (CH$_3$), 30.5 (3CH$_3$), 53.4 (C), 54.2 (CH$_3$), 55.7 (C), 58.9 (CH$_3$), 106.2 (C), 123.1 (C), 126.9 (CH), 128.4 (2CH), 129.0 (C), 130.2 (CH), 130.3 (CH), 134.1 (C), 139.5 (C), 140.2 (C), 143.8 (C), 147.3 (C).

4-Benzylamino-2,3,6,7-tetrahydro-5,6-dimethoxy-7,7-dimethyl-6-trimethylsilyloxy-1*H*-cyclobuta[1,2-*e*]indene (5i): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **5l** as a light yellow oil (59%). $R_f = 0.17$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.25$ (s, 9H), 1.35 (s, 3H), 1.37 (s, 3H), 2.13 (quint., $J = 7.4$ Hz, 2H), 2.77 (t, $J = 7.4$ Hz, 2H), 2.91 (t, $J = 7.4$ Hz, 2H), 3.47 (s, 3H), 3.97 (s, 3H), 4.34 (s, 2H), 7.26 – 7.42 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 1.3$ (CH$_3$), 21.7 (CH$_3$), 24.0 (CH$_3$), 26.3 (CH$_2$), 29.0 (CH$_2$), 31.4 (CH$_2$), 51.6 (CH$_2$), 53.9 (CH$_3$), 55.4 (C), 60.2 (CH$_3$), 106.6 (C), 126.8 (CH), 127.6 (2CH), 128.3 (2CH), 129.1 (C), 131.9 (C), 135.1 (C), 136.8 (C), 137.9 (C), 140.7 (C), 142.9 (C).

4-*tert*-Butylamino-2,3,6,7-tetrahydro-5,6,6,7,7-pentamethoxy-1*H*-cyclobuta[1,2-*e*]indene (5j): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **5m** as a colorless oil (85%). $R_f = 0.20$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.15$ (s, 9H), 2.00 – 2.03 (m, 2H), 2.85 – 2.87 (m, 4H), 3.48 (s, 12H), 3.96 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 26.6$ (CH$_2$), 30.4 (3CH$_3$), 31.6 (CH$_2$), 33.1 (CH$_2$), 51.5 (2CH$_3$), 52.1 (2CH$_3$), 54.9 (C), 59.9 (CH$_3$), 108.9 (C), 109.1 (C), 128.3 (C), 132.3 (C), 133.8 (C), 135.3 (C), 145.6 (C), 148.4 (C); elemental analysis calcd (%) for $C_{20}H_{31}NO_5$: C 65.73, H 8.55, N 3.83; found: C 65.99, H 8.78, N 4.02.

5-*tert*-Butylamino-1,2,3,4,7,8-hexahydro-6,7,7,8,8-pentamethoxycyclobuta[*a*]naphthalene (5k): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **5o** as a colorless oil (87%). $R_f = 0.20$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.13$ (s, 9H), 1.65–1.68 (m, 4H), 2.65–2.69 (m, 2H), 2.76–2.78 (m, 2H), 3.47 (s, 6H), 3.48 (s, 6H), 3.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.8$ (CH_2), 22.7 (CH_2), 26.3 (CH_2), 27.6 (CH_2), 30.5 ($3CH_3$), 51.8 ($2CH_3$), 52.0 ($2CH_3$), 54.6 (C), 59.8 (CH_3), 108.7 (C), 109.3 (C), 126.9 (C), 127.5 (C), 136.6 (C), 137.1 (C), 138.7 (C), 148.2 (C); elemental analysis calcd (%) for $C_{21}H_{33}NO_5$: C 66.46, H 8.76, N 3.69; found: C 66.78, H 8.56, N 3.32.

5-Benzylamino-1,2,3,4,7,8-hexahydro-6,7,7,8,8-pentamethoxycyclobuta[*a*]-naphthalene (5l): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **5p** as a yellow oil (76%). $R_f = 0.23$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.75$–1.77 (m, 4H), 2.70 (t, $J = 5.7$ Hz, 2H), 2.85 (t, $J = 5.7$ Hz, 2H), 3.53 (s, 12H), 3.91 (s, 2H), 25–7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.9$ (CH_2), 22.6 (CH_2), 26.2 (CH_2), 26.6 (CH_2), 51.6 ($2CH_3$), 51.7 ($2CH_3$), 52.2 (CH_2), 60.4 (CH_3), 108.6 (C), 109.3 (C), 126.7 (CH), 127.3 (C), 127.5 (2CH), 128.1 (2CH), 128.8 (C), 132.5 (C), 135.3 (C), 139.3 (C), 140.2 (C), 144.0 (C).

6-*tert*-Butylamino-1,5,8,9-tetrahydro-7,8,8,9,9-pentamethoxy-3,3-dimethyl-cyclobuta[1′,2′:3,4]benzo[*e*][1,3]dioxepine (5m): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 3:1, **5q** as a colorless oil (92%). $R_f = 0.25$; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.06$ (s, 9H), 1.45 (s, 6H), 3.45 (s, 6H), 3.46 (s, 6H), 3.97 (s, 3H), 4.89 (s, 2H), 4.97 (s, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 23.7$ ($2CH_3$), 30.2 ($3CH_3$), 51.6 ($2CH_3$), 52.2 ($2CH_3$), 55.1 (C), 59.9 (CH_3), 61.5 (CH_2), 61.5 (CH_2), 102.1 (C), 108.7 (C), 109.2 (C), 126.9 (C), 127.8 (C), 135.3 (C), 135.7 (C), 140.7 (C), 150.0 (C).

3-Benzylamino-2,7,7,8,8-pentamethoxy-4-phenylbicyclo[4.2.0]octa-1,3,5-triene (5n): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **5s** as a colorless oil (82%). $R_f = 0.28$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.55$ (s, 6H), 3.61 (s, 6H), 3.87 (s, 2H), 4.05 (s, 3H), 6.96 (s, 1H), 7.00–7.49 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 51.1$ ($2CH_3$), 51.4 (CH_2), 52.1 ($2CH_3$), 60.0 (CH_3), 108.7 (C), 109.3 (C), 118.4 (CH), 126.6 (CH), 126.9 (CH), 127.4 (2CH), 127.9 (2CH), 128.2 (2CH), 128.6 (2CH), 129.1 (C), 135.1 (C), 135.6 (C), 139.1 (C), 139.9 (C), 140.3 (C), 145.6 (C); elemental analysis calcd (%) for $C_{26}H_{29}NO_5$: C 71.70, H 6.71, N 3.22; found: C 71.96, H 8.02, N 3.03.

4-*tert*-Butylamino-2,5,6,7-tetrahydro-1,1,2,2,3-pentamethoxy-1*H*-cyclobuta[1′,2′:5,6]benzo[*b*]pyrane (5o): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 3:1, **5t** as a colorless oil (97%). $R_f = 0.36$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.18$ (s, 9H), 1.86–1.91 (m, 2H), 2.76 (dd, $J = 6.4$, 5.6 Hz, 2H), 3.53 (s, 6H), 3.56 (s, 6H), 3.91 (s, 3H), 4.15 (t, $J = 4.9$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 22.1$ (CH_2), 24.5 (CH_2), 30.6 ($3CH_3$), 52.1 ($2CH_3$), 52.4 ($2CH_3$), 55.0 (C), 60.0 (CH_3), 65.9 (CH_2), 108.8 (C), 109.1 (C), 123.3 (C), 124.6 (C), 129.3 (C), 138.5 (C), 143.5 (C), 144.1 (C); elemental analysis calcd (%) for $C_{20}H_{31}NO_6$: C 62.97, H 8.19, N 3.67; found: C 63.16, H 8.41, N 3.28.

Hydrolysis of aniline derivative 5j: Compound **5l** (0.2 mmol) dissolved in THF (2 mL) was treated with a saturated solution of K_2CO_3 in H_2O (2 mL). The mixture was stirred at room temperature for 15 minutes and then extracted with diethyl ether (2 × 10 mL). The organic layer was washed with brine and dried over anhydrous Na_2SO_4. Product **6** was isolated after column chromatography in a mixture of hexane/ethyl acetate 5:1.

4-Benzylamino-2,3,6,7-tetrahydro-5-methoxy-7,7-dimethyl-1*H*-cyclobuta[1,2-*e*]inden-6-one (6): Prepared from **5l** as described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **6** as a light yellow oil (89%). $R_f = 0.28$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.45$ (s, 6H), 2.10–2.20 (m, 2H), 2.81 (t, $J = 7.4$ Hz, 2H), 2.93 (t, $J = 7.4$ Hz, 2H), 4.16 (s, 3H), 4.33 (s, 2H), 7.27–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 22.4$ ($2CH_3$), 26.2 (CH_2), 28.7 (CH_2), 32.2 (CH_2), 51.2 (CH_2), 60.1 (CH_3), 62.2 (C), 127.0 (C), 127.1 (CH), 127.5 (2CH), 128.4 (2CH), 130.0 (C), 134.0 (C), 140.2 (C), 142.4 (C), 143.6 (C), 146.3 (C), 192.7 (C); HRMS (EI): calcd for $C_{21}H_{23}NO_2$: 321.1729; found: 321.1733.

General procedure for the preparation of *cis*-1,2-benzocyclobutene derivatives 7: Compounds **5c**–**e** (1 mmol) dissolved in a mixture THF/H_2O 10:1 were treated with an excess of trifluoroacetic acid (2 mL) at room temperature. After 12 h, volatiles were removed in high vacuum (0.1 mm Hg) and the residue was redissolved in dichloromethane, washed with 0.5 M NaOH and saturated NaCl solutions and dried over anhydrous Na_2SO_4. *cis*-1,2-Diol derivatives were employed in the next reaction step without further purification.

Protection of the hydroxyl groups as trimethylsilyl ethers was carried out by adding chlorotrimethylsilane (2.2 mmol) and triethylamine (2.2 mmol) to the crude obtained in the previous step dissolved in dry THF (10 mL). The mixture was stirred under nitrogen atmosphere for 12 h, hydrolysed with H_2O (10 mL) and extracted with *tert*-butyl methyl ether (2 × 10 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and chromatographed with hexane/ethyl acetate 20:1. When *tert*-butyldimethylsilyl was chosen as protective group, the experimental procedure followed was identical, but 2.2 mmol of TBSCl were used as silylating agent and 4 mmol of imidazole as base.

