From α,β-Unsaturated Fischer Carbene Complexes to Highly Substituted 3-Ethoxycyclopentadienes, Masked Cyclopentenones

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Dedicated to Lawrence T. Scott on the occasion of his 60th birthday

Keywords: Cocyclization / Organometallics / Template synthesis / Cycloadditions / Aldol reactions / Fischer carbenes

The β-amino-substituted α,β-unsaturated Fischer carbene complexes **3** are readily available by a four step one-pot procedure from terminal alkynes, chromium hexacarbonyl and secondary amines (24 examples with yields of 68–99% and 7 examples with yields of 26–63%). The formal [3+2] cycloadditions of complexes **3** with different alkynes including diynes and enynes performed in donor solvents such as pyridine or acetonitrile afforded highly substituted 5-(dialkylamino)-3-ethoxycyclopentadienes **7**, generally in medium to excellent yields (25 examples with yields of 60–95% and 7 examples with yields of 18–53%). The steric and electronic effects of the substituents on the carbene complexes and the incorporated alkynes on the regio- and stereoselectivity of the ring-forming reaction have been elaborated. An interesting 1,5- or, more likely, 1,2-migration of the dimethylamino group was observed for 5-(dimethylamino)-3-ethoxycyclopentadienes with trimethylsilyl and *i*Pr substituents at C-5. Attempted asymmetric syntheses of cyclopentadienes **7** from complexes **3** with chiral amino groups or substituents were only moderately successful. At a center of chirality in the secondary amino group, complexes of type **3** gave compounds **7** with diastereomeric excesses of, at best, 59% in yields of 54%, and with a stereogenic center in the substituent R^1 attached to the vinyl group of **3**, diastereomeric excesses as high as 94% could be achieved, but with poor chemical yields (21%). In general, cyclopentenones **21** could be easily obtained from the cyclopentadienes **7** under acidic conditions in very good yields (4 examples with yields of 81–98%, 1 example with an overall yield of 50% from complex **3**). Intramolecular aldol reactions of dicarbonyl compounds generated by hydrolysis of cyclopentadienes **7** with acetal-protected aldehyde or ketone carbonyl groups in either the 5-substituent R^1 or the *N*-substituent R^2 led to the bicyclic compounds **22** and **23**. The dimethylamino group in cyclopentenones **21** could be either eliminated or transformed into other functional groups via the quaternary ammonium salts **24**. The elimination product, cyclopentadienone **27** can undergo dimerization either by a formal [4+2] or [2+2] cycloaddition. Cyclopentenone **21naaa** with a bromovinyl-terminated side chain undergoes an intramolecular Heck reaction to form 5-methyl-4,6-dimethylenebicyclo[3.3.0]oct-1-en-3-one (**32**) (37% yield).

Introduction

When E. O. Fischer and his co-workers discovered a straightforward route to alkoxycarbene complexes of chromium and other transition metals about four decades ago,[1] it was not obvious that these would soon start to become an important component in the tool box for organic synthesis.[2] In particular, the formal [3+2+1] cycloaddition of an α,β-unsaturated or an α-aryl-substituted Fischer carbene complex and an alkyne with carbon monoxide insertion, the so-called Dötz reaction, was convincingly applied towards the preparation of a large variety of natural products and other interesting molecules.[3] Yet, quite a few α,β-unsaturated Fischer carbene complexes do not undergo the Dötz reaction with alkynes. Depending on the nature of the substituents on the carbene carbon atom and on the vinyl group as well as on the reaction conditions, such complexes can yield a wide variety of different types of products, often with high chemoselectivities upon careful choice of the reaction conditions. This is particularly true for β-amino-substituted α,β-unsaturated Fischer carbene complexes, and thus they can be regarded as chemical multitalents.[4] The [3+2] cocyclization of such a complex with an alkyne, yield-

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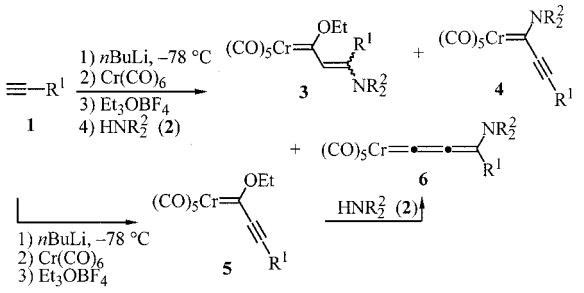
ing a 5-dialkyamino-3-ethoxycyclopentadiene was first reported by us for a β-cyclopropyl-substituted example.[5] Later this was greatly extended and found to be quite general when carried out in a donor solvent, especially pyridine.[6] Here we report on the full scope of the preparation of such β-amino-substituted α,β-unsaturated Fischer carbene complexes and their application towards the synthesis of 5-(dialkylamino)-3-ethoxycyclopentadienes, which have also turned out to be useful building blocks for organic synthesis.[4]

Results and Discussion

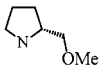
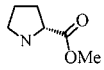
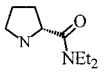
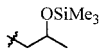
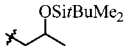
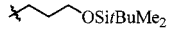
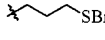
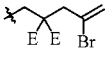
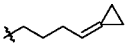
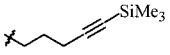
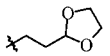
Certainly the most convenient access to β-amino-substituted α,β-unsaturated Fischer carbene complexes **3** is by a Michael-type addition of secondary amines **2** to alkynylidenecarbene complexes **5**. The latter are easily obtained from lithiated terminal alkynes **1**, chromium hexacarbonyl, and triethyloxonium tetrafluoroborate (Scheme 1). In a previous systematic study of this Michael-type reaction of complexes **5**, it was observed that in addition to the 1,4-addition products **3**, 1,2-addition-elimination (formal substitution) **4** and 1,4-addition-elimination products **6** can be formed.[7] The ratio of the three complexes **3**, **4** and **6** largely depends on the polarity of the solvent, the reaction temperature, and the substituents on the alkyne (R^1) and amine (R^2). By working entirely in tetrahydrofuran instead of diethyl ether for the first two steps, however, one can carry out all four steps in a one-pot procedure and obtain complexes **3** consistently in good to very good yields (Table 1) with only a few exceptions.[6]



Scheme 1. Preparation of Fischer carbene complexes **3** in a one-pot procedure; for details see Table 1

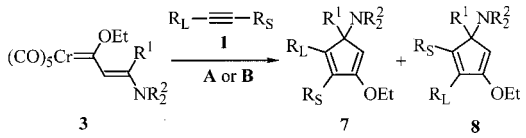
Upon heating a complex of type **3** with a terminal alkyne **1** in a donor solvent, such as pyridine or acetonitrile, at temperatures between 55 and 80 °C, a 1,5-disubstituted 5-(dialkylamino)-3-ethoxycyclopentadiene **7**, in some cases accompanied by its 2,5-disubstituted regioisomer **8**, was obtained in moderate to excellent yield (Scheme 2, Table 2). Internal alkynes gave the 1,2,5-trisubstituted analogues **7/8**. In none of the cases was any Dötz-reaction product detected. As has previously been discussed,[10] a donor solvent molecule acting as a ligand on the intermediate complexes in addition to the strongly donating β-dialkylamino group

Table 1. Preparation of (3-dialkylamino-1-ethoxyalkenylidene)pentacarbonylchromium complexes **3** from terminal alkynes **1**, chromium hexacarbonyl, triethyloxonium tetrafluoroborate and dialkylamines (see Scheme 1)

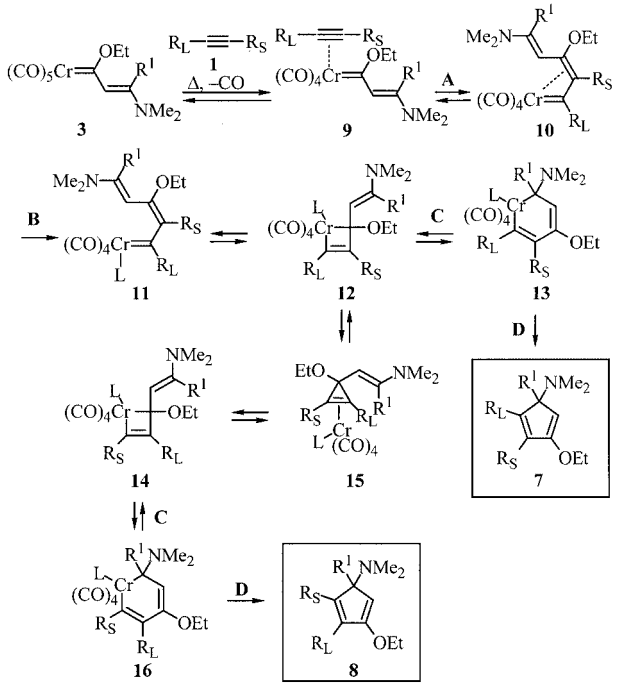
Entry	Alkyne	R^1 [a]	Amine	NR_2^2	Product	Yield (%)[b]
1	**1a**	Me	**2a**	NMe_2	**3aa**	84
2	**1a**	Me	**2b**	NEt_2	**3ab**	93
3	**1a**	Me	**2c**	pyrrolidine	**3ac**	82
4	**1a**	Me	**2d**	piperidine	**3ad**	90
5	**1b**	*n*Pr	**2a**	NMe_2	**3ba**	89
6	**1b**	*n*Pr	**2b**	NEt_2	**3bb**	87
7	**1b**	*n*Pr	**2e**		**3be**	99[c]
8	**1b**	*n*Pr	**2f**		**3bf**	97[c]
9	**1b**	*n*Pr	**2g**		**3bg**	91[c]
10	**1b**	*n*Pr	**2h**		**3bh**	26[c,d]
11	**1b**	*n*Pr	**2i**		**3bi**	100[c]
12	**1b**	*n*Pr	**2j**		**3bj**	76[c,e]
13	**1c**	*c*Pr	**2a**	NMe_2	**3ca**	88
14	**1d**	*i*Pr	**2a**	NMe_2	**3da**	75[f]
15	**1d**	*i*Pr	**2k**	morpholine	**3dk**	76[g]
16	**1e**	*n*Bu	**2b**	NEt_2	**3eb**	90
17	**1f**	*t*Bu	**2a**	NMe_2	**3fa**	97
18	**1f**	*t*Bu	**2k**	morpholine	**3fk**	84
19	**1g**	$SiMe_3$	**2a**	NMe_2	**3ga**	52[h,i]
20	**1h**	Ph	**2a**	NMe_2	**3ha**	71
21	**1i**		**2a**	NMe_2	**3ia**	38
22	**1j**		**2a**	NMe_2	**3ja**	50
23	**1k**		**2a**	NMe_2	**3ka**	85
24	**1l**		**2a**	NMe_2	**3la**	63[j]
25	**1m**		**2a**	NMe_2	**3ma**	75
26	**1n**		**2a**	NMe_2	**3na**	84
27	**1o**		**2a**	NMe_2	**3oa**	94
28	**1p**		**2a**	NMe_2	**3pa**	53
29	**1q**		**2a**	NMe_2	**3qa**	46
30	**1r**		**2a**	NMe_2	**3ra**	68[k]
31	**1s**		**2a**	NMe_2	**3sa**	72[k]

[a] E = CO_2Et. [b] One-pot procedure, if not otherwise mentioned. [c] Two-step procedure, the chemical yield was calculated only for the Michael-type addition to complex **5**. [d] In addition, 13% of **6bh** was isolated. [e] In addition, 5% of **6bj** was isolated. [f] In addition, 17% of **6da** was isolated. [g] In addition, 15% of **6dk** was isolated. [h] In addition, 25% of **4ga** was isolated. [i] Ref.[8]. [j] Ref.[6]. [k] Ref.[9]

prevents the CO insertion, which would lead to the formal [3+2+1] cycloadducts thus favoring the formation of the [3+2] cocyclization products. The same chemoselectivity for the formation of five-membered rings without CO insertion has also been observed by Dötz et al.,[11] Wulff et al.,[12] and Aumann et al.[13]



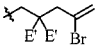
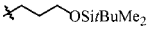
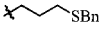
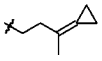
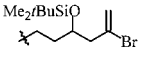
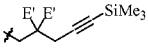
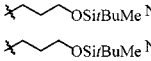
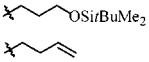
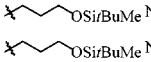
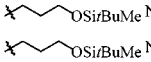
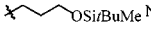
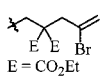
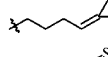
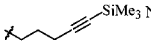
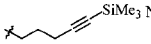
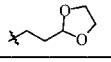
Scheme 2. A general synthesis of highly substituted 5-(dialkylamino)-3-ethoxycyclopentadienes **7/8**; conditions **A**: pyridine, 55−80 °C, 1.5−4 equiv. of alkyne; **B**: MeCN, 80 °C, lower concentration of alkyne; for further details see Table 2 and 3



Scheme 3. Proposed mechanism for the formation of cyclopentadienes **7** and their regioisomers **8**; **A**: alkyne insertion; **B**: coordination with a donor ligand, **C**: 6π-electrocyclization; **D**: reductive elimination

Mechanistically, the formation of the cyclopentadienes **7** and **8** can be rationalized in terms of following the sequence in Scheme 3. Upon heating, complex **3** undergoes thermal, dissociative ligand exchange of a carbonyl group for an alkyne to give **9**. In accordance with the calculations of Hofmann et al., carbene complex **9** then undergoes insertion of the alkyne, in a concerted fashion, to give the carbene/π-chelate complex **10**.[14] This pathway avoids the originally proposed 16-electron chromacyclobutene intermediate (not shown), which would be expected to be of much higher energy than the transition state along the concerted pathway.[14] In the presence of a suitable coordinating agent or solvent, complex **10** is dechelated to give **11**. Complex **11** can then undergo a 4π- and/or 6π-electrocyclization to give the vinylchromacyclobutene **12** and/or the chromacyclo-

Table 2. 5-(Dialkylamino)-3-ethoxycyclopentadienes **7/8** from (3-dialkylamino-1-ethoxyalkenylidene)pentacarbonylchromium complexes **3** and alkynes **1** (see Scheme 2)