***cis*-4-*tert*-Butylamino-2,3,6,7-tetrahydro-5-methoxy-6,7-bis(trimethylsilyloxy)-1*H*-cyclobuta[1,2-*e*]indene (7a)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **7a** as a colorless oil (76%). $R_f = 0.22$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.16$ (s, 9H), 0.21 (s, 9H), 1.12 (s, 9H), 1.83–1.92 (m, 1H), 1.96–2.04 (m, 1H), 2.67–2.85 (m, 4H), 2.94 (brs, 1H), 3.92 (s, 3H), 5.23 (d, $J = 3.5$ Hz, 1H), 5.48 (d, $J = 3.5$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 0.3$ ($3CH_3$), 0.4 ($3CH_3$), 26.8 (CH_2), 30.3 ($3CH_3$), 30.6 (CH_2), 32.9 (CH_2), 55.2 (C), 57.4 (CH_3), 73.6 (CH), 75.2 (CH), 127.6 (C), 131.8 (C), 132.4 (C), 137.5 (C), 145.3 (C), 148.9 (C); HRMS: calcd for $C_{22}H_{40}NO_3Si_2$ $[M+H]^+$: 422.2547; found: 422.2552; MS (FAB+): m/z (%): 422 (9), 326 (65), 313 (28), 281 (41), 207 (100).

***cis*-4-*tert*-Butylamino-6,7-bis(*tert*-butyldimethylsilyloxy)-2,3,6,7-tetrahydro-5-methoxy-1*H*-cyclobuta[1,2-*e*]indene (7b)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **7b** as a colorless oil (62%). $R_f = 0.54$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.11$ (s, 3H), 0.15 (s, 3H), 0.19 (s, 3H), 0.22 (s, 3H), 0.95 (s, 9H), 1.16 (s, 9H), 1.88–2.07 (m, 2H), 2.74–2.90 (m, 4H), 3.93 (s, 3H), 5.39 (d, $J = 3.9$ Hz, 1H), 5.52 (d, $J = 3.9$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -4.7$ (CH_3), -4.2 (CH_3), -3.7 (CH_3), -3.5 (CH_3), 18.2 (C), 18.5 (C), 26.0 ($3CH_3$), 26.2 ($3CH_3$), 26.8 (CH_2), 30.4 ($3CH_3$), 31.1 (CH_2), 32.9 (CH_2), 55.2 (C), 57.9 (CH_3), 75.1 (CH), 76.0 (CH), 128.4 (C), 132.1 (C), 132.9 (C), 138.0 (C), 145.4 (C), 149.1 (C); HRMS: calcd for $C_{28}H_{51}NO_3Si_2$: 505.3407; found: 505.3392; MS (70 eV): m/z (%): 505 (40), 491 (38), 490 (100), 434 (43), 302 (21), 245 (37).

***cis*-5-*tert*-Butylamino-7,8-bis(*tert*-butyldimethylsilyloxy)-1,2,3,4,7,8-hexahydro-6-methoxycyclobuta[*a*]naphthalene (7c)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **7c** as a colorless oil (68%). $R_f = 0.56$; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.08$ (s, 3H), 0.10 (s, 3H), 0.17 (s, 3H), 0.22 (s, 3H), 0.96 (s, 9H), 1.00 (s, 9H), 1.18 (s, 9H), 1.18 (s, 9H), 1.59–1.72 (m, 4H), 2.63–2.79 (m, 4H), 3.89 (s, 3H), 5.36 (d, $J = 3.7$ Hz, 1H), 5.54 (d, $J = 3.7$ Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = -4.1$ (CH_3), -3.9 (CH_3), -3.7 (CH_3), -3.5 (CH_3), 18.3 (C), 18.6 (C), 22.1 (CH_2), 23.1 (CH_2), 25.3 (CH_2), 26.1 ($3CH_3$), 26.3 ($3CH_3$), 27.6 (CH_2), 30.6 ($3CH_3$), 54.9 (C), 57.7 (CH_3), 75.1 (CH), 76.4 (CH), 126.7 (C), 127.8 (C), 134.7 (C), 137.7 (C), 141.5 (C), 148.5 (C); elemental analysis calcd (%) for $C_{29}H_{53}NO_3Si_2$: C 66.99, H 10.28, N 2.69; found: C 67.24, H 10.46, N 2.51.

***cis*-5-Benzylamino-7,8-bis(*tert*-butyldimethylsilyloxy)-1,2,3,4,7,8-hexahydro-6-methoxycyclobuta[*a*]naphthalene (7d)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **7d** as a colorless oil (62%). $R_f = 0.59$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.12$ (s, 3H), 0.18 (s, 3H), 0.18 (s, 3H), 0.24 (s, 3H), 0.97 (s, 9H), 1.00 (s, 9H), 1.73–1.75 (m, 4H), 2.67–2.81 (m, 4H), 3.89 (s, 3H), 4.12 (brs, 2H), 5.36 (d, $J = 3.7$ Hz, 1H), 5.52 (d, $J = 3.7$ Hz, 1H), 7.26–7.49 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -4.1$ (CH_3), -3.7 (CH_3), -3.5 (CH_3), -3.0 (CH_3), 18.3 (C), 18.6 (C), 22.2 (CH_2), 22.6 (CH_2), 23.0 (CH_2), 25.6 (CH_2), 26.1 ($3CH_3$), 26.2 ($3CH_3$), 52.6 (CH_2), 58.5 (CH_3), 75.1 (CH), 74.8 (CH), 127.0 (CH), 127.2 (C), 128.0 (2CH), 128.3 (2CH), 128.8 (C), 130.1 (C), 132.2 (C), 139.7 (C), 140.5 (C), 144.9 (C); HRMS (EI): calcd for $C_{32}H_{51}NO_3Si_2$: 553.3407; found: 553.3413.

***cis*-3-*tert*-Butylamino-7,8-bis(*tert*-butyldimethylsilyloxy)-4-phenyl-2-methoxybicyclo[4.2.0]octa-1,3,5-triene (7e)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **7e** as a colorless oil (86%). $R_f = 0.55$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.24$ (s, 12H), 0.88 (s, 9H), 1.01 (s, 18H), 3.29 (brs, 1H), 4.07 (s, 3H), 5.40 (d, $J = 3.7$ Hz, 1H), 5.62 (d, $J = 3.7$ Hz, 1H), 6.77 (s, 1 H), 7.30–7.46 (m, 5 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = −5.1 (CH$_3$), −4.0 (CH$_3$), −4.0 (CH$_3$), −3.6 (CH$_3$), 18.2 (C), 18.5 (C), 25.9 (3 CH$_3$), 26.2 (3 CH$_3$), 30.2 (3 CH$_3$), 54.7 (C), 57.6 (CH$_3$), 75.2 (CH), 75.8 (CH), 118.2 (CH), 126.5 (CH), 127.9 (2 CH), 129.0 (C), 129.8 (2 CH), 133.9 (C), 141.6 (C), 142.1 (C), 142.2 (C), 150.9 (C); elemental analysis calcd (%) for $C_{31}H_{51}NO_3Si_2$: C 68.71, H 9.49, N 2.58; found: C 68.97, H 9.26, N 2.77.

General procedure for the preparation of benzocyclobutenedione derivatives 9: The synthesis of compounds **9** involved reaction of **5j**, **l**, **n**, **o** (1 mmol) with an excess of trifluoroacetic acid (3 mL) in a mixture THF/H$_2$O 10:1 at room temperature for 12 h. After volatiles had been removed in high vacuum (0.1 mm Hg), the residue was redissolved in dichloromethane, washed with 0.5 M NaOH and saturated NaCl solutions, dried over anhydrous Na$_2$SO$_4$ and cromatographed in a mixture of hexane:ethyl acetate 5:1.

4-*tert*-Butylamino-2,3,6,7-tetrahydro-5-methoxy-1*H*-cyclobuta[1,2-*e*]inden-6,7-dione (9a): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **9a** as a bright yellow solid (85 %). R_f = 0.25; m.p. 83–85 °C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.38 (s, 9 H), 2.23 (quint., *J* = 7.4 Hz, 2 H), 2.90 (t, *J* = 7.4 Hz, 2 H), 3.16 (t, *J* = 7.4 Hz, 2 H), 4.23 (s, 3 H); ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 25.0 (CH$_2$), 30.8 (CH$_2$), 31.0 (3 CH$_3$), 32.4 (CH$_2$), 54.6 (C), 59.7 (CH$_3$), 133.0 (C), 140.1 (C), 141.2 (C), 146.4 (C), 155.6 (C), 156.1 (C), 190.2 (C), 190.5 (C); elemental analysis calcd (%) for $C_{16}H_{19}NO_3$: C 70.31, H 7.01, N 5.12; found: C 70.20, H 7.34, N 5.45.

5-Benzylamino-1,2,3,4,7,8-hexahydro-6-methoxycyclobuta[*a*]naphthalen-7,8-dione (9b): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **9b** as a bright yellow solid (61 %). R_f = 0.32; m.p. 79–81 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.75–1.88 (m, 4 H), 2.58 (dd, *J* = 6.3, 5.7 Hz, 2 H), 2.99–3.01 (m, 2 H), 4.10 (s, 3 H), 4.70 (s, 2 H), 7.24–7.37 (m, 5 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 20.8 (CH$_2$), 22.1 (CH$_2$), 26.0 (CH$_2$), 26.6 (CH$_2$), 50.8 (CH$_2$), 60.1 (CH$_3$), 127.2 (2 CH), 127.4 (CH), 128.6 (2 CH), 128.9 (C), 135.1 (C), 138.7 (C), 139.4 (C), 142.4 (C), 154.3 (C), 159.1 (C), 190.5 (C), 191.0 (C); elemental analysis calcd (%) for $C_{20}H_{19}NO_3$: C 74.75, H 5.96, N 4.36; found: C 74.54, H 6.21, N 4.55.