Entry	Start. Mat.	R^1[a]	NR_2^2	Alkyne	R_L	R_S	Product	Yield (%)[b]
1	**3aa**	Me	NMe_2	**1aa**	Me	Me	**7aaaa**	82
2	**3aa**	Me	NMe_2	**1r**		H	**7aar**	86[c]
3	**3aa**	Me	NMe_2	**1s**		H	**7aas**	78[d]
4	**3ab**	Me	NEt_2	**1aa**	Me	Me	**7abaa**	73
5	**3ac**	Me	pyrrolidine	**1aa**	Me	Me	**7acaa**	60
6	**3ad**	Me	piperidine	**1a**	Me	H	**7ada**	60
7	**3ba**	*n*Pr	NMe_2	**1t**		H	**7bat**	44[e]
8	**3ba**	*n*Pr	NMe_2	**1u**	CH_2SiMe_3	H	**7bau**	53[e]
9	**3ba**	*n*Pr	NMe_2	**1o**		H	**7bao**	69
10	**3ba**	*n*Pr	NMe_2	**1aa**	Me	Me	**7baaa**	95
11	**3ba**	*n*Pr	NMe_2	**1bb**	*n*Pr	*n*Pr	**7babb**	62
12	**3ba**	*n*Pr	NMe_2	**1hh**	Ph	Ph	**7bahh**	80
13	**3ba**	*n*Pr	NMe_2	**1l**		H	**7bal**	74[f]
14	**3ba**	*n*Pr	NMe_2	**1m**		H	**7bam**	75[g]
15	**3ba**	*n*Pr	NMe_2	**1v**		H	**7bav**	18
16	**3ba**	*n*Pr	NMe_2	**1w**		H	**7baw**	85
17	**3ba**	*n*Pr	NMe_2	**1x**		H	**7bax**	81
18	**3bb**	*n*Pr	NEt_2	**1aa**	Me	Me	**7bbaa**	77
19	**3ca**	*c*Pr	NMe_2	**1aa**	Me	Me	**7caaa**	84
20	**3ca**	*c*Pr	NMe_2	**1cc**	*c*Pr	*c*Pr	**7cacc**	64
21	**3ca**	*c*Pr	NMe_2	**1y**		H	**7cay**	87[h]
22	**3la**		NMe_2	**1l**		H	**7lal**	77[i]
23	**3la**		NMe_2	**1z**		H	**7laz**	25[e,j]
24	**3la**		NMe_2	**1b**	*n*Pr	H	**7lab**	40[k]
25	**3la**		NMe_2	**1aa**	Me	Me	**7laaa**	91[l]
26	**3ma**		NMe_2	**1a**	Me	H	**7maa**	78
27	**3na**		NMe_2	**1aa**	Me	Me	**7naaa**	79
28	**3oa**		NMe_2	**1aa**	Me	Me	**7oaaa**	74
29	**3pa**		NMe_2	**1aa**	Me	Me	**7paaa**	69
30	**3qa**		NMe_2	**1g**	$SiMe_3$	H	**7qag**	48[m]
31	**3qa**		NMe_2	**1aa**	Me	Me	**7qaaa**	46
32	**3ra**		NMe_2	**1a**	Me	H	**7raa**	88

[a] E = CO_2Me, E′ = CO_2Et. [b] Conditions **A**, if not otherwise specified. [c] In addition, 7% **8aar** was isolated. [d] In addition, 7% of **8aas** was isolated. [e] Conditions **B**. [f] In addition, 8% of **8bal** was isolated. [g] In addition, 11% of **8bam** was isolated. [h] Hexane was used as solvent. [i] In addition, 8% of **8lal** was isolated. [j] In addition, 11% of **8laz** was isolated. [k] In addition, 6% of **8lab** was isolated. [l] Ref. [6]. [m] In addition, 4% of **8qag** was isolated.

hexadiene **13**, respectively, which would both be formed as low energy 18-electron complexes. These two complexes, **12** and **13**, may interconvert via ring expansion and contraction. Reductive elimination from **13** gives the cyclopentadiene **7**. Reductive elimination from **12** gives the vinylcyclopropene **15**, which would be expected to undergo reinsertion of the chromium into the least congested cyclopropene single bond to give a regiosomeric vinylchromacyclobutene **14**.[15] Ring expansion of **14** to the chromacyclohexadiene **16** and reductive elimination then leads to the regiosiomeric cyclopentadiene **8**.

A high concentration of the coordinating agent L relative to the alkyne **1** is very important in favoring formation of cyclopentadienes **7** and **8** over carbonyl-insertion products.[10] In the presence of high concentrations of an alkyne, the group L in **11** can be replaced by an alkyne to give an alkyne complex (**11**, L = alkyne). Unlike the usual groups L, such as acetonitrile and pyridine, this alkyne ligand can act as a 4π-electron donor and induce carbonyl insertion to give an 18-electron ketene complex (not shown), which will ultimately lead to the formation of carbonyl-containing cocyclization products.

Alkynes with a large variety of substituents, even enynes and diynes can be applied in this formal [3+2] cycloaddition with complete chemoselectivity. Intramolecular annelations[16] of α,β-unsaturated Fischer carbene complexes, i.e. di- and triynyl complexes, and intermolecular cascade cycloadditions[17] of alkyl complexes with enynes, diynes etc. are well known. In the cases reported here, however, additional multiple bonds in the molecule do not participate after the intermolecular cocyclization (Entries 15−17, 27−31, Table 2), and the substituents in the carbene complexes and the alkynes do not influence the chemoselectivity in the formation of the products **7**. In the cocyclization of complex **3ba** with the unsymmetrical diyne **1x**, only one product was detected (Entry 17, Table 2), apparently arising from the fact that the terminal triple bond must be more reactive than the internal one with its two bulky substituents.

In some examples (see Table 2), small amounts of regioisomers **8** as by-products could be detected. The steric bulk of the substituents either in the complexes **3** (R^1) or in the applied alkynes (R_L) appears to have an important effect on the regioselectivity of the cocyclization, and it has more influence on the former than on the latter (Entries 1−8, Table 3). The substituents R^1 in complexes **3** of the first six examples in Table 3 are primary alkyl groups, and the cocyclization products of type **7** obviously still dominate even when alkynes **1f** and **1g** with bulky substituents were applied as reaction partners. In contrast to these cases, complex **3da** with the sterically more demanding isopropyl substituent consistently gave larger fractions of the regioisomeric cyclopentadienes **8**. With trimethylsilylethyne (**1g**) and some internal alkynes **1hh[1]** as well as **1h[2]h[3]**, the products of type **8** became the major regioisomers (Entries 7, 11, 12, Table 3). With even bulkier substituents on the alkyne (e.g. *tert*-butyl, mesityl, adamantyl, etc.), 2-(acylmethylene)pyrrolidines were formed via a completely different reaction process.[18]

Table 3. Steric influence of substituents on the complexes **3** and the alkynes **1** on the regioselectivities of the formation of 5-dialkylamino-3-ethoxycyclopentadienes **7/8**

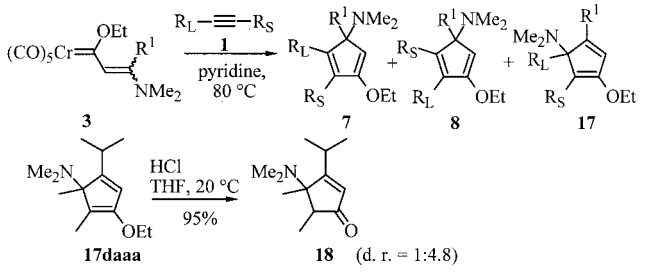
Entry	Start. Mat.	R^1	Alkyne	R_L	R_S	Product	Yield (%)	Combined Yields (%)[a]
1	**3ba**	*n*Pr	**1h**	Ph	H	**7bah**	80	80[b]
						8bah	0	
2	**3ba**	*n*Pr	**1g**	$SiMe_3$	H	**7bag**	53	53
						8bag	0	
3	**3ra**		**1f**	*t*Bu	H	**7raf**	57	57[c]
						8raf	0	
4	**3ra**		**1g**	$SiMe_3$	H	**7rag**	40	49[c]
						8rag	9	
5	**3sa**		**1f**	*t*Bu	H	**7saf**	59	59[c]
						8saf	0	
6	**3sa**		**1g**	$SiMe_3$	H	**7sag**	45	54[c]
						8sag	9	
7	**3da**	*i*Pr	**1g**	$SiMe_3$	H	**7dag**	23	44
						8dag	21	
8	**3da**	*i*Pr	**1h**	Ph	H	**7dah**	28	48
						8dah	20	
9	**3da**	*i*Pr	**1he**	Ph	*n*Hex	**7dahe**	49	70[d]
						8dahe	21	
10	**3da**	*i*Pr	**1hc**	Ph	*c*Pr	**7dahc**	41	70[d]
						8dahc	29	
11	**3da**	*i*Pr	**1hh[1]**	$4\text{-}EtO_2CC_6H_4$	Ph	**7dahh[1]**	16	36[e]
						8dahh[1]	20	
12	**3da**	*i*Pr	**1h[2]h[3]**	$4\text{-}MeOC_6H_4$	$4\text{-}MeO_2CC_6H_4$	**7dah[2]h[3]**	21	44[e]
						8dah[2]h[3]	23	

[a] Conditions **A** are as in Scheme 2 unless otherwise specified. [b] Conditions **B** are as in Scheme 2. [c] Ref.[9]. [d] Although the product mixtures **7dahe/8dahe** and **7dahc/8dahc** could not be separated, the regioisomers **8** are more easily hydrolyzed to cyclopentenones than **7**. After initial separation of the mixtures from other components, slow elution with a mixture of pentane/Et_2O (10:1) allowed the non-polar isomer **7** to be isolated. The structures of **7** and **8** were assigned on the basis of their HMBC-2D NMR spectra. [e] It was not possible to rigorously assign the regioisomers **7dahh[1]/8dahh[1]** and **7dah[2]h[3]/8dah[2]h[3]** so that the ratios may be reverse of those stated.

The internal alkynes 1-phenyloctyne (**1he**) and cyclopropylphenylethyne (**1hc**), upon treatment with **3da**, gave higher proportions of the regioisomer **7** than phenylethyne (Entries 8−10, Table 3). Varying the electronic properties of the substituents on the phenyl groups of diphenylethyne did not influence the ratio between **7** and **8** greatly (Entries 11−12).

Cocyclizations of internal alkynes and the carbene complexes **3** with larger substituents R^1 did not only lead to an increased formation of the regioisomer **8**, but led to yet another isomeric cyclopentadiene **17** which would result from **7** by 1,5-migration of the dimethylamino group (Scheme 4 and Table 4).[19] These 1,4,5-trisubstituted 5-(dimethylamino)-2-ethoxycyclopentadienes **17** have distinctly different NMR spectra compared with the isomers **7** and **8**. Due to the electron donating effect of the ethoxy group, the signals of the olefinic protons in **7/8** appear more upfield than that in **17** (δ = 4.5−5 ppm versus δ = 5.7−6.5 ppm).

The same holds for the corresponding ^{13}C NMR signals (δ = 95−100 ppm versus δ = 110−120 ppm). The constitution of **17daaa**, one specimen of type **17**, was rigorously established by a single-crystal X-ray diffraction study of its hydrolysis product **18** which was obtained by treatment of **17daaa** with hydrochloric acid (Figure 1).[20]



Scheme 4. Steric and electronic effects of substituents in the applied alkynes **1** on the distribution of cyclopentadienes **7**, **8** and **17**; for further details see Table 4

Table 4. Formation of 1,4,5-trisubstituted 5-(dimethylamino)-2-ethoxycyclopentadienes **17** from complexes **3** and internal alkynes (see Scheme 4)

Entry	Start. Mat.	R^1	Alkyne	R_L	R_S	Product	Yield (%)	Ratio 17/7	Combined Yields (%)[a]
1	**3da**	*i*Pr	**1aa**	Me	Me	**7daaa**	38	51:49	77
						17daaa	39		
2	**3ia**		**1aa**	Me	Me	**7iaaa**	0	100:0	26
						17iaaa	26		
3	**3ga**	$SiMe_3$	**1aa**	Me	Me	**7gaaa**	0	100:0	28
						17gaaa	28		
4	**3da**	*i*Pr	**1cc**	*c*Pr	*c*Pr	**7dacc**	78	0:100	78[b]
						17dacc	0		
5	**3da**	*i*Pr	**1h^{4}h^4**	4-$F_3CC_6H_4$		**7dah^{4}h^4**	65	0:100	65
					4-$F_3CC_6H_4$	**17dah^{4}h^4**	0		
6	**3da**	*i*Pr	**1h^{4}z**	4-$F_3CC_6H_4$		**7dah^{4}z**	7	71:29	73
					4-$F_3CC_6H_4C{\equiv}C$	**8dah^{4}z**	49		
						17dah^{4}z	17		
7	**3da**	*i*Pr	**1hz^1**	Ph	Ph−C≡C	**7dahz^1**	22	29:71	68[c]
						8dahz^1	37		
						17dahz^1	9		
8	**3da**	*i*Pr	**1h^{3}z^2**	4-$MeOC_6H_4$		**7dah^{3}z^2**	22	<1:99	57
					4-$MeOC_6H_4C{\equiv}C$	**8dah^{3}z^2**	35		
						17dah^{3}z^2	≤1		

[a] All starting materials had the (*E*) configuration. [b] The product was isolated as a 1:1 mixture of cyclopentadiene **7dacc** and its hydrolysis adduct **21dacc** in 78% yield. Complete hydrolysis of the mixture gave the cyclopentenone **21dacc** in 84% yield. [c] The structures of **7dahz^1**, **8dahz^1** and **17dahz^1** could be assigned on the basis of NOESY-2D NMR spectroscopy, and the resultant information could also be applied towards the assignment of isomers **7dah^{4}z**/**8dah^{4}z**/**17dah^{4}z** and **7dah^{3}z^2**/**8dah^{3}z^2**/**17dah^{3}z^2**.

In contrast to 2-butyne (**1aa**), the sterically more congested and more electron-rich dicyclopropylethyne (**1cc**) did not afford any product of type **17** (Entry 4, Table 4), while complexes **3ia** and **3ga** with 2-butyne (**1aa**) gave only **17iaaa** and **17gaaa**, respectively. Neither **7** nor **8** could even be detected in the spectra of the crude products (Entries 2, 3, Table 4).