3-Benzylamino-4-phenyl-2-methoxybicyclo[4.2.0]octa-1,3,5-trien-7,8-dione (9c): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **9c** as a bright yellow solid (61 %). R_f = 0.27; m.p. 85–87 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.13 (s, 2 H), 4.25 (s, 3 H), 7.07 (d, *J* = 7.7 Hz, 2 H), 7.22–7.50 (m, 9 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 50.3 (CH$_2$), 60.5 (CH$_3$), 117.9 (CH), 127.0 (2 CH), 127.3 (CH), 128.3 (2 CH), 128.4 (2 CH), 128.5 (CH), 128.8 (2 CH), 138.0 (C), 138.4 (C), 138.6 (C), 141.0 (C), 142.1 (C), 153.8 (C), 158.8 (C), 189.9 (C), 190.7 (C); elemental analysis calcd (%) for $C_{22}H_{17}NO_3$: C 76.95, H 4.99, N 4.08; found: C 77.09, H 5.23, N 4.32.

4-*tert*-Butylamino-2,5,6,7-tetrahydro-3-methoxy-1*H*-cyclobuta[1′,2′:5,6]-benzo[*b*]pyran-1,2-dione (9d): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **9d** as a bright yellow solid (61 %). R_f = 0.18; m.p. 76–78 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.33 (s, 9 H), 2.03–2.08 (m, 2 H), 2.66 (t, *J* = 6.3 Hz, 2 H), 4.13 (s, 3 H), 4.27 (t, *J* = 5.1 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.1 (CH$_2$), 23.6 (CH$_2$), 31.2 (3 CH$_3$), 55.8 (C), 59.7 (CH$_3$), 66.0 (CH$_2$), 124.0 (C), 138.4 (C), 144.3 (C), 144.5 (C), 149.1 (C), 152.1 (C), 187.6 (C), 190.1 (C); elemental analysis calcd (%) for $C_{16}H_{19}NO_4$: C 66.42, H 6.62, N 4.84; found: C 66.17, H 6.91, N 4.66.

General procedure for the preparation of *trans*-1,2-benzocyclobutene derivatives 8: Reduction of compounds **9** to the corresponding *trans*-1,2-diol derivatives was carried out according to the experimental procedure reported by Danishefsky and co-workers:[5a] Compounds **9** (1 mmol) were dissolved in methanol (30 mL) and cooled to 0 °C. NaBH$_4$ (2 mmol) was added in small portions, and the resulting mixture was stirred at the same temperature for 30 minutes. The reaction was then quenched with acetone (2 mL) and solvents were removed in vacuum (10 mm Hg). The residue was redissolved in ethyl acetate (30 mL) and filtered through a pad of silica gel. The resulting diols were used in the next reaction step without further purification.

Protection of the hydroxyl groups as trimethylsilyl or *tert*-butyldimethylsilyl ethers was performed by the same experimental procedure described for the analogous *cis*-derivatives **7**. Systems **8** were also purified by column chromatography.

***trans*-4-*tert*-Butylamino-2,3,6,7-tetrahydro-5-methoxy-6,7-bis(trimethylsilyloxy)-1*H*-cyclobuta[1,2-*e*]indene (8a)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **8a** as a colorless oil (63 %). R_f = 0.55; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.17 (s, 9 H), 0.20 (s, 9 H), 1.12 (s, 9 H), 1.93–1.98 (m, 2 H), 2.00–2.77 (m, 2 H), 2.81 (t, *J* = 7.1 Hz, 2 H), 3.00 (brs, 1 H), 3.89 (s, 3 H), 4.86 (s, 1 H), 5.04 (s, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 0.1 (3 CH$_3$), 0.3 (3 CH$_3$), 26.7 (CH$_2$), 30.1 (CH$_2$), 30.3 (3 CH$_3$), 32.8 (CH$_2$), 55.1 (C), 57.3 (CH$_3$), 78.4 (CH), 79.4 (CH), 124.3 (C), 131.5 (C), 132.3 (C), 133.9 (C), 145.2 (C), 148.9 (C); HRMS: calcd for $C_{22}H_{40}NO_3Si_2$ $[M+H]^+$: 422.2547; found: 422.2558; MS (FAB +): *m*/*z* (%): 422 (6), 326 (71), 313 (32), 281 (56), 207 (100).

***trans*-4-*tert*-Butylamino-6,7-bis(*tert*-butyldimethylsilyloxy)-2,3,6,7-tetrahydro-5-methoxy-1*H*-cyclobuta[1,2-*e*]indene (8b)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **8b** as a colorless oil (56 %). R_f = 0.53; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.16 (s, 12 H), 0.94 (s, 9 H), 0.96 (s, 9 H), 1.18 (s, 9 H), 1.97–2.05 (m, 2 H), 2.81 (t, *J* = 7.7 Hz, 2 H), 2.87 (t, *J* = 7.2 Hz, 2 H), 3.95 (s, 3 H), 4.93 (brs, 1 H), 5.09 (brs, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = −4.6 (CH$_3$), −4.4 (CH$_3$), −4.1 (CH$_3$), −4.0 (CH$_3$), 17.9 (C), 18.1 (C), 25.7 (3 CH$_3$), 25.8 (3 CH$_3$), 26.9 (CH$_2$), 30.4 (3 CH$_3$), 30.6 (CH$_2$), 32.9 (CH$_2$), 55.2 (C), 57.5 (CH$_3$), 78.8 (CH), 80.0 (CH), 125.1 (C), 131.8 (C), 132.5 (C), 134.4 (C), 145.2 (C), 148.9 (C); HRMS: calcd for $C_{28}H_{51}NO_3Si_2$: 505.3407; found: 505.3411; MS (70 eV): *m*/*z* (%): 505 (35), 491 (24), 490 (100), 434 (23), 302 (7), 245 (31).

***trans*-5-Benzylamino-1,2,3,4,7,8-hexahydro-6-methoxy-7,8-trimethylsilyloxycyclobuta[*a*]naphthalene (8c)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **8c** as a colorless oil (64 %). R_f = 0.57; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.29 (s, 9 H), 0.32 (s, 9 H), 1.82–1.91 (m, 4 H), 2.69–2.82 (m, 4 H), 3.98 (s, 3 H), 4.13 (d, *J* = 13.4 Hz, 1 H), 4.19 (d, *J* = 13.4 Hz, 1 H), 5.02 (s, 1 H), 5.12 (s, 1 H), 7.29–7.44 (m, 5 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 0.2 (3 CH$_3$), 0.4 (3 CH$_3$), 22.0 (CH$_2$), 22.9 (CH$_2$), 24.5 (CH$_2$), 26.0 (CH$_2$), 52.4 (CH$_2$), 57.4 (CH$_3$), 78.5 (CH), 79.0 (CH), 123.8 (C), 125.7 (C), 126.6 (CH), 127.7 (2 CH), 128.0 (2 CH), 132.2 (C), 134.9 (C), 136.4 (C), 140.4 (C), 144.9 (C); HRMS (EI): calcd for $C_{26}H_{39}NO_3Si_2$: 469.2468; found: 469.2475.

***trans*-5-Benzylamino-7,8-bis(*tert*-butyldimethylsilyloxy)-1,2,3,4,7,8-hexahydro-6-methoxycyclobuta[*a*]naphthalene (8d)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **8d** as a colorless oil (86 %). R_f = 0.59; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.15 (s, 3 H), 0.17 (s, 3 H), 0.18 (s, 3 H), 0.22 (s, 3 H), 0.98 (s, 9 H), 1.01 (s, 9 H), 1.78–1.81 (m, 4 H), 2.72–2.75 (m, 4 H), 3.97 (s, 3 H), 4.14 (d, *J* = 13.5 Hz, 1 H), 4.20 (d, *J* = 13.5 Hz, 1 H), 5.02 (brs, 1 H), 5.12 (s, ancho, 1 H), 7.27–7.44 (m, 5 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = −4.2 (2 CH$_3$), −4.1 (CH$_3$), −3.9 (CH$_3$), 17.9 (C), 18.2 (C), 22.2 (CH$_2$), 23.1 (CH$_2$), 24.9 (CH$_2$), 25.7 (3 CH$_3$), 25.8 (3 CH$_3$), 26.2 (CH$_2$), 52.6 (CH$_2$), 57.8 (CH$_3$), 79.1 (CH), 79.7 (CH), 124.9 (C), 126.4 (C), 126.9 (CH), 127.9 (2 CH), 128.2 (2 CH), 132.3 (C), 135.5 (C), 136.8 (C), 140.7 (C), 144.9 (C); HRMS (EI): calcd for $C_{32}H_{51}NO_3Si_2$: 553.3407; found: 553.3402.

***trans*-3-Benzylamino-2-methoxy-7,8-trimethylsilyloxy-4-phenylbicyclo[4.2.0]octa-1,3,5-triene (8e)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **8e** as a colorless oil (59 %). R_f = 0.57; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.24 (s, 9 H), 0.26 (s, 9 H), 3.79 (d, *J* = 13.4 Hz, 1 H), 3.88 (d, *J* = 13.4 Hz, 1 H), 4.05 (s, 3 H), 4.91 (s, 1 H), 5.15 (s, 1 H), 6.68 (s, 1 H), 7.07–7.10 (m, 2 H), 7.19–7.26 (m, 3 H), 7.32–7.42 (m, 5 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 0.0 (3 CH$_3$), 0.3 (3 CH$_3$), 52.0 (CH$_2$), 57.8 (CH$_3$), 78.6 (CH), 790 (CH), 117.8 (CH), 125.3 (C), 126.7 (CH), 126.8 (CH), 127.8 (2 CH), 128.1 (2 CH), 128.3 (2 CH), 129.0 (2 CH), 135.5 (C), 136.3 (C), 136.3 (C), 140.3 (C), 140.9 (C), 146.5 (C); HRMS: calcd for $C_{28}H_{38}NO_3Si_2$ $[M+H]^+$: 492.2390; found: 492.2377; MS (FAB +): *m*/*z* (%):492 (3), 475 (12), 355 (21), 281 (85), 221 (100), 207 (92).