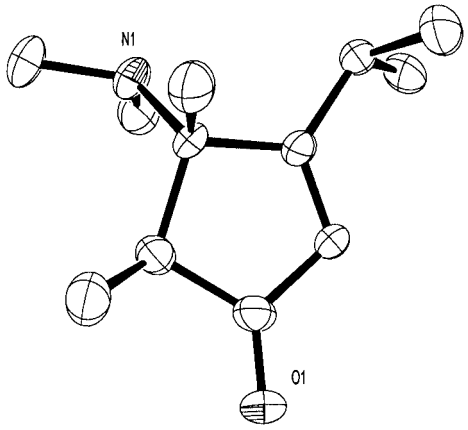
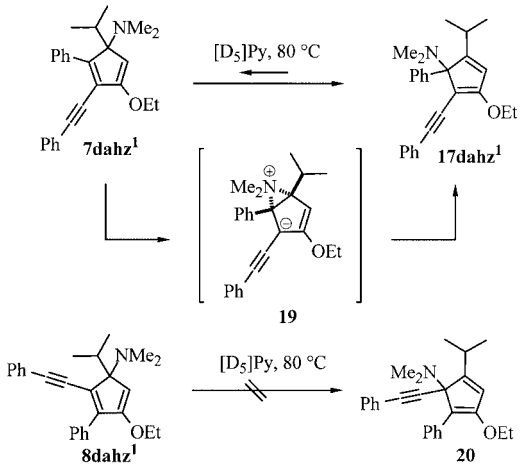


Figure 1. Structure of 4-(dimethylamino)-3-isopropyl-4,5-dimethylcyclopent-2-enone (**18**) in the crystal[20]

1,4-Diphenylbutadiyne (**1hz^1**) can be regarded as an internal alkyne with a phenyl and a phenylethynyl substituent with the latter being more strongly electron withdrawing than the former. With this acetylene, the cocyclization product **17dahz^1** was isolated in 9% yield (Entry 7, Table 4). In order to determine the mode of formation of **17dahz^1**, isolated samples of **7dahz^1** and **8dahz^1** in [D_5]pyridine were heated to 80 °C. In the sample of **7dahz^1**, the signal of **17dahz^1** appeared slowly. After 17 days, 67% of **7dahz^1** had been converted into **17dahz^1**, while the isomer **8dahz^1** remained unchanged even upon prolonged heating (Scheme 5). This shift of the dimethylamino group is reversible but the rate constant for the transformation of **7dahz^1** to **17dahz^1** must be larger than that of the reverse reaction. When pure **17dahz^1** was heated in [D_5]pyridine at 80 °C for 2 days, a 21% conversion to **7dahz^1** could be observed. Under the same conditions, 40% of **7dahz^1** was converted into **17dahz^1**.

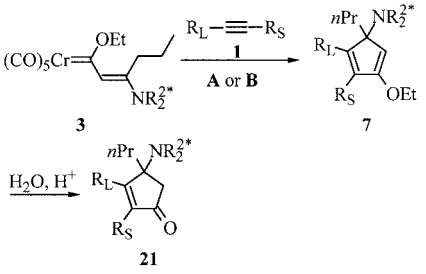


Scheme 5. A possible mode of formation of 1,4,5-trisubstituted 5-(dimethylamino)-3-ethoxycyclopentadiene **17dahz^1** by 1,2-migration of the dimethylamino group in **7dahz^1** via a bridged zwitterionic intermediate

These results seem to indicate that **17dahz**[1] is not formed by a 1,5-shift of the dimethylamino group, but rather a 1,2-migration via the bridged zwitterionic intermediate **19** which would be significantly stabilized by the strongly electron withdrawing phenylethynyl substituent and the electron donating ethoxy group. Indeed, even with the more strongly electron withdrawing *p*-trifluorophenylethynyl substituent provided by 1,4-bis(*p*-trifluoromethylphenyl)butadiyne (**1h**[4]**z**), the ratio between **17** and **7** increased by around six-fold. In contrast, the bis-donor-substituted diphenylbutadiyne **1h**[3]**z**[2] did afford traces (≤1%) of a product of type **17** (Entry 8, Table 4). Di(*p*-trifluoromethylphenyl)ethyne (**1h**[4]**h**[4]) also yielded none of the product **17dah**[4]**h**[4].

Asymmetric Induction in the Formation of 5-(Dialkylamino)-3-ethoxycyclopentadienes

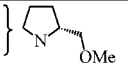
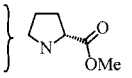
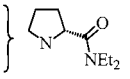
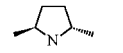
The 5-(dialkylamino)-3-ethoxycyclopentadienes **7**, **8** and **17** are chiral with one stereogenic center each in their five-membered rings. The stereochemical information contained in enantiomerically pure derivatives would be carried over into the 3-(dialkylamino)cyclopent-2-enones **21** which are easily obtained, e.g. from **7**,[9] and can be applied favorably towards the construction of complex molecules.[9,19,21] It was therefore desirable to prepare cyclopentadienes of type **7** in enantiomerically pure form. In view of the numerous examples of the successful application of chiral auxiliaries derived from proline, e.g. in the SAMP/RAMP methodology developed by Enders et al.,[22] pyrrolidinyl residues were introduced into the α,β-unsaturated carbene complexes **3** using the established methodology (see above, Scheme 1). In the best example, however, the diastereomeric excess was only 59% with a chemical yield of only 54% (Scheme 6 and Table 5). In two cases yields were better, but the diastereomeric excesses were lower, and in four cases the yields and diastereoselectivities were unsatisfactory.



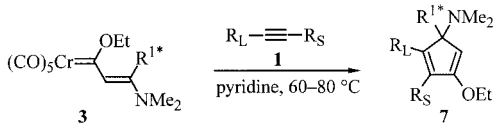
Scheme 6. Asymmetric induction in the formation of cyclopentadienes **7** by chiral amino group auxiliaries in the complexes **3**; **A**: 80 °C, pyridine; **B**: 80 °C, MeCN; for further details see Table 5

The chiral complex **3bi** with a *cis*-dimethylaziridinyl group and the chiral one **3bj** did not yield any cocyclization products **7** with alkynes, and the chiral complex **3bh** with a *trans*-2,5-dimethylpyrrolidinyl group in a reaction with 2-butyne (**1aa**) gave the corresponding cyclopentadiene **7bhaa**, isolated as its hydrolysis product **21bhaa** in poor yield (22%) with only a 50% diastereomeric excess (Table 5).[23]

Table 5. Stereodirected synthesis of 5-(dialkylamino)-3-ethoxycyclopentadienes **7** from chirally modified β-(dialkylamino)alkenylidenechromium complexes **3** (see Scheme 6)

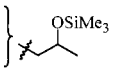
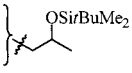
Start. Mat.	NR_2^2	Alkyne	R_L	R_S	Conditions	Product	Yield (%)	de (%)
3be		**1f**	*t*Bu	H	B	**21bef**	54	59
3be		**1aa**	Me	Me	A	**21beaa**	98	31
3bf		**1f**	*t*Bu	H	B	**21bff**	72	39
3bf		**1aa**	Me	Me	A	**21bfaa**	78	23
3bg		**1f**	*t*Bu	H	B	**7bgf**	47	2
3bg		**1h**	Ph	H	B	**7bgh**	40	5
3bg		**1aa**	Me	Me	A	**7bgaa**	74	5
3bh		**1aa**	Me	Me	A	**21bhaa**	22	50

Substituents R^1 in the carbene complexes **3** with stereogenic centers in the 1- and 2-positions relative to the double bond were also tested for the asymmetric synthesis of cyclopentadienes **7** (Scheme 7, Table 6). Although the diastereomeric excesses obtained with complex **3ia** containing a 1-methoxyethyl substituent were quite good, especially when the reactions were carried out at low temperatures, the chemical yields were insufficient. Chemical yields were better with the 2-(*tert*-butyldimethylsilyloxy)propyl-substituted complex **3ka**, but diastereomeric excesses were consistently lower.



Scheme 7. Asymmetric synthesis of cyclopentadienes **7** with chiral substituents R^1 on the complexes **3**; for further details see Table 6

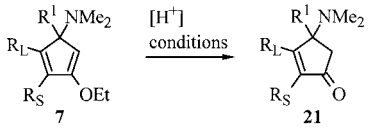
Table 6. Asymmetric synthesis of cyclopentadienes **7** with chiral substituents R^1 on the complexes **3**; for further details see Scheme 7

Start. Mat.	R^{1*}	Alkyne	R_L	R_S	Temp. [°C]	Time [h]	Product	Yield (%)	de (%)
3ia		**1f**	*t*Bu	H	80	24	**7iaf**	29	75
					60	42	**7iaf**	33	79
					40	528	**7iaf**	21	>88
					20	336	**7iaf**	17	>88
3ia		**1h**	Ph	H	80	42	**7iah**	21	94
3ja		**1f**	*t*Bu	H	80	96	**7jaf**	31	47
3ja		**1h**	Ph	H	80	96	**7jah**	48	31
3ja		**1aa**	Me	Me	80	48	**7jaaa**	15	31
3ka		**1f**	*t*Bu	H	80	72	**7kaf**	43	44
3ka		**1h**	Ph	H	80	72	**7kah**	63	29
3ka		**1aa**	Me	Me	80	72	**7kaaa**	27	35

Synthetic Applications of (Dialkylamino)ethoxycyclopentadienes 7/8

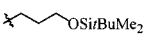
Many biologically active compounds contain highly substituted cyclopentenone subunits, and the variously substi-

tuted 5-(dialkylamino)-3-ethoxycyclopentadienes **7** as well as their regioisomers **8** and **17** are just enol ethers of functionally substituted cyclopentenones. As such, they can easily be hydrolyzed under acidic conditions to furnish cyclopentenones **21** in good to very good yields (Scheme 8 and Table 7). The latter can also be obtained in a one-pot procedure directly from the carbene complexes **3** and alkynes **1** by immediate addition of two to three drops of concentrated hydrochloric acid to the reaction mixture before workup (Entry 2, Table 7). The silyl protecting group on the hydroxy groups is retained when hydrogen chloride is used for hydrolysis but can be cleaved off afterwards, or simultaneously, with aqueous hydrogen fluoride (40%) (Entries 3 and 5, Table 7).



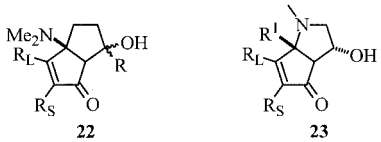
Scheme 8. Selected examples of the hydrolysis of ethoxycyclopentadienes **7** to cyclopentenones **21**; for further details see Table 7

Table 7. Selected examples of the hydrolysis of ethoxycyclopentadienes **7** to cyclopentenones **21** (see Scheme 8)

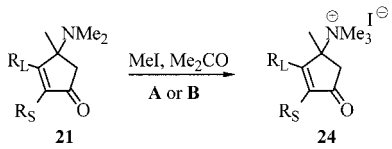
Entry	Start. Mat.	R^1	R_L	R_S	Conditions[a]	Product	Yield (%)
1	**7aaaa**	Me	Me	Me	A	**21aaaa**	98
2	**3aa**	Me	Ph	Ph	A	**21aahh**	50[b]
3	**7bal**	*n*Pr		H	A	**21bal**	93[c,d]
4	**7caaa**	*c*Pr	Me	Me	A	**21caaa**	95
5	**7laaa**		Me	Me	B	**21laaa**	81[e]

[a] **A**: 2 N HCl. **B**: 40% HF. [b] Overall yield for the one-pot procedure from the complex **3aa**. [c] Without removal of the protecting group. [d] The remaining silyl protecting group in **21bal** could be removed in 67% yield with hydrogen fluoride solution. [e] Including removal of the silyl protecting group.

When an acetal-protected aldehyde or ketone carbonyl group is present in either the 5-substituent R^1 or the *N*-substituent R^2 on the cyclopentadiene **7**, they will be cleaved under hydrolytic conditions, and the resultant diones will immediately undergo an intramolecular Aldol reaction to afford 5-(dimethylamino)bicyclo[3.3.0]oct-3-en-2-ones **22** or 6-azabicyclo[3.3.0]oct-3-en-2-ones **23**,[9] which can serve as oligofunctional building blocks for the synthesis of terpenes and terpene analogues.[19,21]



The dialkylamino group, especially the dimethylamino group, in a cyclopentenone of type **21** can be transformed into a better leaving group by alkylation with methyl iodide. In acetone at ambient temperature and pressure, the quaternary ammonium salts **24** are formed in good yields (Scheme 9, Table 8). Under high pressure, the chemical yields can be improved to excellent levels.

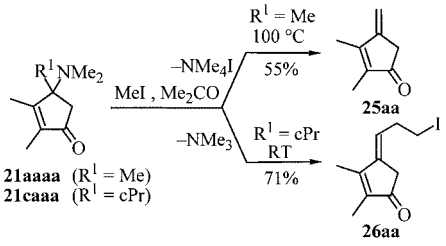


Scheme 9. Quaternization of 4-(dimethylamino)cyclopentenones **21**; **A**: 10 kbar, 25 °C, 20 h − 3 days; **B**: 25 °C, 3 days; for further details see Table 8

Table 8. Quaternization of 4-(dimethylamino)cyclopentenones **21** (see Scheme 9)

Entry	Starting material	R_L	R_S	Conditions	Product	Yield (%)
1	**21aaaa**	Me	Me	**A**	**24aaaa**	93
2	**21aaaa**	Me	Me	**B**	**24aaaa**	70
3	**21aahh**	Ph	Ph	**A**	**24aahh**	96
4	**21aahh**	Ph	Ph	**B**	**24aahh**	70

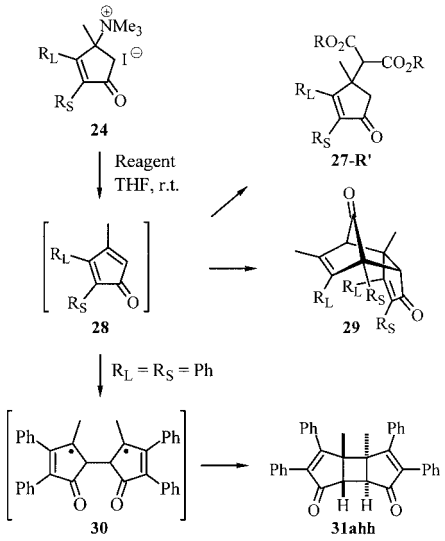
Upon heating the cyclopentenone **21aaaa** with methyl iodide in acetone solution in a sealed thick-walled screw-cap bottle at 100 °C for 2 h, the elimination product **25aa** was formed directly and isolated in 55% yield (Scheme 10) instead of the quaternary ammonium salt **24aaaa**. The ammonium salt **24caaa** from the cyclopropyl-substituted cyclopentenone **21caaa** could not be isolated even at ambient temperature, but underwent ring opening by nucleophilic attack of the iodide ion and elimination of trimethylamine to yield 4-(3′-iodopropylidene)cyclopent-2-enone **26aa** (71%).