***trans*-3-*tert*-Butylamino-7,8-bis(*tert*-butyldimethylsilyloxy)-2-methoxy-4-phenylbicyclo[4.2.0]octa-1,3,5-triene (8f)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **8f** as a colorless oil (54 %). R_f = 0.55; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.21 (s, 3 H), 0.24 (s, 3 H), 0.26 (s, 3 H), 0.29 (s, 3 H), 1.01 (s, 9 H), 1.01 (s, 9 H), 3.85 (d, *J* = 13.1 Hz, 1 H), 3.91 (d, *J* = 13.1 Hz, 1 H), 4.11 (s, 3 H), 4.98 (brs, 1 H), 5.19 (brs, 1 H), 6.76 (s, 1 H), 7.13–7.51 (m, 10H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -5.2$ (CH$_3$), -4.7 (CH$_3$), -4.3 (CH$_3$), -3.6 (CH$_3$), 17.8 (C), 17.9 (C), 25.7 (3CH$_3$), 25.8 (3CH$_3$), 52.1 (CH$_2$), 58.1 (CH$_3$), 78.9 (CH), 79.3 (CH), 118.0 (CH), 125.6 (C), 126.7 (CH), 126.8 (CH), 127.8 (2CH), 128.1 (2CH), 128.3 (2CH), 129.0 (2CH), 135.2 (C), 136.2 (C), 136.4 (C), 140.4 (C), 141.0 (C), 146.6 (C); elemental analysis calcd (%) for $C_{34}H_{49}NO_3Si_2$: C 70.91, H 8.58, N 2.43; found: C 71.12, H 8.95, N 2.14.

***trans*-4-*tert*-Butylamino-1,2-bis(*tert*-butyldimethylsilyloxy)-2,5,6,7-tetrahydro-3-methoxy-1*H*-cyclobuta[1′,2′:5,6]benzo[*b*]pyrane (8g)**: Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 20:1, **8g** as a colorless oil (33%). $R_f = 0.45$; ^{1}H NMR (300 MHz, CDCl$_3$): 0.09 (s, 3H), 0.12 (s, 3H), 0.16 (s, 6H), 0.92 (s, 9H), 0.95 (s, 9H), 1.27 (s, 9H), 1.72–1.79 (m, 2H), 2.67–2.68 (m, 2H), 3.91 (s, 3H), 3.96–4.12 (m, 2H), 4.95 (s, 1H), 5.05 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -5.1$ (CH$_3$), -5.0 (CH$_3$), -4.5 (CH$_3$), -4.2 (CH$_3$), 17.9 (C), 18.2 (C), 22.5 (CH$_2$), 24.3 (CH$_2$), 25.7 (3CH$_3$), 25.8 (3CH$_3$), 30.6 (3CH$_3$), 55.1 (C), 57.4 (CH$_3$), 65.3 (CH$_2$), 77.7 (CH), 79.8 (CH), 122.7 (C), 124.5 (C), 125.4 (C), 135.0 (C), 143.8 (C), 144.4 (C); elemental analysis calcd (%) for $C_{28}H_{51}NO_4Si_2$: C 64.44, H 9.85, N 2.68; found: C 64.67, H 9.98, N 2.39.

General procedure for the thermal reaction of *trans*-1,2-bis(trialkylsilyloxy)benzocyclobutene derivatives 8 and dienophiles: A solution of benzocyclobutene **8** (0.3 mmol) and the corresponding dienophile (1 mmol) in dry toluene (10 mL) was refluxed under nitrogen atmosphere until TLC analysis revealed the complete disappearance of the starting material and the formation of a new compound. Cycloadducts were purified in all the cases by column chromatography.

Transformation of compound **11a** in its derivative **12a** was performed by stirring a mixture of **11a** (0.2 mmol) and a 1M solution of tetrabutylammonium fluoride (TBAF) in THF (2 mL, ca. 1% of H$_2$O) at room temperature for 10 minutes. After removal of the solvent in vacuum (10 mm Hg), dichloromethane (10 mL) was added and the organic layer was washed with brine and dried over anhydrous Na$_2$SO$_4$. Compound **12a** was purified by filtration through a pad of silica gel.

(±)-(6*R*,9*S*)-Methyl[4-*tert*-butylamino-6,9-bis(*tert*-butyldimethylsilyloxy)-2,3,6,9-tetrahydro-5-methoxy-1*H*-cyclopenta[*a*]naphthalene-7-carboxylate] and (±)-(6*S*,9*S*)-methyl[4-*tert*-butylamino-6,9-bis(*tert*-butyldimethylsilyloxy)-2,3,6,9-tetrahydro-5-methoxy-1*H*-cyclopenta[*a*]naphthalene-8-carboxylate] (10, regioisomeric ratio 1:1): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 3:1, **10** as a light yellow oil (62%) and as a 1:1 mixture of regioisomers. $R_f = 0.47$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.09$ (s, 3H), 0.11 (s, 3H), 0.12 (s, 3H), 0.14 (s, 3H), 0.16 (s, 6H), 0.18 (s, 3H), 0.92 (s, 18H), 0.94 (s, 9H), 0.95 (s, 9H), 1.31 (s, 18H), 1.98–2.05 (m, 4H), 2.62–2.67 (m, 4H), 2.80–2.85 (m, 4H), 3.60 (s, 3H), 3.61 (s, 3H), 3.89 (s, 6H), 4.90 (s, 1H), 4.91 (s, 1H), 5.03 (s, 2H), 7.88 (brs, 1H), 7.92 (brs, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -4.7$ (CH$_3$), -4.6 (CH$_3$), -4.4 (CH$_3$), -4.1 (CH$_3$), -4.0 (2CH$_3$), -3.9 (CH$_3$), -3.7 (CH$_3$), 17.8 (2C), 18.0 (C), 18.1 (C), 25.5 (CH$_2$), 25.6 (CH$_2$), 25.7 (3CH$_3$), 25.7 (3CH$_3$), 30.1 (3CH$_3$), 30.1 (3CH$_3$), 30.3 (CH$_2$), 30.6 (CH$_2$), 31.4 (2CH$_2$), 50.3 (2CH$_3$), 58.0 (CH), 58.0 (CH), 58.1 (CH$_3$), 58.3 (CH$_3$), 78.6 (CH), 78.6 (CH), 79.5 (CH), 79.6 (CH), 126.4 (C), 126.6 (C), 131.9 (C), 132.2 (C), 139.6 (2C), 147.7 (C), 148.9 (2CH), 150.5 (C), 150.6 (C), 170.2 (C), 170.3 (C); HRMS: calcd for $C_{32}H_{55}NO_5Si_2$: 589.3619; found: 589.3630; MS (FAB+): *m*/*z* (%): 589 (100), 558 (11), 532 (15), 402 (16).

Dimethyl(4-*tert*-butylamino-6-*tert*-butyldimethylsilyloxy-2,3-dihydro-5-methoxy-1*H*-cyclopenta[*a*]naphthalene-7,8-dicarboxylate) (11a): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **11a** as a white solid (82%). M.p. 126–128 °C; $R_f = 0.39$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.04$ (s, 6H), 0.99 (s, 9H), 1.33 (s, 9H), 2.21 (quint., $J = 7.4$ Hz, 2H), 3.11 (t, $J = 7.4$ Hz, 2H), 3.24 (t, $J = 7.4$ Hz, 2H), 3.64 (s, 3H), 3.89 (s, 3H), 3.90 (s, 3H), 7.98 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -3.7$ (2CH$_3$), 18.4 (C), 24.7 (CH$_2$), 26.1 (3CH$_3$), 31.3 (3CH$_3$), 31.9 (CH$_2$), 34.8 (CH$_2$), 52.2 (CH$_3$), 54.3 (C), 61.2 (CH$_3$), 121.4 (C), 122.1 (CH), 123.0 (C), 124.1 (C), 127.6 (C), 137.7 (C), 138.3 (C), 139.9 (C), 146.5 (C), 148.5 (C), 167.0 (C), 168.1 (C); elemental analysis calcd (%) for $C_{28}H_{41}NO_6Si$: C 65.21, H 8.01, N 2.72; found: C 65.49, H 7.72, N 2.20.

Dimethyl (7-benzylamino-1-*tert*-butyldimethylsilyloxy-8-methoxy-6-phenylnaphthalene-2,3-dicarboxylate) (11b): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **11b** as a yellow solid (85%). M.p. 135–137 °C; $R_f = 0.43$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.07$ (s, 3H), 0.08 (s, 3H), 0.99 (s, 9H), 3.51 (s, 3H), 3.89 (s, 3H), 3.92 (s, 3H), 3.99 (s, 2H), 7.10–7.12 (m, 2H), 7.19–7.29 (m, 4H), 7.41–7.60 (m, 3H), 7.62–7.63 (m, 2H), 8.04 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -3.8$ (CH$_3$), 1.0 (CH$_3$), 18.4 (C), 26.0 (3CH$_3$), 51.5 (CH$_2$), 52.2 (CH$_3$), 52.3 (CH$_3$), 61.4 (CH$_3$), 122.3 (C), 123.5 (C), 123.6 (C), 12.8 (CH), 127.1 (CH), 127.1 (CH), 127.6 (CH), 127.8 (2CH), 128.4 (2CH), 128.6 (2CH), 128.7 (2CH), 129.7 (C), 135.0 (C), 139.3 (C), 140.0 (C), 140.1 (C), 144.5 (C), 147.6 (C), 166.5 (C), 168.0 (C); elemental analysis calcd (%) for $C_{34}H_{39}NO_6Si$: C 69.71, H 6.71, N 2.39; found: C 70.02, H 6.45, N 2.08.

Dimethyl (4-*tert*-butylamino-2,3-dihydro-6-hydroxy-5-methoxy-1*H*-cyclopenta[*a*]naphthalene-7,8-dicarboxylate) (12a): Prepared from **11a** according to the experimental procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **12a** as a white solid (94%). M.p. 132–134 °C; $R_f = 0.29$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.28$ (s, 9H), 2.24 (quint., $J = 7.4$ Hz, 2H), 3.00 (t, $J = 7.4$ Hz, 2H), 3.26 (t, $J = 7.4$ Hz, 2H), 3.26 (t, $J = 7.4$ Hz, 2H), 3.91 (s, 3H), 3.96 (s, 3H), 3.99 (s, 3H), 7.83 (s, 1H), 10.66 (brs, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 23.8$ (CH$_2$), 30.7 (CH$_3$), 31.9 (CH$_2$), 32.4 (CH$_2$), 52.3 (CH$_3$), 52.6 (CH$_3$), 55.7 (C), 60.1 (CH$_3$), 113.8 (C), 119.1 (CH), 124.5 (C), 127.5 (C), 135.6 (C), 138.0 (C), 141.2 (C), 141.2 (C), 147.0 (C), 152.5 (C), 166.6 (C), 168.9 (C); elemental analysis calcd (%) for $C_{22}H_{27}NO_6$: C 65.82, H 6.78, N 3.49; found: C 65.98, H 6.44, N 3.61.