Scheme 10. Direct formation of elimination products **25** and **26** from in situ formed quaternary ammonium salts

When the quaternary ammonium salts **24aaaa** and **24aahh** in tetrahydrofuran were treated with the sodium enolate of a dialkyl malonate, three types of products were obtained namely the formal substitution product **27**, the [4+2] dimer **29** and the [2+2] dimer **31** of the cyclopentadienone **28**, respectively, formed by elimination of trimethylamine from **24** (Scheme 11, Table 9). The ratio of the three products **27**:**29**:**31** depends upon the applied reagents

(or bases) and the substituents R_L and R_S in the cyclopentenone **24**.



Scheme 11. Further transformations of quaternary ammonium salts **24**; for further details see Table 9

Table 9. Further transformations of quaternary ammonium salts **24** (see Scheme 11)

Starting Material (R_L, R_S)	Reagent	Product	Yield (%)	Combined Yields (%)
24aaaa (Me, Me)	$NaCH(CO_2Me)_2$	**27aaa**-Me	33	89
		29aaa	56	
24aaaa (Me, Me)	$NaCH(CO_2Et)_2$	**27aaa**-Et	74	74
24aahh (Ph, Ph)	$NaCH(CO_2Et)_2$	**27ahh**-Et	75	75
24aahh (Ph, Ph)	$NaCH(CO_2tBu)_2$	**27ahh**-*t*Bu	45	91
		31ahh	46	
24aahh (Ph, Ph)	NaOMe	**31ahh**	96	96

With diethyl sodiomalonate, only the formal substitution product **27aaa**-Et, most probably formed by elimination to **28aaa** and subsequent Michael addition, was isolated from the dimethylcyclopentenone derivative **24aaaa**, while the same starting material **24aaaa** upon treatment with dimethyl sodiomalonate gave, along with the Michael addition adduct **27aaa**-Me (33%), the [4+2] dimer **29aaa** as the major product (56%). The diphenylcyclopentenone derivative **24aahh** reacted with diethyl sodiomalonate in the same way as the dimethyl derivative **24aaaa** to give only the elimination-addition product **27ahh**-Et. With di-*tert*-butyl sodiomalonate, however, equal amounts of the Michael adduct **27ahh**-*t*Bu and the [2+2] dimer **31ahh** of the intermediate 4-methyl-2,3-diphenylcyclopentadienone (**28ahh**) were isolated. The [2+2] dimer of the latter, namely **31ahh**, was obtained as the sole product upon treatment of **24aahh** with sodium methoxide in tetrahydrofuran (96% yield). Its structure was rigorously established from a single-crystal X-ray diffraction study (Figure 2).[24] The formal [2+2] cycloadduct of type **31** apparently forms only from the diphenyl-substituted cyclopentadienone **28ahh** and most probably via a 1,4-diradical intermediate **30**. This preference must be due to the efficient stabilization of **30** by two phenyl substituents in the two allylic positions, which would also cause a significant lowering of the energy of the transition state leading to **30**.[25]

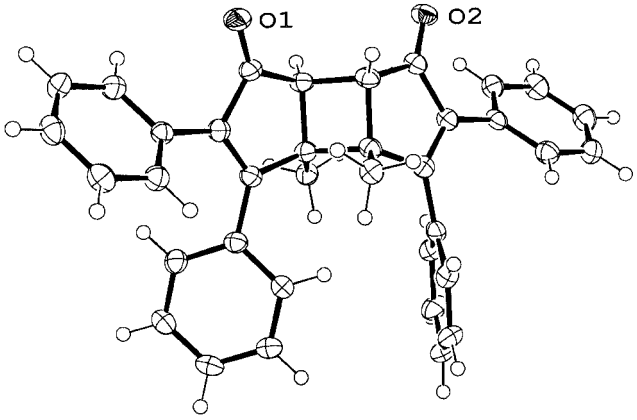
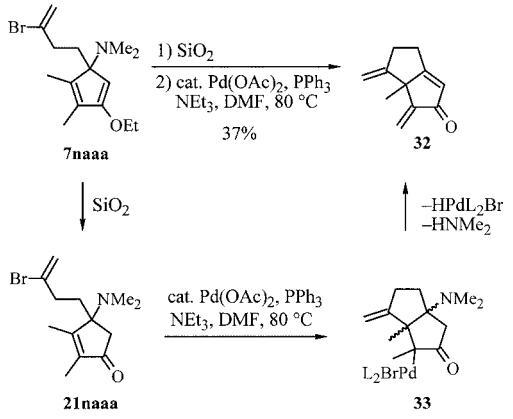


Figure 2. Structure of the cyclopentadienone dimer **31ahh** in the crystal[24]

To demonstrate the utility of the highly functionalized cyclopentadienes accessible by this methodology, the (dimethylamino)ethoxycyclopentadiene **7naaa** with a 5-(3′-bromobut-3′-enyl) substituent was hydrolyzed to the corresponding cyclopentenone **21naaa**, and the latter was subjected to conditions appropriate for an intramolecular Heck-type coupling. This led to the formation of the interesting 5-methyl-4,6-dimethylenebicyclo[3.3.0]oct-1-en-3-one (**32**) in an overall yield of 37%. Under the basic conditions of the Heck reaction, the cyclization product **33** apparently undergoes facile elimination of dimethylamine to furnish the α,β-unsaturated ketone.



Scheme 12. An intramolecular Heck reaction leading to 5-methyl-4,6-dimethylenebicyclo[3.3.0]oct-1-en-3-one (**32**)

Conclusion

Using the recently developed optimized conditions,[6] a wide range of β-amino-substituted α,β-unsaturated Fischer carbenechromium complexes **3** (which are easily accessible in a four-step one-pot procedure from terminal acetylenes, chromium hexacarbonyl, triethyloxonium tetrafluoroborate and secondary amines) react with terminal and internal acetylenes forming di- and trisubstituted 5-(dialkylamino)-3-ethoxycyclopentadienes **7/8**, generally in good to very good yields. The products are protected cyclopentenones and, in a sense, even doubly protected cyclopentadienones, and thus they open up multiple synthetic avenues to complex skeletons of natural products and their analogues, e.g. sesquiterpenes, including triquinanes,[19,21] (+)-nortaylorione-,[26a] and steroid-like compounds.[21a]

Experimental Section

General: ^{1}H and ^{13}C NMR spectroscopy: Bruker AM 250 (250 and 62.9 MHz, respectively) and Bruker AMX 300 (300 and 75 MHz, respectively) instruments. IR: Bruker IFS 66 (FT-IR) spectrometer. Low-resolution EI MS: Varian MAT CH 7, MAT 731 instrument, ionizing voltage 70 eV. High-resolution EI MS (HR EIMS): Varian MAT 311 A spectrometer. X-ray crystal structure determination: the data were collected on a Stoe−Siemens-AED diffractometer. Melting points were determined with a Büchi melting point apparatus and are uncorrected. Elemental analyses: Mikroanalytisches Laboratorium der Georg-August-Universität Göttingen. Chromatography: Merck silica gel 60 (230−400 mesh) or ICN neutral alumina (Super I, activity grade II). Solvents for chromatography were technical grade and freshly distilled before use. Tetrahydrofuran was distilled from sodium benzophenone ketyl and pyridine was distilled from calcium hydride. The following were prepared according to published procedures: 3-Methoxybut-1-yne (**1i**),[27] 4-(trimethylsilyloxy)pent-1-yne (**1j**),[28] 4-(*tert*-butyldimethylsilyloxy)pent-1-yne (**1k**),[29] 5-[*tert*-butyl(dimethyl)silyloxy]pent-1-yne (**1l**),[30] 4-pentynyl benzyl sulfide (**1m**),[26b] diethyl 6-bromo-6-hepten-1-yne-4,4-dicarboxylate (**1o**),[31] 6-cyclopropylidenehex-1-yne (**1p**),[32] 1-(trimethylsilyl)hepta-1,6-diyne (**1q**),[32] 2-[(*E*)-ethoxy]-1-ethynylcyclopropane (**1y**),[33] 1-hexen-5-yne (**1z**),[33] hexylphenylethyne (**1he**),[34] cyclopropylphenylethyne (**1hc**),[34] ethyl *p*-phenylethynylbenzoate (**1hh^1**),[35] methyl 4-(4-methoxyphenylethynyl)benzoate (**1h^{2}h^3**),[35] bis(*p*-trifluoromethylphenyl)ethyne (**1h^{4}h^4**),[35] 1,4-bis(*p*-trifluoromethylphenyl)-1,3-butadiyne (**1h^{4}z**),[36] 1,4-bis(*p*-methoxyphenyl)-1,3-butadiyne (**1h^{3}z^2**),[36] (2*S*)-methoxymethyl-pyrrolidine (**2e**),[37] methyl (2*S*)-pyrrolidinecarboxylate (**2f**),[38] diethyl (2*S*)-*N*′,*N*′-diethylpyrrolidinecarboxamide (**2g**),[39] (2*R*,5*R*)-dimethylpyrrolidine (**2h**),[40] *trans*-2,3-dimethylaziridine (**2i**),[41] (1*S*)-(1-phenyl)ethylmethylamine (**2j**),[42] pentacarbonyl[(2*E*)-3-(dimethylamino)-1-ethoxy-3-(trimethylsilyl)-2-propen-1-ylidene]chromium (**3ga**),[8] pentacarbonyl(1-ethoxy-2-hexyn-1-ylidene)chromium (**5**, R^1 = *n*Pr)[43].

For the experimental and spectroscopic data of all compounds not presented here see the Supporting Informations (see also the footnote on the first page of this article).

General Procedures for the Preparation of β-Amino-Substituted α,β-Unsaturated Fischer Carbene Complexes 3

1) One-Pot Procedure from Terminal Alkynes (GP1A): To a solution of a terminal alkyne **1** (20 mmol) in THF (100 mL) was added at −78 °C a solution of *n*-butyllithium (20 mmol). The mixture was stirred at this temperature for an additional 1−3 h. After addition of chromium hexacarbonyl (4.40 g, 20.0 mmol), the solution was warmed to room temperature, stirred for another 30 min, and triethyloxonium tetrafluoroborate (Et_3OBF_4, 20.5 mmol) was then added at 0 °C. After an additional 10 min, 1.0−1.1 equiv. of a secondary amine was added to the dark red solution in THF upon which the color changed to yellow or orange as the reaction proceeded to completion. After filtration through Celite and removal of solvent, the residue was purified by flash column chromatography.

2) Michael Addition of a Secondary Amine to an Alkynylidenecarbene Complex 5 (GP1B): To a 2 M solution of an alkynylidenecarbene complex **5** in Et_2O was added at ambient temperature 1.0−1.1 equiv. of a secondary amine. The progress of the reaction was monitored by TLC. After removal of the solvent, the residue was purified by flash column chromatography.

General Procedure for Cocyclizations of Complexes 3 with Alkynes 1

1) In Pyridine as a Solvent (GP2A): A thick-walled, screw-cap Pyrex bottle equipped with a magnetic stirring bar was charged with a 0.05 M solution of the respective complex **3** in anhydrous pyridine. Dry nitrogen was bubbled through the solution for 5 min, and 2−4 equiv. of the respective alkyne **1** was added immediately. The sealed bottle was kept in an oil bath at 60−80 °C for 2−5 days. The solvent was then removed under reduced pressure, the residue diluted with Et_2O, and the solution exposed to air for 2 h. After filtration and removal of the solvent, the residue was purified by column chromatography on aluminum oxide (activity grade II) or silica gel.

2) In Acetonitrile as a Solvent (GP2B): To a 0.05 M solution of the complex **3** in anhydrous acetonitrile at 50−80 °C was added 2−4 equiv. of the respective alkyne **1** via a syringe pump over a period of 8−36 h. After 2 h − 4 d, complex **3** was completely consumed (TLC), and the solvent could then be removed. The mixture was diluted with pentane (10 mL), left open to air for 1 h, and filtered through Celite. The filtrate was concentrated under reduced pressure, and the residue purified by chromatography on aluminum oxide (activity grade II) or silica gel.

General Procedure for the Hydrolysis of (Dimethylamino)ethoxycyclopentadienes 7 to (Dimethylamino)cyclopentenones 21 (GP3): To a 0.5 M solution of the respective ethoxycyclopentadiene **7** in THF was added two drops of 2 N hydrochloric acid and a small amount of silica gel (1−3 g). After stirring at room temperature for 5 min and removal of the solvent, the residue was purified by column chromatography on silica gel.

General Procedure for the Methylation of (Dimethylamino)cyclopentenones 21 with Methyl Iodide

1) Under a Pressure of 10 kbar (GP4A): To a solution of the respective cyclopentenone **21** (0.61 mmol) in of acetone (8 mL) was added 2−7 equiv. of methyl iodide and the mixture was sealed in Teflon bags which were pressurized at ambient temperature to 10 kbar for 20 h−3 days. The reaction mixture was diluted with Et_2O (50 mL) and filtered. The collected solid was washed with Et_2O three times and dried under reduced pressure.

2) At Ambient Pressure (GP4B): As for GP4A, but at 1 atm.

General Procedure for the Transformation of the Quaternary Ammonium Salts (GP5): To a solution of the respective quaternary ammonium salt **24** (0.15 mmol) in THF (10 mL) was added dropwise a solution of a dialkylsodium malonate (or sodium meth-

oxylate) (0.40 mmol) in THF (5 mL), and the mixture was stirred at ambient temperature for an additional 1 h. The mixture was then treated with H_2O (10 mL) and extracted with Et_2O (3 × 20 mL). The organic solution was dried with $MgSO_4$, and the solvent removed under reduced pressure.

Pentacarbonyl[(2*E*)-3-(dimethylamino)-1-ethoxy-2-buten-1-ylidene]-chromium (3aa): According to GP1A, propyne (**1a**) (1.60 g, 40.0 mmol) in THF (80 mL) was treated with *n*-butyllithium (8.5 mL, 2.36 M in *n*-hexane, 20 mmol), chromium hexacarbonyl (4.51 g, 20.5 mmol), Et_3OBF_4 (4.56 g, 24.0 mmol) and then gaseous dimethylamine. Flash chromatography on silica gel (50 g) eluting with pentane/Et_2O (from 3:1 to 1:1) gave 5.60 g (84%) of **3aa** [R_f = 0.41 (Et_2O)] as a yellow solid. The spectroscopic data are consistent with those previously reported.[44]

Pentacarbonyl[(2*E*)-3-(diethylamino)-1-ethoxy-2-buten-1-ylidene]-chromium (3ab): According to GP1A, propyne (**1a**) (1.31 mL, 22.0 mmol) in THF (120 mL) was treated with *n*-butyllithium (12.5 mL, 1.60 M in *n*-hexane, 20.0 mmol), chromium hexacarbonyl (4.40 g, 20.0 mmol), Et_3OBF_4 (4.18 g, 22.0 mmol) and diethylamine (2.47 mL, 24.0 mmol). Flash chromatography on silica gel (40 g) eluting with pentane/Et_2O (3:1) gave 6.72 g (93%) of **3ab** [R_f = 0.32 (Et_2O)] as a yellow solid, m.p. 63 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2984 cm^{-1} (C−H), 2045 (C=O), 1890 (C=O), 1446, 1292, 1261, 1081, 912. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.28 [m, 6 H, $N(CH_2CH_3)_2$], 1.47 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.36 (s, 3 H, CH_3), 3.49 [m, 4 H, $N(CH_2CH_3)_2$], 4.66 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 6.46 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.6 [+, $N(CH_2CH_3)_2$], 15.7 (+, OCH_2CH_3), 19.1 (+, C-4), 46.2 [−, $N(CH_2CH_3)_2$], 73.5 (−, OCH_2CH_3), 117.3 (+, C-2), 154.4 ($C_{quat.}$, C-3), 219.4, 224.3 ($C_{quat.}$, CO), 283.9 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 361 (7) [M^+], 333 (11) [M^+ − CO], 305 (5) [M^+ − 2CO], 277 (11) [M^+ − 3CO], 249 (14) [M^+ − 4CO], 221 (100) [M^+ − 5CO], 192 (25), 164 (28), 162 (7), 149 (14), 124 (11), 123 (11), 122 (13), 94 (6), 93 (5), 52 (6) [Cr^+]. $C_{15}H_{19}CrNO_6$ (361.3): calcd. C 49.86, H 5.30; found C 49.88, H 5.20.

Pentacarbonyl{(2*E*)-1-ethoxy-3-[(2′*S*)-(2′-methoxymethyl)pyrrolidino]-2-hexen-1-ylidene}chromium (3be): According to GP1B, complex **5** (989 mg, 3.13 mmol) (R^1 = *n*Pr) in Et_2O (63 mL) was treated with (2*S*)-methoxymethylpyrrolidine (**2e**) (360 mg, 3.13 mmol). Flash chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/CH_2Cl_2 (3:1) gave 1.34 g (99%) of **3be** [R_f = 0.23 (pentane/CH_2Cl_2, 3:1); ratio of rotamers 2:1] as an orange solid, m.p. 44 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2975 cm^{-1} (C−H), 2042 (C=O), 1959 (C=O), 1486, 1240, 1075, 943. **Major Rotamer:** ^1H NMR (250 MHz, C_6D_6): δ = 0.74 (t, ^3J = 7.3 Hz, 3 H, 6-H), 1.05−1.50 (m, 6 H, 4,5,4′-H), 1.10 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.99−2.18 (m, 2 H, 3′-H), 2.45−3.30 (m, 4 H, 5′-H, CH_2OCH_3), 3.02 (s, 3 H, CH_2OCH_3), 3.90−3.98 (m, 1 H, 2′-H), 4.67 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 6.51 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 14.2, 15.5 (+, C-6, OCH_2CH_3), 21.4 (−, C-5), 22.6 (−, C-4′), 28.2 (−, C-3′), 35.4 (−, C-5′), 48.9 (−, CH_2OCH_3), 58.8, 59.9 (+, C-2′, CH_2OCH_3), 71.0 (−, OCH_2CH_3), 74.0 (−, C-4), 119.1 (+, C-2), 157.9 ($C_{quat.}$, C-3), 220.3, 224.8 ($C_{quat.}$, CO), 283.3 ($C_{quat.}$, C-1) ppm. **Minor Rotamer:** ^1H NMR (250 MHz, C_6D_6): δ = 0.74 (t, ^3J = 7.3 Hz, 3 H, 6-H), 1.05−1.63 (m, 6 H, 4,5,4′-H), 1.10 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.35−3.30 (m, 6 H, 3′,5′-H, CH_2OCH_3), 2.84 (s, 3 H, CH_2OCH_3), 3.51−3.66 (m, 1 H, 2′-H), 4.67 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 6.48 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 14.2, 15.5 (+, C-6, OCH_2CH_3), 21.4 (−, C-5), 22.2 (−, C-4′), 27.8 (−, C-3′), 34.9 (−, C-5′), 48.6 (−, CH_2OCH_3), 58.8, 59.9 (+, C-2′, CH_2OCH_3), 71.0 (−, OCH_2CH_3), 73.6 (−, C-4), 119.1 (+, C-2), 157.8 ($C_{quat.}$, C-3), 220.3, 224.8 ($C_{quat.}$, CO), 284.7 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 431 (11) [M^+], 403 (8) [M^+ − CO], 388 (4), 347 (16) [M^+ − 3CO], 319 (18) [M^+ − 4CO], 291 (100) [M^+ − 5CO], 266 (16), 262 (50), 234 (31), 232 (12), 217 (10), 210 (10), 206 (17), 194 (10), 181 (12), 165 (31), 70 (35) [$C_4H_8N^+$], 52 (7) [Cr^+]. $C_{19}H_{25}CrNO_7$ (431.4): calcd. C 52.90, H 5.84, N 3.25; found C 52.73, H 5.77, N 3.24.

Pentacarbonyl{(2*E*)-1-ethoxy-3-[(2′*S*)-(2′-methoxycarbonyl)-pyrrolidin-1′-yl]-2-hexen-1-ylidene}chromium (3bf): According to GP1B, complex **5** (651 mg, 2.06 mmol) (R^1 = *n*Pr) in Et_2O (41 mL) was treated with (2*S*)-(methoxycarbonyl)pyrrolidine (**2f**) (266 mg, 2.06 mmol). Flash chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/CH_2Cl_2 (3:1) gave 889 mg (97%) of **3bf** [R_f = 0.55 (Et_2O); rotamer ratio = 3:1] as an orange solid, m.p. 75 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} (C−H), 2046 (C=O), 1907 (C=O), 1505, 1251, 1099, 943. **Major Rotamer:** ^1H NMR (250 MHz, C_6D_6): δ = 0.76 (t, ^3J = 7.3 Hz, 3 H, 6-H), 0.85−1.60 (m, 2 H, 4′-H), 1.08 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.15−1.33 (m, 2 H, 5-H), 1.33−1.55 (m, 2 H, 4-H), 1.86−2.13 (m, 1 H, 3′-H), 2.22−2.70 (m, 2 H, 3′,5′-H), 2.82−3.06 (m, 1 H, 5′-H), 3.42 (s, 3 H, OCH_3), 4.19 (d, ^3J = 8.0 Hz, 1 H, 2′-H), 4.66 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 6.36 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 14.2, 15.5 (+, C-6, OCH_2CH_3), 21.3, 23.2 (−, C-3′,4′), 30.3 (−, C-5), 35.1 (−, C-5′), 48.9 (−, C-4), 52.8 (+, C-2′), 61.5 (+, OCH_3), 74.1 (−, OCH_2CH_3), 118.8 (+, C-2), 155.8 ($C_{quat.}$, C-3), 171.2 ($C_{quat.}$, CO_2CH_3), 219.1, 224.3 ($C_{quat.}$, CO), 286.9 ($C_{quat.}$, C-1) ppm. **Minor Rotamer:** ^1H NMR (250 MHz, C_6D_6): δ = 0.76 (t, ^3J = 7.3 Hz, 3 H, 6-H), 0.85−1.60 (m, 2 H, 4′-H), 1.08 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.15−1.33 (m, 2 H, 5-H), 1.33−1.55 (m, 2 H, 4-H), 1.86−2.13 (m, 1 H, 3′-H), 2.51−3.06 (m, 2 H, 3′,5′-H), 3.15−3.36 (m, 1 H, 5′-H), 3.15 (s, 3 H, OCH_3), 3.89 (d, ^3J = 8.0 Hz, 1 H, 2′-H), 4.66 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 6.60 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 14.2, 15.5 (+, C-6, OCH_2CH_3), 21.8, 22.9 (−, C-3′,4′), 30.3 (−, C-5), 31.2 (−, C-5′), 48.9 (−, C-4), 49.9 (+, C-2′), 60.9 (+, OCH_3), 74.1 (−, OCH_2CH_3), 118.8 (+, C-2), 154.8 ($C_{quat.}$, C-3), 171.9 ($C_{quat.}$, CO_2CH_3), 219.1, 224.3 ($C_{quat.}$, CO), 290.5 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 445 (36) [M^+], 417 (2) [M^+ − CO], 389 (5) [M^+ − 2CO], 361 (28) [M^+ − 3CO], 333 (34) [M^+ − 4CO], 305 (100) [M^+ − 5CO], 276 (36), 262 (50), 244 (15), 179 (33), 108 (14), 70 (44) [$C_4H_8N^+$], 52 (62) [Cr^+]. $C_{19}H_{23}CrNO_8$ (445.4): calcd. C 51.23, H 5.21, N 3.14; found C 51.30, H 5.33, N 3.25.

Pentacarbonyl[(2*E*)-1-ethoxy-4,4-dimethyl-3-morpholino-2-penten-1-ylidene)]chromium (3fk): 3,3-Dimethylbutyne (**1f**) (2.60 mL, 21.2 mmol) in THF (100 mL) was treated with *n*-butyllithium (8.50 mL, 2.36 M in *n*-hexane, 20.1 mmol), chromium hexacarbonyl (4.58 g, 20.8 mmol) and Et_3OBF_4 (4.17 g, 21.9 mmol). After evaporation of the solvent, the residue was dissolved in pentane (50 mL) to which morpholine (1.97 mL, 22.6 mmol) was added. Flash chromatography on silica gel (100 g) eluting with pentane/Et_2O (from 10:1 to 0:1) gave 7.07 g (84%) of **3fk** [R_f = 0.74 (Et_2O)] as a yellow solid, m.p. 106−108 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2976 cm^{-1} (C−H), 2045 (C=O), 1968 (C=O), 1873 (C=O), 1525 (C=C), 1489, 1427, 1375, 1121, 667. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34 [s, 9 H, $C(CH_3)_3$], 1.47 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 3.50 (t, ^3J = 4.6 Hz, 4 H, NCH_2CH_2O), 3.79 (t, ^3J = 4.6 Hz, 4 H, NCH_2CH_2O), 4.68 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 6.35 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 15.8 (+, OCH_2CH_3), 29.5 [+, $C(CH_3)_3$], 38.4 [$C_{quat.}$, $C(CH_3)_3$], 54.6 (−, NCH_2CH_2O), 66.4 (−, NCH_2CH_2O), 73.0 (−, OCH_2CH_3), 116.2 (+, C-2), 170.3 ($C_{quat.}$, C-3), 220.3, 224.8 ($C_{quat.}$, CO), 276.10 ($C_{quat.}$, C-1) ppm.

MS (70 eV): *m/z* (%) = 417 (6) [M^+], 361 (5) [$M^+ - 2CO$], 333 (21) [$M^+ - 3CO$], 305 (18) [$M^+ - 4CO$], 277 (67) [$M^+ - 5CO$], 249 (30) [$M^+ - 5CO - C_2H_4$], 219 (100) [$M^+ - 5CO - C_4H_{10}$], 203 (11), 192 (11), 137 (12), 52 (10) [Cr^+]. $C_{18}H_{23}CrNO_7$ (417.4): calcd. C 51.80, H 5.55; found C 52.03, H 5.75.

Pentacarbonyl[(2*E*)-5-*tert*-butyldimethylsiloxy-3-(dimethylamino)-1-ethoxyhex-2-en-1-ylidene]chromium (3ka): According to GP1A, 4-(*tert*-butyldimethylsilyloxy)pent-1-yne (**1k**) (1.98 g, 9.98 mmol) in THF (50 mL) was treated with *n*-butyllithium (4.25 mL, 2.36 M in *n*-hexane, 10.0 mmol), chromium hexacarbonyl (2.20 g, 10.0 mmol), Et_3OBF_4 (2.30 g, 12.1 mmol) and a 40% aqueous solution of dimethylamine (1.3 mL, 10.0 mmol). Flash chromatography on silica gel (40 g) eluting with pentane/Et_2O (1:1) gave 4.19 g (85%) of **3ka** [R_f = 0.63 (Et_2O/pentane, 1:1)] as a yellow solid, m.p. 72−75 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2929 cm^{-1} (C−H), 2044 (C=O), 1913 (C=O), 1567, 1535, 1433, 1273, 1091, 933. ^1H NMR (250 MHz, C_6D_6): δ = −0.12 [s, 3 H, $SiCH_3$], −0.06 [s, 3 H, $SiCH_3$], 0.82 [s, 9 H, $SiC(CH_3)_3$], 1.00 (d, ^3J = 7.0 Hz, 3 H, 6-H), 1.05 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.94 (dd, ^2J = 11.4, ^3J = 11.9 Hz, 1 H, 4-H), 2.32 [s, 3 H, $N(CH_3)_2$], 2.36 [s, 3 H, $N(CH_3)_2$], 2.87 (dd, ^2J = 11.4, ^3J = 2.5 Hz, 1 H, 4-H), 4.02 (m, 1 H, 5-H), 4.62 (m, 2 H, OCH_2CH_3), 6.41 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.0, −4.9 [+, $Si(CH_3)_2$], 15.7 (+, OCH_2CH_3), 24.6 (+, C-6), 25.82 [+, $SiC(CH_3)_3$], 25.85 [$C_{quat.}$, $SiC(CH_3)_3$], 40.6 (−, C-4), 40.9, 41.6 [+, $N(CH_3)_2$], 69.3 (+, C-5), 73.9 (−, OCH_2CH_3), 118.0 (+, C-2), 156.0 ($C_{quat.}$, C-3), 220.4, 224.2 ($C_{quat.}$, CO), 285.3 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m/z* (%) = 491 (2) [M^+], 463 (7) [$M^+ - CO$], 435 (4) [$M^+ - 2CO$], 407 (8) [$M^+ - 3CO$], 379 (2) [$M^+ - 4CO$], 351 (100) [$M^+ - 5CO$], 322 (14), 307 (18), 305 (18), 294 (18), 281 (18), 170 (12), 168 (17), 126 (20), 124 (17), 52 (5) [Cr^+]. $C_{21}H_{33}CrNO_7Si$ (491.6): calcd. C 51.31, H 6.77; found C 51.25, H 6.89.