(±)-(4a*R*,5R,10*S*,10a*S*)-7-Benzylamino-5,10-bis(*tert*-butyldimethylsilyloxy)-1,4,5,10-tetrahydro-6-methoxy-8-phenylantracen-1,4-dione (13): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **13** as a red solid (40%). M.p. 145–147 °C; $R_f = 0.50$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.06$ (s, 3H), 0.08 (s, 3H), 0.18 (s, 3H), 0.20 (s, 3H), 0.76 (s, 9H), 0.77 (s, 9H), 3.83 (s, 3H), 4.08 (d, $J = 13.8$ Hz, 1H), 4.15 (d, $J = 13.8$ Hz, 1H), 5.64 (s, 1H), 5.99 (s, 1H), 6.82 (s, 2H), 6.95 (s, 1H), 7.03–7.38 (m, 10H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -5.1$ (CH$_3$), -4.8 (CH$_3$), -4.3 (CH$_3$), -4.2 (CH$_3$), 18.1 (C), 18.3 (C), 25.7 (3CH$_3$), 25.9 (3CH$_3$), 51.0 (CH$_2$), 57.7 (CH$_3$), 59.5 (CH), 62.8 (CH), 126.9 (CH), 127.3 (CH), 127.3 (CH), 127.8 (2CH), 128.3 (2CH), 128.6 (2CH), 128.9 (2CH), 129.7 (C), 130.3 (C), 133.1 (C), 136.2 (CH), 136.3 (CH), 139.2 (C), 139.2 (C), 140.0 (C),141.8 (C),141.9 (C),148.7 (C),186.8 (C), 187.2 (C); HRMS: calcd for $C_{40}H_{52}NO_5Si_2$: 682.3384; found: 682.3371 $[M+H]^+$; MS (FAB+): *m*/*z* (%): 682 (9), 624 (23), 550 (21), 460 (12), 419 (100); elemental analysis calcd (%) for $C_{40}H_{51}NO_5Si_2$: C 70.44, H 7.54, N 2.05; found: C 70.62, H 7.79, N 1.76.

4-*tert*-Butylamino-2,3,7,10-tetrahydro-5-methoxy-1*H*-cyclopenta[*a*]antracen-7,10-dione (14a): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **14a** as a red solid (67 or 72%). M.p. 145–147 °C; $R_f = 0.29$; ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 1.37$ (s, 9H), 2.29 (tdd, $J = 7.7$, 7.4, 7.2 Hz, 2H), 3.07 (dd, $J = 7.7$, 7.2 Hz, 2H), 3.36 (dd, $J = 7.7$, 7.4 Hz, 2H), 3.89 (s, 3H), 7.03 (s, 2H), 8.47 (s, 1H), 8.78 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 24.2$ (CH$_2$), 30.9 (CH$_3$), 31.7 (CH$_2$), 33.2 (CH$_2$), 55.2 (C), 60.4 (CH$_3$), 123.3 (CH), 125.8 (CH), 126.1 (C), 127.4 (C), 127.6 (C), 130.0 (C), 138.3 (C), 139.1 (C), 139.9 (CH), 140.0 (CH), 142.1 (C), 146.7 (C), 184.9 (C), 185.0 (C); HRMS: calcd for $C_{22}H_{23}NO_3$: 349.1678; found: 349.1686; MS (70 eV): *m*/*z* (%): 349 (32), 334 (14), 278 (100), 260 (21), 204 (32); elemental analysis calcd (%) for $C_{22}H_{23}NO_3$: C 75.62, H 6.63, N 4.01; found: C 75.88, H 6.90, N 3.73.

7-Benzylamino-1,4-dihydro-6-methoxy-8-phenylantracen-1,4-dione (14b): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **14b** as a red solid (45%). M.p. 153–155 °C ; $R_f = 0.47$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 3.87$ (s, 3H), 4.27 (s, 2H), 7.03 (s, 2H), 7.14–7.15 (m, 2H), 7.22–7.26 (m, 3H), 7.44–7.46 (m, 5H), 7.61 (s, 1H), 8.47 (s, 1H), 8.74 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 50.6$ (CH$_2$), 60.8 (CH$_3$), 121.7 (CH), 126.1 (C), 127.3 (CH), 127.6 (2CH), 128.1 (CH), 128.2 (CH), 128.5 (2CH), 128.5 (C), 128.8 (2CH), 128.9 (2CH), 129.1 (CH), 129.4 (C), 129.9 (C), 137.4 (C), 138.5 (C), 139.6 (C), 139.8 (CH), 139.8 (C), 140.2 (CH), 144.2 (C), 184.5 (C), 185.0 (C); HRMS: calcd for $C_{28}H_{22}NO_3$ $[M+H]^+$: 420.1600; found: 420.1602; MS (FAB+): *m*/*z* (%): 420 (65), 355 (29), 307 (40), 281 (100), 221 (62); elemental analysis calcd (%) for $C_{28}H_{21}NO_3$: C 80.17, H 5.05, N 3.34; found: C 80.50, H 5.23, N 3.02.

(±)-(6*R*,6a*R*,9a*S*,10*S*)-4-*tert*-Butylamino-2,3,6,6a,7,9,9a-octahydro-5-methoxy-6,10-bis(trimethylsilyloxy)-1*H*-cyclopenta[1′,2′:6,7]naphtho[2,3-*c*]pyr-

role-7,9-dione (15a): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **15a** as a white solid (86%). M.p. 131–133 °C; $R_f = 0.31$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = -0.06$ (s, 9H), 0.05 (s, 9H), 1.25 (s, 9H), 1.98–2.20 (m, 2H), 2.89 (dd, $J = 7.7$, 6.3 Hz, 2H), 3.01 (dd, $J = 7.7$, 6.8 Hz, 2H), 3.21–3.31 (m, 2H), 3.79 (s, 3H), 5.44 (d, $J = 4.8$ Hz, 1H), 5.71 (d, $J = 5.1$ Hz, 1H), 7.26–7.30 (m, 2H), 7.37–7.42 (m, 1H), 7.47–7.51 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -0.1$ (3CH$_3$), 0.0 (3CH$_3$), 25.3 (CH$_2$), 30.7 (3CH$_3$), 31.3 (CH$_2$), 32.2 (CH$_2$), 46.4 (CH), 47.1 (CH), 55.0 (C), 60.2 (CH$_3$), 61.3 (CH), 64.6 (CH), 126.8 (2CH), 128.3 (CH), 129.0 (2CH), 129.1 (C), 129.9 (C), 132.4 (C), 137.0 (C), 137.6 (C), 139.9 (C), 150.8 (C), 176.1 (C), 176.2 (C); HRMS: calcd for $C_{32}H_{47}N_2O_5Si_2$ $[M+H]^+$: 595.3024; found: 595.3008; MS (FAB+): *m/z* (%): 595 (55), 594 (100), 579 (14), 505 (81), 449 (15); elemental analysis calcd (%) for $C_{32}H_{46}N_2O_5Si_2$: C 64.61, H 7.79, N 4.71; found: C 63.87, H 7.46, N 4.58.

(±)-(6*R*,6a*R*,9a*S*,10*S*)-4-*tert*-Butylamino-6,10-bis(*tert*-butyldimethylsilyloxy)-2,3,6,6a,7,9,9a-octahydro-5-methoxy-8-phenyl-1*H*-cyclopenta[1′,2′:6,7]naphtho[2,3-*c*]pyrrole-7,9-dione (15b): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **15b** as a white solid (84%). M.p. 129–130 °C; $R_f = 0.30$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.09$ (s, 3H), 0.11 (s, 3H), 0.20 (s, 3H), 0.22 (s, 3H), 0.72 (s, 9H), 0.79 (s, 9H), 1.26 (s, 9H), 2.01–2.17 (m, 2H), 2.85–2.92 (m, 2H), 2.97–3.19 (m, 2H), 3.26 (dd, $J = 6.2$, 5.4 Hz, 1H), 3.31 (dd, $J = 6.2$, 5.4 Hz, 1H), 3.80 (s, 3H), 5.45 (d, $J = 5.4$ Hz, 1H), 5.72 (d, $J = 5.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -5.3$ (CH$_3$), -5.0 (CH$_3$), -4.4 (CH$_3$), -3.8 (CH$_3$), 18.3 (C), 18.5 (C), 25.3 (CH$_2$), 26.3 (3CH$_3$), 26.6 (3CH$_3$), 30.7 (3CH$_3$), 31.7 (CH$_2$), 32.4 (CH$_2$), 46.7 (CH), 46.8 (CH), 55.1 (C), 60.0 (CH$_3$), 61.7 (CH), 64.8 (CH), 126.9 (2CH), 128.4 (CH), 129.0 (2CH), 129.6 (C), 130.0 (C), 132.2 (C), 137.0 (C), 137.7 (C), 140.0 (C), 151.1 (C), 175.7 (C), 176.0 (C); elemental analysis calcd (%) for $C_{38}H_{58}N_2O_5Si_2$: C 67.21, H 8.61, N 4.13; found: C 67.43, H 8.29, N 4.44.