Pentacarbonyl[(2*E*)-6-bromo-3-(dimethylamino)-1-ethoxy-2,6-heptadien-1-ylidene]chromium (3na): According to GP1A, 2-bromohex-1-en-5-yne (**1n**) (3.18 g, 20.0 mmol) in Et_2O (100 mL) was treated with *n*-butyllithium (8.47 mL, 2.36 M in *n*-hexane, 20.0 mmol), chromium hexacarbonyl (4.40 g, 20.0 mmol), Et_3OBF_4 (4.37 g, 23.0 mmol) and a 40% aqueous solution of dimethylamine (2.59 mL, 21.6 mmol). Flash chromatography on silica gel (120 g) eluting with pentane/Et_2O (from 5:1 to 0:1) gave 7.60 g (84%) of **3na** [R_f = 0.51 (Et_2O)] as a yellow solid, m.p. 77−78 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2979 cm^{-1}, 2938, 2864 (C−H), 2046 (C=O), 1629 (C=C), 1443, 1344, 1144, 882, 743. ^1H NMR (250 MHz, C_6D_6): δ = 1.10 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.80−2.32 [m, 8 H, 5-H, $N(CH_3)_2$], 2.46 (m_c, 2 H, 4-H), 4.63 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 5.15 (s, 1 H, 7-H), 5.18 (s, 1 H, 7-H), 6.35 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 15.6 (+, OCH_2CH_3), 30.0 (−, C-4), 38.9 (−, C-5), 40.9 [+, $N(CH_3)_2$], 74.4 (−, OCH_2CH_3), 110.2 ($C_{quat.}$, C-6), 117.3 (−, C-7), 118.2 (+, C-2), 156.4 ($C_{quat.}$, C-3), 220.1, 224.8 ($C_{quat.}$, CO), 287.9 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m/z* (%) = 453/451 (3/2) [M^+], 425/423 (3/2) [$M^+ - CO$], 369/367 (22/20) [$M^+ - 3CO$], 180 (100) [$M^+ - Cr(CO)_5 - Br$], 152 (18), 101 (31), 55 (41), 52 (2) [Cr^+]. $C_{16}H_{18}BrCrNO_6$ (452.2): calcd. C 42.50, H 4.01, N 3.10; found C 42.67, H 4.05, N 3.07.

Pentacarbonyl[(2*E*)-7-bromo-5,5-bis(ethoxycarbonyl)-3-(dimethylamino)-1-ethoxy-2,7-octadien-1-ylidene]chromium (3oa): According to GP1A, diethyl 6-bromo-6-hepten-1-yne-4,4-dicarboxylate (**1o**) (1.30 g, 4.10 mmol) in THF (100 mL) was treated with *n*-butyllithium (1.74 mL, 2.36 M in *n*-hexane, 4.10 mmol), chromium hexacarbonyl (0.90 g, 4.09 mmol), Et_3OBF_4 (0.95 g, 5.00 mmol) and a 40% aqueous solution of dimethylamine (0.56 mL, 4.66 mmol). Flash chromatography on silica gel (40 g) eluting with pentane/Et_2O (from 8:1 to 0:1) gave 2.36 g (94%) of **3oa** [R_f = 0.62 (Et_2O)] as an orange solid, m.p. 87 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2918 cm^{-1} (C−H), 2045 (C=O), 1735 (C=O), 1617 (C=C), 1533, 1330, 812, 673. ^1H NMR (250 MHz, C_6D_6): δ = 0.87 (t, ^3J = 7.2 Hz, 6 H, $CO_2CH_2CH_3$), 1.26 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.36 [s, 6 H, $N(CH_3)_2$], 3.32 (s, 2 H, 6-H), 3.36 (s, 2 H, 4-H), 3.92 (q, ^3J = 7.2 Hz, 4 H, $CO_2CH_2CH_3$), 4.78 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 5.32 (s, 1 H, 8-H), 5.40 (s, 1 H, 8-H), 6.38 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 12.7 (+, 2 × $CO_2CH_2CH_3$), 15.1 (+, OCH_2CH_3), 32.6 (−, C-6), 40.9 [+, $N(CH_3)_2$], 45.6 (−, C-4), 57.1 ($C_{quat.}$, C-5), 61.1 (−, 2 × $CO_2CH_2CH_3$), 73.1 (−, OCH_2CH_3), 118.7 (+, C-2), 120.6 (−, C-8), 127.0 ($C_{quat.}$, C-7), 154.1 ($C_{quat.}$, C-3), 168.2 ($C_{quat.}$, 2 × $CO_2CH_2CH_3$), 219.1, 223.5 ($C_{quat.}$, CO), 286.2 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m/z* (%) = 583/581 (1/1) [$M^+ - CO$], 527/525 (3/3), 471/469 (37/36) [$M^+ - 5CO$], 338 (61) [$M^+ - Cr(CO)_5 - Br$], 237 (100), 193 (99), 149 (79), 52 (90) [Cr^+]. $C_{23}H_{28}BrCrNO_{10}$ (610.4): calcd. C 45.26, H 4.62, N 2.29; found C 45.43, H 4.72, N 2.11.

5-(Dimethylamino)-3-ethoxy-1,2,5-trimethyl-1,3-cyclopentadiene (7aaaa): According to GP2A, a solution of complex **3aa** (1.66 g, 4.98 mmol) in pyridine (100 mL) was treated with 2-butyne (**1aa**) (798 mg, 14.8 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (60 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 1:2) gave 797 mg (82%) of **7aaaa** [R_f = 0.46, (pentane/Et_2O, 3:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2979 cm^{-1}, 2818, 2779 (C−H), 1633 (C=C), 1594 (C=C), 1457, 1204, 1042, 740. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.16 (s, 3 H, CH_3), 1.31 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.63 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 2.10 [s, 6 H, $N(CH_3)_2$], 3.81 (m, 2 H, OCH_2CH_3), 4.77 (s, 1 H, 4-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.8 (+, CH_3), 9.7 (+, CH_3), 14.4 (+, OCH_2CH_3), 22.1 (+, CH_3), 39.9 [+, $N(CH_3)_2$], 64.3 (−, OCH_2CH_3), 71.3 ($C_{quat.}$, C-5), 95.5 (+, C-4), 128.4 ($C_{quat.}$, C-2), 144.4 ($C_{quat.}$, C-1), 160.2 ($C_{quat.}$, C-3) ppm.

5-Dimethyamino-1-[2′-(1′′,3′′-dioxolan-2′′-yl)ethyl]-3-ethoxy-5-methyl-1,3-cyclopentadiene (7aar) and 5-(Dimethylamino)-2-[2′-(1′′,3′′-dioxolan-2′′-yl)ethyl]-3-ethoxy-5-methyl-1,3-cyclopentadiene (8aar): According to GP2A, a solution of complex **3aa** (660 mg, 1.98 mmol) in pyridine (40 mL) was treated with 2-(pent-3′-ynyl)-1,3-dioxolane (**1r**) (750 mg, 5.95 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (40 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 0:1) gave 458 mg (86%) of **7aar** [R_f = 0.70 (Et_2O)] and 38 mg (7%) of **8aar** [R_f = 0.20 (Et_2O)] as colorless oils. **7aar:** IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 2818, 2775 (C−H), 1635 (C=C), 1581 (C=C), 1444, 1403, 1198, 1032, 733. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.21 (s, 3 H, CH_3), 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.88 (m_c, 2 H, 2′-H), 2.13 [s, 6 H, $N(CH_3)_2$], 2.16 (m_c, 2 H, 1′-H), 3.79−3.99 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 4.84 (d, ^4J = 1.8 Hz, 1 H, 4-H), 4.91 (t, ^3J = 4.6 Hz, 1 H, 2′′-H), 5.63 (d, ^4J = 1.8 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.5 (+, OCH_2CH_3), 20.6 (−, C-2′), 22.5 (+, CH_3), 31.0 (−, C-1′), 39.9 [+, $N(CH_3)_2$], 64.4, 64.9 (−, OCH_2CH_2O, OCH_2CH_3), 72.9 ($C_{quat.}$, C-5), 97.0 (+, C-4), 104.1 (+, C-2′′), 121.0 (+, C-2), 157.5 ($C_{quat.}$, C-1), 159.2 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 267 (51) [M^+], 238 (100) [$M^+ - C_2H_5$], 229 (9), 163 (26), 148 (48), 136 (20), 108 (13), 99 (57), 84 (40), 73 (34), 45 (15). $C_{15}H_{25}NO_3$ (267.4): calcd. C 67.38, H 9.43; found C 67.26, H 9.43.

8aar: IR (film): $\tilde{\nu}$ = 2977 cm^{-1}, 2883, 2779 (C−H), 1636 (C=C), 1584 (C=C), 1446, 1372, 1199, 1042, 737. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (s, 3 H, CH_3), 1.24 (t, ^3J = 7.0 Hz, 3 H,

OCH_2CH_3), 1.81 (m_c, 2 H, 2′-H), 2.19 [s, 6 H, $N(CH_3)_2$], 2.21 (m_c, 2 H, 1′-H), 3.79−3.90 (m, 6 H, OCH_2CH_2O, OCH_2CH_3), 4.77 (d, ^5J = 1.8 Hz, 1 H, 4-H), 4.81 (t, ^3J = 4.6 Hz, 1 H, 2′′-H), 5.77 (d, ^4J = 1.8 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3 (+, OCH_2CH_3), 20.9 (−, C-2′), 21.6 (+, CH_3), 31.8 (−, C-1′), 40.3 [+, $N(CH_3)_2$], 64.4, 64.7 (−, OCH_2CH_2O, OCH_2CH_3), 69.9 ($C_{quat.}$, C-5), 102.1 (+, C-4), 104.0 (+, C-2′′), 135.6 (+, C-1), 139.6 ($C_{quat.}$, C-2), 158.2 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 267 (71) [M^+], 238 (44) [$M^+ - C_2H_5$], 222 (14), 166 (31), 152 (88), 136 (33), 109 (16), 99 (100), 73 (29), 45 (11).

5-(Dimethylamino)-3-ethoxy-5-methyl-1-[2′-(2′′-methyl-1′′,3′′-dioxolan-2′′-yl)ethyl]-1,3-cyclopentadiene (7aas) and 5-(Dimethylamino)-3-ethoxy-5-methyl-2-[2′-(2′′-methyl-1′′,3′′-dioxolan-2′′-yl)ethyl]-1,3-cyclopentadiene (8aas): According to GP2A, a solution of complex **3aa** (2.00 g, 6.00 mmol) in pyridine (100 mL) was treated with 2-(but-3′-ynyl)-2-methyldioxolane (**1s**) (1.10 g, 7.85 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (60 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 0:1) gave 1.32 g (78%) of **7aas** [R_f = 0.30 (Et_2O)] and 110 mg (7%) of **8aas** [R_f = 0.08, (Et_2O)] as colorless oils. **7aas**: IR (film): $\tilde{\nu}$ = 2967 cm^{-1} (C−H), 2879 (C−H), 1609 (C=C), 1456, 1260, 1211, 1084, 1052, 974, 948. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (s, 3 H, CH_3), 1.30 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.32 (s, 3 H, CH_3), 1.85 (m_c, 2 H, 2′-H), 2.09−2.13 [m, 8 H, $N(CH_3)_2$, 1′-H], 3.82 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 3.91 (br. s, 4 H, OCH_2CH_2O), 4.81 (d, ^4J = 1.2 Hz, 1 H, 4-H), 5.58 (d, ^4J = 1.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 20.5 (−, C-1′), 22.5, 23.9 (+, CH_3), 36.1 (−, C-2′), 39.9 [+, $N(CH_3)_2$], 64.4, 64.6 (−, OCH_2CH_3, OCH_2CH_2O), 72.9 ($C_{quat.}$, C-5), 96.7 (+, C-4), 109.6 ($C_{quat.}$, C-2′′), 120.1 (+, C-2), 157.8 ($C_{quat.}$, C-1), 159.2 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 281 (28) [M^+], 252 (61) [$M^+ - CH_2CH_3$], 236 (8) [$M^+ - HN(CH_3)_2$], 224 (8), 166 (10), 150 (25), 136 (10), 108 (9), 87 (100) [$CH_3C(OCH_2CH_2O)^+$], 44 (37) [$N(CH_3)_2^+$]. $C_{16}H_{27}NO_3$ (281.4): calcd. C 68.29, H 9.67; found C 67.50, H 9.48.

8aas: IR (film): $\tilde{\nu}$ = 2979 cm^{-1} (C−H), 2891 (C−H), 2776 (C−H), 1623 (C=C), 1448, 1256, 1188, 1056, 859. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.29 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.79 (m_c, 2 H, 2′-H), 2.18−2.26 [m, 8 H, $N(CH_3)_2$, 1′-H], 3.76 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 3.89 (br. s, 4 H, OCH_2CH_2O), 4.78 (s, 1 H, 4-H), 5.76 (s, 1 H, 1-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 21.0 (−, C-1′), 21.6, 23.6 (+, CH_3), 36.9 (−, C-2′), 40.3 [+, $N(CH_3)_2$], 64.4, 64.5 (−, OCH_2CH_3, OCH_2CH_2O), 69.9 ($C_{quat.}$, C-5), 102.0 (+, C-4), 109.7 ($C_{quat.}$, C-2′′), 135.0 (+, C-1), 140.1 ($C_{quat.}$, C-2), 158.3 ($C_{quat.}$, C-3) ppm.

1-[2′,2′-Bis(methoxycarbonylethyl]-5-dimethyamino-3-ethoxy-5-propyl-1,3-cyclopentadiene (7bat): According to GP2B, to a solution of complex **3ba** (300 mg, 0.83 mmol) in acetonitrile (7 mL) at 80 °C was slowly added a solution of dimethyl prop-1-yn-3-ylmalonate (**1t**) (425 mg, 2.50 mmol) in acetonitrile (2 mL) over a period of 18 h, and the mixture was stirred at this temperature for an additional 2 h. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (5:1) gave 125 mg (44%) of **7bat** [R_f = 0.21 (pentane/Et_2O, 5:1)] as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.78−0.92 (m, 5 H, $CH_2CH_2CH_3$), 1.28 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.48 (m_c, 1 H, $CH_2CH_2CH_3$), 1.79 (m_c, 1 H, $CH_2CH_2CH_3$), 2.12 [s, 6 H, $N(CH_3)_2$], 2.64 (m_c, 2 H, 1′-H), 3.55−3.72 (m, 7 H, CO_2CH_3, 2′-H), 3.81 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.70 (s, 1 H, 4-H), 5.57 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3, 14.6 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 16.3 (−, $CH_2CH_2CH_3$), 36.6 (−, $CH_2CH_2CH_3$), 39.67 [+, $N(CH_3)_2$], 49.4 (−, C-1′), 52.5 (+, C-2′), 64.5 (−, OCH_2CH_3), 79.3 ($C_{quat.}$, C-5), 81.3 (+, CO_2CH_3), 96.0 (+, C-4), 122.8 (+, C-2), 151.8 ($C_{quat.}$, C-1), 159.4 ($C_{quat.}$, C-3), 169.3 ($C_{quat.}$, CO_2CH_3) ppm. MS (70 eV): *m/z* (%) = 339 (27) [M^+], 310 (79) [$M^+ - C_2H_5$], 296 (15), 208 (24), 163 (18), 111 (49), 59 (18), 41 (10). HRMS (EI) calcd. for $C_{18}H_{29}NO_5$: 339.2045 (correct HRMS).

5-(Dimethylamino)-3-ethoxy-5-propyl-1-(trimethylsilylmethyl)-1,3-cyclopentadiene (7bau): Following GP2B, to a solution of complex **3ba** (200 mg, 0.55 mmol) in acetonitrile (5.5 mL) at 80 °C was slowly added a solution of 1-(trimethylsilyl)prop-2-yne (**1u**) (187 mg, 1.67 mmol) in acetonitrile (2 mL) over a period of 10 h, and the mixture was stirred at this temperature for an additional 2 h. Chromatography on aluminum oxide (20 g, activity grade II) eluting with pentane/Et_2O (5:1) gave 83 mg (53%) of **7bau** [R_f = 0.23 (pentane/Et_2O, 5:1)] as a yellow oil. IR (film): $\tilde{\nu}$ = 2993 cm^{-1}, 2838 (C−H), 1608 (C=C), 1345, 1207, 835, 688, 531. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 [s, 9 H, $Si(CH_3)_3$], 0.71−0.98 (m, 5 H, $CH_2CH_2CH_3$), 1.34 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 1.68−1.84 (m, 2 H, $CH_2CH_2CH_3$), 2.13 (s, 2 H, $SiCH_2$), 2.16 [s, 6 H, $N(CH_3)_2$], 3.87 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 4.67 (s, 1 H, 4-H), 5.69 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −0.7 [+, $Si(CH_3)_3$], 14.5, 14.7 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 14.9 (−, $CH_2CH_2CH_3$), 16.6 (−, $SiCH_2$), 36.2 (−, $CH_2CH_2CH_3$), 39.9 [+, $N(CH_3)_2$], 64.3 (−, OCH_2CH_3), 77.4 ($C_{quat.}$, C-5), 94.0 (+, C-4), 123.3 (+, C-2), 153.2 ($C_{quat.}$, C-1), 160.2 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 281 (18) [M^+], 252 (67) [$M^+ - C_2H_5$], 238 (100), 209 (83), 181 (72), 73 (54) [$Si(CH_3)_3^+$], 42 (11). HRMS (EI) calcd. for $C_{16}H_{31}NOSi$: 281.2174 (correct HRMS).

1-[2′,2′-Bis(ethoxycarbonyl)-4′-bromopent-4′-enyl)-5-(dimethylamino)-3-ethoxy-5-propyl-1,3-cyclopentadiene (7bao): According to GP2A, a solution of complex **3ba** (300 mg, 0.83 mmol) in pyridine (17 mL) was treated with diethyl 6-bromo-6-hepten-1-yne-4,4-dicarboxylate (**1o**) (525 mg, 1.66 mmol), and the mixture was stirred at 80 °C for 20 h. Chromatography on aluminum oxide (20 g, activity grade II) gave 280 mg (69%) of **7bao** as a colorless oil. IR (film): $\tilde{\nu}$ = 2959 cm^{-1}, 2935 (C−H), 1733 (C=O), 1636 (C=C), 1334, 1191, 1043, 747, 666. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.73 (t, ^3J = 7.2 Hz, 3 H, $CH_2CH_2CH_3$), 0.85 (m_c, 2 H, $CH_2CH_2CH_3$), 1.15 (t, ^3J = 7.1 Hz, 6 H, 2 $CO_2CH_2CH_3$), 1.25 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.39 (m_c, 1 H, $CH_2CH_2CH_3$), 1.73 (m_c, 1 H, $CH_2CH_2CH_3$), 2.08 [s, 6 H, $N(CH_3)_2$], 2.60 (d, ^2J = 19.0 Hz, 1 H, 1′-H), 2.83 (d, ^2J = 19.0 Hz, 1 H, 1′-H), 3.29 (s, 2 H, 3′-H), 3.76 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 4.12 (m_c, 4 H, 2 $CO_2CH_2CH_3$), 4.66 (s, 1 H, 5′-H), 5.44 (d, ^4J = 1.6 Hz, 1 H, 4-H), 5.59 (s, 1 H, 5′-H), 5.65 (d, ^4J = 1.6 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.5 (+, OCH_2CH_3), 14.1 (+, 2 × $CO_2CH_2CH_3$), 14.3 (+, $CH_2CH_2CH_3$), 16.0 (−, $CH_2CH_2CH_3$), 28.7 (−, C-3′), 29.4 (−, $CH_2CH_2CH_3$), 36.4 [+, $N(CH_3)_2$], 43.1 (−, C-1′), 55.5 ($C_{quat.}$, C-2′), 61.3 (−, OCH_2CH_3), 64.1 (−, 2 × $CO_2CH_2CH_3$), 76.3 ($C_{quat.}$, C-5), 95.7 (+, C-4), 121.3 (−, C-5′), 122.7 (+, C-2), 127.2 ($C_{quat.}$, C-4′), 149.6 ($C_{quat.}$, C-1), 159.0 ($C_{quat.}$, C-3) 169.8 ($C_{quat.}$, 2 × CO_2Et) ppm. MS (70 eV): *m/z* (%) = 487/485 (7/6) [M^+], 458/456 (11/10) [$M^+ - C_2H_5$], 406 (18) [M^+ − Br], 361 (5), 208 (100), 178 (22), 163 (9), 72 (4). $C_{23}H_{36}BrNO_5$ (486.5): calcd. C 56.79, H 7.46; found C 56.88, H 7.48.

5-(Dimethylamino)-1,2-dimethyl-3-ethoxy-5-propyl-1,3-cyclopentadiene (7baaa): According to GP2A, a solution of complex **3ba** (300 mg, 0.83 mmol) in pyridine (6 mL) was treated with 2-butyne (**1aa**) (250 mg, 4.62 mmol), and the mixture was stirred at 55 °C for 6 days. Chromatography on aluminum oxide (30 g, activity

grade II) eluting with pentane/Et_2O (from 20:1 to 5:1) gave 177 mg (95%) of **7baaa** [R_f = 0.48 (pentane/Et_2O, 5:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2955 cm^{-1}, 2870 (C−H), 1658 (C=C), 1593, 1378, 1343, 1311, 1118, 918, 742. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.74−0.89 (m, 5 H, $CH_2CH_2CH_3$), 1.31 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.45 (m_c, 1 H, $CH_2CH_2CH_3$), 1.57 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3), 1.75 (m_c, 1 H, $CH_2CH_2CH_3$), 2.12 [s, 6 H, $N(CH_3)_2$], 3.83 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.62 (s, 1 H, 4-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.5, 10.2 (+, 2 × CH_3), 14.4, 14.7 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 16.6 (−, $CH_2CH_2CH_3$), 36.7 (−, $CH_2CH_2CH_3$), 39.8 [+, $N(CH_3)_2$], 64.3 (−, OCH_2CH_3), 74.8 ($C_{quat.}$, C-5), 93.7 (+, C-4), 130.4 ($C_{quat.}$, C-2), 142.3 ($C_{quat.}$, C-1), 160.9 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 223 (57) [M^+], 194 (79) [$M^+ - C_2H_5$], 180 (78) [$M^+ - C_3H_7$], 151 (100) [$M^+ - C_2H_5 - C_3H_7$], 123 (82), 91 (23), 67 (16). $C_{14}H_{25}NO$ (223.4): calcd. C 75.28, H 11.28; found C 75.11, H 11.10.

1-[3′-(*tert*-Butyldimethylsilyloxy)propyl]-5-(dimethylamino)-3-ethoxy-5-propyl-1,3-cyclopentadiene (7bal) and 2-[3′-(*tert*-Butyldimethylsilyloxy)propyl]-5-(dimethylamino)-3-ethoxy-5-propyl-1,3-cyclopentadiene (8bal): According to GP2A, a solution of complex **3ba** (1.99 g, 5.51 mmol) in pyridine (110 mL) was treated with (*tert*-butyltrimethylsilyloxy)pent-4-yne (**1l**) (1.64 g, 8.27 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (100 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 1.51 g (74%) of **7bal** [R_f = 0.59 (pentane/Et_2O, 3:1)] and 163 mg (8%) of **8bal** [R_f = 0.43 (pentane/Et_2O, 3:1)] as colorless oils. **7bal**: IR (film): $\tilde{\nu}$ = 2955 cm^{-1}, 2857 (C−H), 1660 (C=C), 1617, 1385, 1105, 964, 776. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.02 [s, 6 H, $Si(CH_3)_2$], 0.77−0.96 (m, 5 H, $CH_2CH_2CH_3$), 0.87 [s, 9 H, $SiC(CH_3)_3$], 1.33 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.45 (m_c, 1 H, $CH_2CH_2CH_3$), 1.68−1.85 (m, 3 H, $CH_2CH_2CH_3$, 2′-H), 1.98 (t, ^3J = 6.7 Hz, 2 H, 1′-H), 2.16 [s, 6 H, $N(CH_3)_2$], 3.66 (dt, ^3J = 6.4, ^4J = 2.2 Hz, 2 H, 3′-H), 3.86 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.67 (d, ^4J = 1.8 Hz, 1 H, 4-H), 5.68 (d, ^4J = 1.8 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.3 [+, $Si(CH_3)_2$], 14.5, 14.7 (+, OCH_2CH_3, $CH_2CH_2CH_3$), 16.6 (−, $CH_2CH_2CH_3$), 18.2 [$C_{quat.}$, $SiC(CH_3)_3$], 23.0 (−, $CH_2CH_2CH_3$), 25.9 [+, $SiC(CH_3)_3$], 29.8 (−, C-2′), 36.7 (−, C-1′), 39.8 [+, $N(CH_3)_2$], 62.9 (−, C-3′), 64.4 (−, OCH_2CH_3), 76.3 ($C_{quat.}$, C-5), 94.8 (+, C-4), 122.4 (+, C-2), 155.8 ($C_{quat.}$, C-1), 160.1 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 367 (51) [M^+], 338 (100) [$M^+ - C_2H_5$], 323 (17) [$M^+ - C_3H_8$], 237 (18), 206 (15), 164 (11), 138 (18), 91 (13), 75 (39), 73 (27), 45 (46). $C_{21}H_{41}NO_2Si$ (367.7): calcd. C 68.61, H 11.24, N 3.81; found C 68.77, H 11.13, N 3.68.

8bal: IR (film): $\tilde{\nu}$ = 3026 cm^{-1}, 2929 (C−H), 1653 (C=C), 1592, 1380, 1118, 702. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.02 [s, 6 H, $Si(CH_3)_2$], 0.78−1.00 (m, 5 H, $CH_2CH_2CH_3$), 0.89 [s, 9 H, $SiC(CH_3)_3$], 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.55−1.69 (m_c, 3 H, $CH_2CH_2CH_3$, 2′-H), 1.74 (t, ^3J = 6.7 Hz, 2 H, 1′-H), 1.82 (m, 1 H, $CH_2CH_2CH_3$), 2.26 [s, 6 H, $N(CH_3)_2$], 3.62 (t, ^3J = 6.4 Hz, 2 H, 3′-H), 3.82 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.80 (d, ^4J = 1.8 Hz, 1 H, 4-H), 5.82 (d, ^4J = 1.8 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.5 [+, $Si(CH_3)_2$], 14.5, 14.8 (+, OCH_2CH_3, $CH_2CH_2CH_3$), 18.4 [$C_{quat.}$, $SiC(CH_3)_3$], 18.6 (−, $CH_2CH_2CH_3$), 22.7 (−, $CH_2CH_2CH_3$), 26.0 [+, $SiC(CH_3)_3$], 31.1 (−, C-2′), 37.5 (−, C-1′), 40.2 [+, $N(CH_3)_2$], 62.9 (−, C-3′), 64.5 (−, OCH_2CH_3), 76.3 ($C_{quat.}$, C-5), 100.9 (+, C-4), 134.2 (+, C-1), 141.0 ($C_{quat.}$, C-2), 158.9 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 367 (42) [M^+], 338 (52) [$M^+ - C_2H_5$], 323 (82) [$M^+ - C_3H_8$], 238 (12), 220 (30), 205 (100), 164 (18), 73 (12), 53 (11). $C_{21}H_{41}NO_2Si$ (367.7): calcd. C 68.61, H 11.24; found C 67.55, H 10.80.