(±)-(7*R*,7a*R*,10a*S*,11*S*)-5-Benzylamino-1,2,3,4,7,7a,8,10,10a,11-decahydro-6-methoxy-7,11-bis(trimethylsilyloxy)-9-phenylphenantreno[2,3-*c*]pyrrole-8,10-dione (15c): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **15c** as a white solid (73%). M.p. 127–129 °C; $R_f = 0.33$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.01$ (s, 9H), 0.08 (s, 9H), 1.78–1.83 (m, 4H), 2.50–2.56 (m, 2H), 2.91–2.94 (m, 2H), 3.27–3.29 (m, 2H), 3.85 (s, 3H), 4.29 (d, $J = 13.3$ Hz, 1H), 4.50 (d, $J = 13.3$ Hz, 1H), 5.72 (dd, $J = 3.1$, 1.8 Hz, 1H), 5.81 (dd, $J = 3.4$, 2.1 Hz, 1H), 7.28–7.56 (m, 10H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -0.1$ (3CH$_3$), 0.3 (3CH$_3$), 22.4 (CH$_2$), 22.6 (CH$_2$), 25.8 (CH$_2$), 26.5 (CH$_2$), 45.8 (CH), 47.3 (CH), 51.5 (CH$_2$), 60.3 (CH$_3$), 60.8 (CH$_2$), 62.2 (CH$_2$), 126.8 (2CH), 127.1 (CH), 127.8 (2CH), 128.3 (C), 128.4 (CH), 128.5 (2CH), 129.1 (2CH), 129.5 (C), 129.8 (C), 130.5 (C), 132.4 (C), 140.0 (C), 140.4 (C), 146.3 (C), 176.2 (C), 176.5 (C); elemental analysis calcd (%) for $C_{36}H_{46}N_2O_5Si_2$: C 67.25, H 7.21, N 4.36; found: C 67.52, H 7.49, N 4.67.

(±)-(3a*R*,4*R*,9*S*,9a*S*)-6-Benzylamino-3,3a,4,9,9a,10-hexahydro-5-methoxy-4,9-bis(trimethylsilyloxy)-7-phenylnaphtho[2,3-*c*]pyrrole-1,3-dione (15d): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **15d** as a white solid (82%). M.p. 124–125 °C; $R_f = 0.31$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.00$ (s, 9H), 0.01 (s, 9H), 3.34–3.36 (m, 2H), 3.88 (s, 3H), 4.12 (s, 2H), 5.30 (d, $J = 4.3$ Hz, 1H), 5.81 (d, $J = 4.3$ Hz, 1H), 6.92 (s, 1H), 7.06–7.09 (m, 2H), 7.20–7.51 (m, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -0.2$ (3CH$_3$), 0.1 (3CH$_3$), 46.4 (CH), 46.8 (CH), 50.9 (CH$_2$), 60.5 (CH$_3$), 60.6 (CH), 67.6 (CH), 125.9 (CH), 126.8 (2CH), 126.9 (CH), 127.4 (CH), 127.7 (2CH), 128.3 (2CH), 128.4 (CH), 128.6 (2CH), 128.8 (2CH), 130.5 (C), 130.8 (C), 132.3 (C), 134.0 (C), 139.2 (C), 139.7 (C), 139.8 (C), 148.0 (C), 175.9 (C), 175.9 (C); elemental analysis calcd (%) for $C_{38}H_{44}N_2O_5Si_2$: C 68.64, H 6.67, N 4.21; found: C 68.93, H 6.34, N 4.02.

(±)-(3a*R*,4*R*,9*S*,9a*S*)-6-Benzylamino-4,9-bis(*tert*-butyldimethylsilyloxy)-3,3a,4,9,9a,10-hexahydro-5-methoxy-7-phenylnaphtho[2,3-*c*]pyrrole-1,3-dione (15e): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **15e** as a white solid (82%). M.p. 134–136 °C; $R_f = 0.36$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.07$ (s, 3H), 0.10 (s, 3H), 0.10 (s, 3H), 0.17 (s, 3H), 0.78 (s, 9H), 0.81 (s, 9H), 3.32 (dd, $J = 10.8$, 5.7 Hz, 1H), 3.40 (dd, $J = 10.8$, 5.7 Hz, 1H), 3.87 (s, 3H), 4.05 (d, $J = 14.0$ Hz, 1H), 4.14 (d, $J = 14.0$ Hz, 1H), 5.32 (d, $J = 5.7$ Hz, 1H), 5.79 (d, $J = 5.7$ Hz, 1H), 6.92 (s, 1H), 7.02–7.05 (m, 2H), 7.18–7.51 (s, 13H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -5.1$ (CH$_3$), -4.8 (CH$_3$), -4.7 (CH$_3$), -4.0 (CH$_3$), 18.3 (C), 18.5 (C), 26.4 (3CH$_3$), 26.5 (3CH$_3$), 46.2 (CH), 46.8 (CH), 51.1 (CH$_2$), 60.5 (CH$_3$), 61.0 (CH), 67.7 (CH), 126.0 (C), 126.9 (2CH), 127.0 (CH), 127.5 (CH), 127.8 (2CH), 128.4 (2CH), 128.4 (CH), 128.7 (2CH), 128.8 (2CH), 129.0 (2CH), 129.1 (CH), 130.9 (C), 132.3 (C), 132.3 (C), 134.1 (C), 139.2 (C), 139.2 (C), 148.2 (C), 175.5 (C), 175.5 (C); elemental analysis calcd (%) for $C_{44}H_{56}N_2O_5Si_2$ C 70.55, H 7.54, N 3.74; found: C 70.21, H 7.32, N 3.95.

5-Benzylamino-1,2,3,4,8,10-hexahydro-6-methoxy-9-phenylphenantreno[2,3-*c*]pyrrole-8,10-dione (16): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **16** as a yellow solid (49%). M.p. 131–132 °C; $R_f = 0.42$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.92$–1.94 (m, 4H), 2.69–2.73 (m, 2H), 3.20 (t, $J = 6.1$ Hz, 2H), 3.85 (s, 3H), 4.62 (s, 2H), 7.27–7.57 (m, 10H), 8.54 (s, 1H), 8.61 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): 22.2 (CH$_2$), 22.4 (CH$_2$), 26.3 (CH$_2$), 26.4 (CH$_2$), 51.2 (CH$_2$), 60.6 (CH$_3$), 118.3 (CH), 120.6 (CH), 124.0 (C), 126.6 (2CH), 126.7 (C), 127.5 (CH), 127.8 (2CH), 127.9 (CH), 128.7 (2CH), 129.1 (2CH), 129.7 (C), 130.4 (C), 131.5 (C), 131.8 (C), 132.1 (C), 134.1 (C), 140.0 (C), 142.0 (C), 167.7 (C), 167.8 (C); elemental analysis calcd (%) for $C_{30}H_{26}N_2O_3$ C 77.90, H 5.67, N 6.06; C 78.13, H 5.99, N 5.83.

General procedure for the thermal reaction of *cis*-1,2-bis(trialkylsilyloxy)benzocyclobutene derivatives 7 and dienophiles: A solution of benzocyclobutene **7** (0.3 mmol) and the corresponding dienophile (1 mmol) in dry toluene (10 mL) was introduced in a sealed tube and heated at 160 °C under nitrogen atmosphere. The evolution of the reactions was monitored by ^{1}H NMR analysis in 6 h intervals. When all the starting material had been consumed and a new compound had been formed, typically after 24 to 48 h, the crude mixture was directly chromatographed.

Analytical and spectroscopical data of compound **11a**, which was achieved in 52% yield from **7b** and DMAD, have been reported in the previous section. The cycloadduct derived from thermal treatment of **7c** and DMAD in the standard experimental conditions could not be properly purified by column chromatography, so it was necessary to carry out the deprotection of the *tert*-butyldimethylsilyl moiety in the crude mixture: treatment of the crude **11b** with a 1M solution of tetrabutylammonium fluoride (TBAF) in THF (2 mL, ca. 1% of H$_2$O) at room temperature for 10 minutes, removal of the solvent in vacuo (10 mm Hg), extractive workup and column chromatography afforded **12b**.

Dimethyl(6-*tert*-butylamino-7,8,9,10-tetrahydro-4-hydroxy-5-methoxyphenantreno-2,3-dicarboxylate) (12b): Prepared according to the experimental procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **12b** as a light yellow solid (53%). M.p. 160–162 °C; $R_f = 0.36$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.30$ (s, 9H), 1.87–1.90 (m, 4H), 2.67–2.69 (m, 2H), 3.05–3.14 (m, 2H), 3.92 (s, 3H), 3.93 (s, 3H), 4.00 (s, 3H), 8.09 (s, 1H), 10.72 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta =$ 22.2 (CH$_2$), 22.5 (CH$_2$), 26.4 (CH$_2$), 26.5 (CH$_2$), 30.6 (3CH$_3$), 52.4 (CH$_3$), 52.6 (CH$_3$), 55.8 (C), 59.7 (CH$_3$), 114.1 (C), 117.5 (CH), 118.3 (C), 124.2 (C), 130.1 (C), 131.0 (C), 134.1 (C), 136.9 (C), 146.0 (C), 152.2 (C), 166.8 (C), 169.0 (C); HRMS: calcd for $C_{23}H_{30}NO_6$ $[M+H]^+$: 416.2073; found: 416.2067; MS (FAB+): *m/z* (%): 416 (9), 415 (43), 401 (42), 355 (24), 281 (79), 221 (100); elemental analysis calcd (%) for $C_{23}H_{29}NO_6$: C 66.49, H 7.04, N 3.37; found: C 66.74, H 7.35, N 3.76.

(±)-(1*S*,4*S*)-Dimethyl[7-*tert*-Butylamino-1,4-bis(*tert*-butyldimethylsilyloxy)-1,4-dihydro-8-methoxy-6-phenylnaphthalen-2,3-dicarboxylate] (17): Prepared according to the general procedure described above to afford, after flash chromatography with hexane/ethyl acetate 3:1, **17** a white solid (85%). M.p. 118–119 °C; $R_f = 0.50$; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.08$ (s, 3H), 0.11 (s, 3H), 0.16 (s, 3H), 0.17 (s, 3H), 0.80 (s, 9H), 0.91 (s, 9H), 0.95 (s, 9H), 3.81 (s, 6H), 3.84 (s, 6H), 5.81 (s, 1H), 6.10 (s, 1H), 7.17 (s, 1H), 7.26–7.40 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = -5.0$ (CH$_3$), -4.3 (CH$_3$), 18.0 (C), 18.1 (C), 25.6 (3CH$_3$), 25.7 (3CH$_3$), 30.3 (3CH$_3$), 52.0 (CH$_3$), 52.2 (CH$_3$), 54.9 (C), 60.2 (CH$_3$), 61.4 (CH), 67.9 (CH), 121.9 (CH), 127.0 (CH), 128.3 (2CH), 128.9 (C), 129.4 (2CH), 131.1 (C), 135.0 (C), 136.8 (C), 137.7 (C), 141.0 (C), 151.8 (C), 153.2 (C), 164.8 (C), 167.2 (C); elemental analysis calcd (%) for $C_{31}H_{45}NO_7Si_2$: C 62.07, H 7.56, N 2.33; found: C 61.79, H 7.35, N 2.01.

(±)-(6*S*,6a*R*,9a*S*,10*S*)-4-*tert*-Butylamino-8-phenyl-2,3,6,6a,7,9,9a-octahydro-5-methoxy-6,10-bis(trimethylsilyloxy)-1*H*-cyclopenta[1′,2′:6,7]naphtho[2,3-*c*]pyrrole-7,9-dione (18a): Prepared according to the experimental procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **18a** as a white solid (66%, with a conversion of

63% based on compound **7a**). M.p. 125–126 °C; $R_f=0.33$; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.11$ (s, 9H), 0.26 (s, 9H), 1.22 (s, 9H), 1.75–2.05 (m, 2H), 2.73–2.81 (m, 2H), 2.98–3.10 (m, 1H), 3.24–3.40 (m, 1H), 3.43 (dd, $J=8.5$, 6.4 Hz, 1H), 3.60 (dd, $J=8.5$, 3.1 Hz, 1H), 3.71 (s, 3H), 5.74 (d, $J=3.1$ Hz, 1H), 5.92 (d, $J=6.4$ Hz, 1H), 6.76–6.81 (m, 2H), 7.27–7.33 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=0.0$ (3 CH_3), 0.0 (3 CH_3), 25.6 (CH_2), 30.7 (3 CH_3), 31.7 (CH_2), 33.0 (CH_2), 45.3 (CH), 49.0 (CH), 55.2 (C), 60.3 (CH_3), 65.1 (CH), 68.1 (CH), 126.4 (2CH), 128.3 (CH), 128.9 (2CH), 131.7 (C), 135.2 (C), 136.9 (C), 142.3 (C), 149.9 (C), 174.7 (C), 175.6 (C); HRMS: calcd for $C_{32}H_{47}N_2O_5Si_2$ $[M+H]^+$: 595.3024; found: 595.3016; MS (FAB +): m/z (%): 595 (58), 594 (100), 579 (12), 505 (65), 449 (70), 433 (34); elemental analysis calcd (%) for $C_{32}H_{46}N_2O_5Si_2$: C 64.61, H 7.79, N 4.71; found : C 63.45, H 7.47, N 4.99.

(±)-(6*S*,6a*R*,9a*S*,10*S*)-4-*tert*-Butylamino-6,10-bis(*tert*-butyldimethylsilyloxy)-2,3,6,6a,7,9,9a-octahydro-5-methoxy-8-phenyl-1*H*-cyclopenta[1′,2′:6,7]naphtho[2,3-*c*]pyrrole-7,9-dione (18b): Prepared according to the experimental procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **18b** as a white solid (61%). M.p. 129–130 °C; $R_f=0.32$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-0.12$ (s, 3H), 0.19 (s, 3H), 0.26 (s, 6H), 0.90 (s, 9H), 1.05 (s, 9H), 1.22 (s, 9H), 1.74–1.85 (m, 1H), 1.98–2.08 (m, 1H), 2.73–2.82 (m, 2H), 3.00–3.12 (m, 1H), 3.48 (dd, $J=8.5$, 6.4 Hz), 3.61 (dd, $J=8.5$, 2.8 Hz, 1H), 3.68 (s, 3H), 5.71 (d, $J=2.8$ Hz, 1H), 6.03 (d, $J=6.4$ Hz, 1H), 6.69–6.73 (m, 2H), 7.29–7.34 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-5.6$ (CH_3), -4.9 (2 CH_3), -4.6 (CH_3), 17.8 (C), 18.2 (C), 25.7 (3 CH_3), 25.8 (CH_2), 26.0 (3 CH_3), 30.7 (3 CH_3), 31.7 (CH_2), 33.5 (CH_2), 45.4 (CH), 49.4 (CH), 55.3 (C), 60.2 (CH_3), 65.4 (CH), 68.9 (CH), 126.2 (C), 126.5 (2CH), 128.4 (CH), 129.0 (2CH), 129.0 (C), 131.7 (C), 134.9 (C), 136.7 (C), 142.5 (C), 149.8 (C), 174.7 (C), 175.7 (C); HRMS: calcd for $C_{38}H_{58}N_2O_5Si_2$: 678.3884; found: 678.3891; MS (FAB +): m/z (%): 678 (100), 663 (14), 621 (62), 547 (69), 491 (46); elemental analysis calcd (%) for $C_{38}H_{58}N_2O_5Si_2$: C 67.21, H 8.61, N 4.13; found: C 67.43, H 8.29, N 4.44.

(±)-(3a*R*,4*S*,9*S*,9a*S*)-6-*tert*-Butylamino-4,9-bis(*tert*-butyldimethylsilyloxy)-3,3a,4,9,9a,10-hexahydro-5-methoxy-2,7-diphenylnaphtho[2,3-*c*]pyrrole-1,3-dione (18c): Prepared according to the experimental procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **18c** as a white solid (23%). M.p. 141–143 °C; $R_f=0.34$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-0.10$ (s, 3H), 0.20 (s, 3H), 0.24 (s, 3H), 0.27 (s, 3H), 0.90 (s, 9H), 0.93 (s, 9H), 1.00 (s, 9H), 3.48 (brs, 1H), 3.54 (dd, $J=8.3$, 7.4 Hz, 1H), 3.67 (dd, $J=8.3$, 3.1 Hz, 1H), 3.82 (s, 3H), 5.80 (d, $J=3.1$ Hz, 1H), 5.82 (d, $J=7.4$ Hz, 1H), 6.75–6.78 (m, 2H), 7.24–7.42 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-5.5$ (CH_3), -5.1 (CH_3), -4.9 (2 CH_3), 17.8 (C), 18.4 (C), 25.6 (3 CH_3), 25.8 (3 CH_3), 30.3 (3 CH_3), 44.6 (CH), 49.4 (CH), 55.2 (C), 59.9 (CH_3), 64.8 (CH), 66.7 (CH), 121.2 (CH), 126.4 (2CH), 127.0 (CH), 127.3 (C), 128.4 (2CH), 128.4 (CH), 128.9 (2CH), 129.3 (2CH), 131.8 (C), 133.5 (C), 136.6 (C), 139.6 (C), 140.9 (C), 151.3 (C), 173.6 (C), 175.4 (C); HRMS: calcd for $C_{41}H_{59}N_2O_5Si_2$ $[M+H]^+$: 715.3963; found: 715.3952; MS (FAB +): m/z (%): 715 (55), 714 (90), 699 (40), 657 (100), 583 (32); elemental analysis calcd (%) for $C_{41}H_{58}N_2O_5Si_2$: C 68.86, H 8.18, N 3.92; found: C 69.04, H 8.35, N 3.66.

(±)-(3a*R*,4*R*,9*R*,9a*S*)-6-*tert*-Butylamino-4,9-bis(*tert*-butyldimethylsilyloxy)-3,3a,4,9,9a,10-hexahydro-5-methoxy-2,7-diphenylnaphtho[2,3-*c*]pyrrole-1,3-dione (19): Prepared according to the experimental procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **18c** as a white solid (34%). M.p. 124–126 °C; $R_f=0.30$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-0.19$ (s, 3H), 0.11 (s, 3H), 0.20 (s, 3H), 0.28 (s, 3H), 0.78 (s, 9H), 0.95 (s, 9H), 0.97 (s, 9H), 3.14 (brs, 2H), 3.86 (s, 3H), 5.57–5.59 (m, 1H), 5.76 (brs, 1H), 7.26–7.49 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-5.6$ (CH_3), -5.2 (CH_3), -4.4 (CH_3), -3.9 (CH_3), 17.7 (C), 18.3 (C), 25.5 (3 CH_3), 26.1 (3 CH_3), 30.3 (3 CH_3), 47.7 (CH), 48.5 (CH), 55.2 (C), 60.5 (CH_3), 64.1 (CH), 67.5 (CH), 122.1 (CH), 126.4 (2CH), 126.4 (C), 127.1 (CH), 128.2 (CH), 128.4 (2CH), 129.0 (2CH), 129.3 (2CH), 132.0 (C), 135.6 (C), 136.5 (C), 138.9 (C), 140.9 (C), 150.4 (C), 175.2 (C), 177.0 (C); HRMS: calcd for $C_{41}H_{59}N_2O_5Si_2$ $[M+H]^+$: 715.3963; found: 715.3958; MS (FAB +): m/z (%): 715 (20), 714 (31), 657 (100), 583 (28), 527 (19); elemental analysis calcd (%) for $C_{41}H_{58}N_2O_5Si_2$: C 68.86, H 8.18, N 3.92; found: C 69.04, H 8.35, N 3.66.

General procedure for the thermal treatment of benzocyclobutenedione derivatives 9 in methanol: A solution of benzocyclobutene **9** (0.5 mmol) in dry methanol (10 mL) was introduced in a sealed tube and heated at 100 °C under nitrogen atmosphere until ^{1}H NMR analyses revealed that all the starting material had been consumed. The benzo[*c*]furane derivatives **20** were purified by chromatography.

4-*tert*-Butylamino-2,3,6,8-tetrahydro-2,5-dimethoxy-1*H*-inden[3,4-*e*]furan-6-one (20a): Prepared according to the experimental procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **20a** as a yellow oil (92%). $R_f=0.26$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.30$ (s, 9H), 2.07 (quint., $J=7.4$ Hz, 2H), 3.84 (t, $J=7.4$ Hz, 2H), 3.15 (t, $J=7.4$ Hz, 2H), 3.84 (s, 3H), 3.95 (s, 3H), 7.21 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=25.5$ (CH_2), 31.1 (3 CH_3), 32.1 (CH_2), 33.2 (CH_2), 52.5 (CH_3), 54.7 (C), 55.7 (CH_3), 111.2 (CH), 120.6 (C), 137.4 (C), 140.8 (C), 142.6 (C), 149.7 (C), 165.9 (C), 185.4 (C); HRMS: calcd for $C_{17}H_{23}NO_4$: 305.1627; found: 305.1616; MS (70 eV): m/z (%): 305 (47), 290 (53), 246 (28), 190 (100).

6-Benzylamino-1,3-dihydro-3,7-dimethoxy-5-phenylbenzo[*c*]furan-1-one (20b): Prepared according to the experimental procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **20b** as a yellow oil (88%). $R_f=0.27$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.91$ (s, 3H), 3.93 (s, 3H), 3.95 (s, 2H), 5.14 (brs, 1H), 7.04 (dd, $J=7.4$, 2.0 Hz, 2H), 7.21–7.26 (m, 3H), 7.35–7.40 (m, 5H), 7.43 (d, $J=1.9$ Hz, 1H), 7.50 (d, $J=1.9$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=50.4$ (CH_2), 52.5 (CH_3), 56.0 (CH_3), 108.3 (CH), 122.0 (C), 127.0 (C), 127.2 (2CH), 127.3 (CH), 127.4 (CH), 128.4 (2CH), 128.4 (2CH), 129.1 (2CH), 130.0 (CH), 139.3 (C), 139.7 (C), 143.0 (C), 148.5 (C), 164.8 (C), 184.2 (C).

5-*tert*-Butylamino-3,4,7,9-tetrahydro-6,9-dimethoxy-2*H*-furan[3′,4′:5,6]-benzo[1,2-*b*]pyran-6-one (20c): The title compound was prepared according to the procedure described above to afford, after flash chromatography with hexane/ethyl acetate 5:1, **20c** as a yellow oil (90%). $R_f=0.17$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.26$ (s, 9H), 1.93–2.03 (m, 2H), 2.62–2.69 (m, 2H), 3.79 (s, 3H), 3.88 (s, 3H), 4.07–4.14 (m, 2H), 7.23 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=21.6$ (CH_2), 22.7 (CH_2), 31.0 (3 CH_3), 52.1 (CH_3), 55.4 (CH_3), 55.5 (C), 66.2 (CH_2), 108.0 (CH), 114.1 (C), 116.9 (C), 144.2 (C), 146.9 (C), 152.4 (C), 166.8 (C), 184.8 (C); HRMS: calcd for $C_{17}H_{23}NO_5$: 321.1576; found: 321.1577; MS (70 eV): m/z (%): 321 (39), 306 (18), 262 (43), 206 (100), 178 (12).

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[1] M. P. Cava, D. R. Napier, *J. Am. Chem. Soc.* **1956**, *78*, 500.

[2] H. Nemeto, K. Fukumoto, *Tetrahedron* **1998**, *54*, 5425.

[3] Recent reviews of benzocyclobutene chemistry: a) P. Y. Michellys, H. Pellisier, M. Santelli, *Org. Prep. Proced. Int.* **1996**, *28*, 545; b) G. Mehta, S. Kotha, *Tetrahedron* **2001**, *57*, 625.

[4] Recent reviews: a) N. Martín, C. Seoane, M. Hanack, *Org. Prep. Proced. Int.* **1991**, *23*, 237; b) T. S. Chou, *Rev. Heteroatom. Chem.* **1993**, *8*, 65; c) J. L. Segura, N. Martín, *Chem. Rev.* **1999**, *99*, 3199.

[5] a) J. G. Allen, M. F. Hentemann, S. J. Danishefsky, *J. Am. Chem. Soc.* **2000**, *122*, 571; b) M. F. Hentemann, J. G. Allen, S. J Danishefsky, *Angew. Chem.* **2000**, *112*, 2013; *Angew. Chem. Int. Ed.* **2000**, *39*, 1937; c) J. G. Allen, S. J. Danishefsky, *J. Am. Chem. Soc.* **2001**, *123*, 351.

[6] a) L. S. Liebeskind, L. J. Lescosky, C. M. McSwain, Jr., *J. Org. Chem.* **1989**, *54*, 1435; b) H. Dürr, H. Nickels, *J. Org. Chem.* **1980**, *45*, 973; c) M. S. South, L. S. Liebeskind, *J. Org. Chem.* **1982**, *47*, 3815.

[7] For reviews of the cyclization reactions of Fischer carbene complexes see: a) K. H. Dötz, *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587; b) W. D. Wulff in *Comprehensive Organometallic Chemistry II, Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, New York, **1995**, p. 469; c) D. F. Harvey, D. M. Sigano, *Chem. Rev.* **1996**, *96*, 271; d) F. Zaragoza Dörwald, *Metal Carbenes in Organic Synthesis*, Wiley-VCH, **1999**.

[8] a) K. H. Dötz, *Angew. Chem.* **1975**, *87*, 674; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 644; b) Review: K. H. Dötz, P. Tomuschat, *Chem. Soc. Rev.* **1999**, *28*, 187.

[9] For a recent review of the reactivity of metallahexatrienes, see: R. Aumann, *Eur. J. Org. Chem.* **2000**, 17.

[10] Photochemical processes: a) C. A. Merlic, D. Xu, *J. Am. Chem. Soc.* **1991**, *113*, 7418; b) C. A. Merlic, W. M. Roberts, *Tetrahedron Lett.* **1993**, *34*, 7379; c) C. A. Merlic, D. Xu, B. G. Gladstone, *J. Org. Chem.* **1993**, *58*, 538; thermal processes: d) J. Barluenga, F. Aznar, M. A. Palomero, S. Barluenga, *Org. Lett.* **1999**, *1*, 541; e) H. P. Wu, R. Aumann, R. Frölich, B. Wibbeling, *Eur. J. Org. Chem.* **2000**, 1183; f) P. Mathur, S. Ghosh, A. Sarkar, A. L. Rheingold, I. Guzei, *Tetrahedron* **2000**, *56*, 4995.

[11] Reactions of Fischer carbene complexes and isocyanides have been extensively studied and reviewed up to the year 1988: a) R. Aumann, *Organometallics in Organic Synthesis*: *Aspects of a Modern Interdisciplinary Field* (Eds.: H. tom Dieck, A. de Meijere), Springer Verlag, Heidelberg, **1987**, p. 69; b) R. Aumann, *Angew. Chem.* **1988**, *100*, 1512; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1456.

[12] a) R. Aumann, H. Heinen, *Chem. Ber.* **1986**, *119*, 3801; b) C. A. Merlic, E. E. Burns, D. Q. Xu, S. Y. Chen, *J. Am. Chem. Soc.* **1992**, *114*, 8722; c) C. A. Merlic, D. M. McInnes, Y. You, *Tetrahedron Lett.* **1997**, *38*, 6787; d) C. A. Merlic, C. C. Aldrich, J. Albaneze-Walker, A. Saghatelian, *J. Am. Chem. Soc.* **2000**, *122*, 3224; e) C. A. Merlic, C. C. Aldrich, J. Albaneze-Walker, A. Saghatelian, J. Mammen, *J. Org. Chem.* **2001**, *66*, 1297.

[13] R. Aumann, B. Jasper, R. Fröhlich, *Organometallics* **1995**, *14*, 231.

[14] R. Aumann, *Chem. Ber.* **1993**, *126*, 1867.

[15] Similar transformations were carried out in another research groups. See refs. [10e, f].

[16] J. Barluenga, F. Aznar, M. A. Palomero, *Angew. Chem.* **2000**, *112*, 4514; *Angew. Chem. Int. Ed.* **2000**, *39*, 4346.

[17] W. D. Wulff, K. L. Faron, J. Su, J. P. Springer, A. L. Rheingold, *J. Chem. Soc. Perkin Trans. 1* **1999**, 197.

[18] F. Camps, A. Llebaría, J. M. Moretó, S. Ricart, J. M. Viñas, *Tetrahedron Lett.* **1990**, *31*, 2479.

[19] The reduction step gave rise to 12:1–20:1 *trans*/*cis* ratios of the diols, but both isomers of 1,2-bis(trialkylsililoxy)benzocyclobutene derivatives could be separated by column chromatography.

[20] Regioselective elimination of a TBSO group in a similar substrate has been justified by both electronic and steric effects, but the latter are not suitable to rationalize this particular example, since both *peri* substituents have roughly the same sterical bulkiness. See ref. [5a].

[21] All X-ray analyses were performed by Dr. M. A. Maestro, from the University of La Coruña, Spain.

[22] a) R. B. Woodward, R. Hoffmann in *Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, **1970**; b) W. R. Dolvier, H. Koroniak, K. N. Houk, C. Sheu, *Acc. Chem. Res.* **1996**, *29*, 471.

[23] Review: A. D. Allen, J. Ma, M. A. McAllister, T. T. Tidwell, D. C. Zhao, *Acc. Chem. Res.* **1995**, *28*, 265.

[24] T. Mosandl, C. Wentrup, *J. Org. Chem.* **1993**, *58*, 747.

[25] a) J. Barluenga, F. Aznar, S. Barluenga, M. Fernández, A. Martín, S. García-Granda, A. Piñera-Nicolás, *Chem. Eur. J.* **1998**, *4*, 2280; b) J. Barluenga, F. Aznar, M. A. Palomero, *Chem. Eur. J.* **2001**, *7*, 5318; c) experimental details for the preparation of analogous (alkenylethynyl)carbene complexes have also been published by another research group: R. Aumann, R. Frölich, J. Prigge, O. Meyer, *Organometallics* **1999**, *18*, 1369.

[26] G. H. Posner, T. D. Nelson, *Tetrahedron* **1990**, *46*, 4573.

[27] Q. H. Zheng, J. Su, *Synth. Commun.* **1999**, *29*, 3467.

[28] J. W. Scheeren, R. J. F. M. Staps, R. J. F. Nivard, *Recl. Trav. Chim. Pays Bas* **1973**, *92*, 11.

[29] W. D. Wulff, K. L. Faron, J. Su, J. P. Springer, A. L. Rheingold, *J. Chem. Soc. Perkin Trans. 1* **1999**, 197.

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