1-[5′-Bromo-3′-(*tert*-butyldimethylsilyloxy)hex-5′-enyl]-5-(dimethylamino)-3-ethoxy-5-propyl-1,3-cyclopentadiene (7baw): According to GP2A, a solution of complex **3ba** (300 mg, 0.83 mmol) in pyridine (17 mL) was treated with 4-(*tert*-butyldimethylsilyloxy)-2-bromooct-1-en-7-yne (**1w**) (300 mg, 0.94 mmol), and the mixture was stirred at 80 °C for 4 days. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 345 mg (85%) of **7baw** [R_f = 0.27 (pentane/Et_2O, 5:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2955 cm^{-1}, 2856, 2820 (C−H), 1653, 1635 (C=C), 1584, 1472, 1337, 1256, 1096, 836, 775. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.05 [s, 6 H, $Si(CH_3)_2$], 0.83 (t, ^3J = 7.1 Hz, 3 H, $CH_2CH_2CH_3$), 0.85 [s, 9 H, $SiC(CH_3)_3$], 1.33 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.45 (m_c, 1 H, 2′-H), 1.62−1.98 (m, 5 H, 2′-H, 4′-H, $CH_2CH_2CH_3$), 1.99−2.14 (m, 2 H, $CH_2CH_2CH_3$), 2.15 [s, 6 H, $N(CH_3)_2$], 2.57 (m_c, 2 H, 1′-H), 3.85 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.06 (m_c, 1 H, 3′-H), 4.69 (s, 1 H, 4-H), 5.40 (d, ^2J = 1.2 Hz, 1 H, 6′-H), 5.58 (s, 1 H, 2-H), 5.66 (d, ^2J = 1.2 Hz, 1 H, 6′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −4.5 [+, $Si(CH_3)_2$], 14.5 (+, $CH_2CH_2CH_3$), 14.7 (+, OCH_2CH_3), 16.6 (−, $CH_2CH_2CH_3$), 18.0 (−, C-2′), 20.9 (−, C-1′), 21.8 [$C_{quat.}$, $SiC(CH_3)_3$], 25.8 [+, $SiC(CH_3)_3$], 33.1 (−, $CH_2CH_2CH_3$), 33.4 (−, C-4′), 39.8 [+, $N(CH_3)_2$], 64.4 (−, OCH_2CH_3), 69.2 (+, C-3′), 76.4 ($C_{quat.}$, C-5), 94.9 (+, C-4), 119.0 (−, C-6′), 122.0 (+, C-2), 131.2 ($C_{quat.}$, C-5′), 155.8 ($C_{quat.}$, C-1), 160.0 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 487/485 (100/95) [M^+], 458/456 (97/91) [$M^+ - C_2H_5$], 406 (16) [M^+ − Br], 321 (22), 222 (42), 139 (45), 107 (29), 59 (16). HRMS (EI) calcd. for $C_{24}H_{44}BrNO_2Si$ (486.6): 485.2324 (correct HRMS).

1-[2′,2′-Bis(ethoxycarbonyl)-3-ethoxy-5′-(trimethylsilyl)pent-4′-ynyl]-5-(dimethylamino)-5-propyl-1,3-cyclopentadiene (7bax): According to GP2A, a solution of complex **3ba** (500 mg, 1.38 mmol) in pyridine (28 mL) was treated with diethyl 1-(trimethylsilyl)-1,6-heptadiynyl-4,4-dicarboxylate (**1x**) (925 mg, 3.00 mmol), and the mixture was stirred at 60 °C for 36 h. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 5:1) gave 534 mg (81%) of **7bax** [R_f = 0.47 (pentane/Et_2O, 5:1)] as a pale-yellow oil. IR (film): $\tilde{\nu}$ = 3012 cm^{-1}, 2889 (C−H), 2176 (C≡C), 1729 (C=O), 1636 (C=C), 1181, 1032, 837. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.09 [s, 9 H, $Si(CH_3)_3$], 0.77−1.11 (m, 6 H, OCH_2CH_3, $CH_2CH_2CH_3$), 1.12 (m_c, 6 H, $CO_2CH_2CH_3$), 1.55 (m_c, 2 H, $CH_2CH_2CH_3$), 1.81 (m_c, 2 H, $CH_2CH_2CH_3$), 2.18 [s, 6 H, $N(CH_3)_2$], 2.70 (d, ^2J = 21.7 Hz, 1 H, 1′-H), 2.96 (d, ^2J = 21.7 Hz, 1 H, 1′-H), 3.08 (s, 2 H, 3′-H), 3.83 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.16 (m_c, 4 H, $CO_2CH_2CH_3$), 4.73 (d, ^4J = 1.5 Hz, 1 H, 4-H), 5.63 (d, ^4J = 1.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −0.2 [+, $Si(CH_3)_3$], 13.9 (+, OCH_2CH_3), 14.3 (+, $CH_2CH_2CH_3$), 14.7 (+, 2 × $CO_2CH_2CH_3$), 16.0 (−, $CH_2CH_2CH_3$), 23.9 (−, C-3′), 29.0 (−, $CH_2CH_2CH_3$), 36.6 (−, C-1′), 39.7 [+, $N(CH_3)_2$], 55.6 ($C_{quat.}$, C-2′), 61.5 (−, 2 × $CO_2CH_2CH_3$), 64.4 (−, OCH_2CH_3), 86.3, 88.0 ($C_{quat.}$, C-5,4′), 95.2 (+, C-4), 101.5 ($C_{quat.}$, C-5′), 122.6 (+, C-2), 149.7 ($C_{quat.}$, C-1), 159.6 ($C_{quat.}$, C-3), 169.8 ($C_{quat.}$, 2 × CO_2Et) ppm. MS (70 eV): *m/z* (%) = 477 (7) [M^+], 448 (89) [$M^+ - C_2H_5$], 404 (100), 359 (9), 208 (96), 164 (25), 75 (80), 44 (43). $C_{26}H_{43}NO_5Si$ (477.7): calcd. C 65.37, H 9.07; found C 65.49, H 9.10.

5-Cyclopropyl-5-(dimethylamino)-3-ethoxy-1-(2′-ethoxycyclopropyl)-1,3-cyclopentadiene (7cay): According to GP2A, a solution of complex **3ca** (200 mg, 0.56 mmol) in hexane (11 mL) was treated with (*E*)-2-ethoxy-1-ethynylcyclopropane (**1y**) (123 mg, 1.12 mmol), and the mixture was stirred at 80 °C for 42 h. Chromatography on silica gel (30 g) eluting with pentane/Et_2O (5:1) gave 134 mg (87%) of **7cay** [R_f = 0.27 (pentane/Et_2O, 5:1); *dr* 1.3:1] as a

colorless oil. IR (film): $\tilde{\nu}$ = 2977 cm^{-1}, 2938 (C−H), 1632 (C=C), 1582, 1454, 1343, 1198, 1033, 938, 742. ^1H NMR (250 MHz, $CDCl_3$): δ = −0.85 (m_c, 1 H, *c*Pr-H), 0.17 (m_c, 1 H, *c*Pr-H), 0.32 (m_c, 1 H, *c*Pr-H), 0.72 (m_c, 1 H, *c*Pr-H), 0.98−1.17 (m, 8 H, 2 × OCH_2CH_3, *c*Pr-H), 1.28 (m_c, 1 H, *c*Pr-H), 1.87−2.16 (m, 1 H, *c*Pr-H), 2.40 [s, 6 H, $N(CH_3)_2$], 3.17 (m_c, 1 H, *c*Pr-H), 3.30−3.72 (m, 4 H, OCH_2CH_3), 4.30 (m_c, 1 H, 4-H), 5.23 (m_c, 1 H, 2-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, plus APT). **Major Diastereomer:** δ = −0.1, 8.1 (−, *c*Pr-C), 11.2 (+, *c*Pr-C), 15.4 (+, OCH_2CH_3), 16.2 (+, *c*Pr-C), 17.2 (−, *c*Pr-C), 17.2 (+, OCH_2CH_3), 40.8 [+, $N(CH_3)_2$], 62.1 (+, *c*Pr-C), 64.0, 65.9 (−, OCH_2CH_3), 77.8 (−, C-5), 98.0 (+, C-4), 115.9 (+, C-2), 159.7 (−, C-1), 162.8 (−, C-3). **Minor Diastereomer:** δ = −0.2, 8.1 (−, *c*Pr-C), 11.7 (+, *c*Pr-C), 15.5 (+, OCH_2CH_3), 17.0 (+, *c*Pr-C), 17.1 (−, *c*Pr-C), 17.5 (+, OCH_2CH_3), 40.6 [+, $N(CH_3)_2$], 63.99 (+, *c*Pr-C), 64.5, 65.8 (−, OCH_2CH_3), 77.8 (−, C-5), 97.8 (+, C-4), 116.4 (+, C-2), 159.6 (−, C-1), 162.8 (−, C-3) ppm. MS (70 eV): *m*/*z* (%) = 277 (2) [M^+], 248 (21) [$M^+ - C_2H_5$], 232 (79) [$M^+ - OC_2H_5$], 203 (42), 175 (23), 132 (18), 102 (100), 91 (19), 58 (37), 41 (6). HRMS (EI) calcd. for $C_{17}H_{27}NO_2$: 277.2041 (correct HRMS).

1,5-Bis(3′-*tert*-butyldimethylsilyloxypropyl)-5-(dimethylamino)-3-ethoxy-1,3-cyclopentadiene (7lal) and 2,5-Bis(3′-*tert*-butyldimethylsilyloxypropyl)-5-(dimethylamino)-3-ethoxy-1,3-cyclopentadiene (8lal): According to GP2A, a solution of complex **3la** (500 mg, 1.02 mmol) in pyridine (20 mL) was treated with *tert*-butyl-trimethylsilyloxypent-4-yne (**1l**) (605 mg, 3.05 mmol), and the mixture was stirred at 80 °C for 20 h. Chromatographic purification on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (3:1) gave 389 mg (77%) of **7lal** [R_f = 0.68 (pentane/Et_2O, 5:1)] and 40 mg (8%) of **8lal** [R_f = 0.19 (pentane/Et_2O, 5:1)] as colorless oils. **7lal**: IR (film): $\tilde{\nu}$ = 2957 cm^{-1}, 2855 (C−H), 1636 (C=C), 1472, 1339, 1144, 1043, 839, 663, 540. ^1H NMR (250 MHz, $CDCl_3$): δ = −0.01 (s, 6 H, $SiCH_3$), 0.01 (s, 6 H, $SiCH_3$), 0.86 [s, 18 H, 2 × $SiC(CH_3)_3$], 1.11 (m_c, 2 H, $OCH_2CH_2CH_2$), 1.31 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.49 (m_c, 2 H, $OCH_2CH_2CH_2$), 1.68−2.12 (m, 4 H, $CH_2CH_2CH_2O$), 2.15 [s, 6 H, $N(CH_3)_2$], 3.49 (t, ^3J = 6.3 Hz, 2 H, $OCH_2CH_2CH_2$), 3.65 (t, ^3J = 6.3 Hz, 2 H, $OCH_2CH_2CH_2$), 3.83 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.67 (s, 1 H, 4-H), 5.69 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.3 [+, 2 × $Si(CH_3)_2$], 14.5 (+, OCH_2CH_3), 18.3 [$C_{quat.}$, 2 × $SiC(CH_3)_3$], 23.0 (−, $CH_2CH_2CH_2O$), 25.9 [+, 2 × $SiC(CH_3)_3$], 26.9 (−, $CH_2CH_2CH_2O$), 29.9, 30.5 (−, 2 × $CH_2CH_2CH_2O$), 39.9 [+, $N(CH_3)_2$], 63.0, 63.7 (−, 2 × $CH_2CH_2CH_2O$), 64.4 (−, OCH_2CH_3), 76.2 ($C_{quat.}$, C-5), 94.8 (+, C-4), 122.4 (+, C-2), 155.7 ($C_{quat.}$, C-1), 160.3 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 497 (100) [M^+], 468 (92) [$M^+ - C_2H_5$], 324 (10), 73 (24) [$SiMe_3^+$], 59 (5). HRMS (EI) calcd. for $C_{27}H_{55}NO_3Si_2$: 497.3720 (correct HMRS).

8lal: IR (film): $\tilde{\nu}$ = 2953 cm^{-1}, 2857 (C−H), 1635 (C=C), 1472, 1255, 1101, 774, 572. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.02 [s, 6 H, $Si(CH_3)_2$], 0.04 [s, 6 H, $Si(CH_3)_2$], 0.87 [s, 9 H, $SiC(CH_3)_3$], 0.89 [s, 9 H, $SiC(CH_3)_3$], 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.51 (m_c, 2 H, $CH_2CH_2CH_2O$), 1.69−1.80 (m, 4 H, $CH_2CH_2CH_2O$), 2.18−2.21 (m, 2 H, $CH_2CH_2CH_2O$), 2.26 [s, 6 H, $N(CH_3)_2$], 3.55 (t, ^3J = 6.3 Hz, 2 H, $OCH_2CH_2CH_2$), 3.62 (t, ^3J = 6.3 Hz, 2 H, $OCH_2CH_2CH_2$), 3.83 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.78 (d, ^5J = 0.6 Hz, 1 H, 4-H), 5.80 (d, ^5J = 0.6 Hz, 1 H, 1-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus. DEPT): δ = −5.3 [+, 2 × $Si(CH_3)_2$], 14.5 (+, OCH_2CH_3), 18.4 [$C_{quat.}$, 2 × $SiC(CH_3)_3$], 22.7 (−, $CH_2CH_2CH_2O$), 26.0 [+, 2 × $SiC(CH_3)_3$], 28.6 (−, $CH_2CH_2CH_2O$), 31.3 (−, 2 × $CH_2CH_2CH_2O$), 40.3 [+, $N(CH_3)_2$], 62.9, 63.8 (−, 2 × $CH_2CH_2CH_2O$), 64.5 (−, OCH_2CH_3), 73.1 ($C_{quat.}$, C-5), 100.9 (+, C-4), 134.1 (+, C-1), 141.3 ($C_{quat.}$, C-2), 159.0 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 497 (61) [M^+], 468 (32) [$M^+ - C_2H_5$], 324 (100), 188 (37), 164 (14), 75 (38), 47 (10). HRMS (EI) calcd. for $C_{27}H_{55}NO_3Si_2$: 497.3720 (correct HRMS).

1-(3′-Butenyl)-5-(3′′-*tert*-butyldimethylsilyloxypropyl)-5-(dimethylamino)-3-ethoxy-1,3-cyclopentadiene (7laz) and 2-(3′-Butenyl)-5-(3′′-*tert*-butyldimethylsilyloxypropyl)-5-(dimethylamino)-3-ethoxy-1,3-cyclopentadiene (8laz): According to GP2B, to a solution of complex **3la** (750 mg, 1.53 mmol) in CH_3CN (31 mL) at 80 °C was slowly added a solution of 1-hexen-5-yne (**1z**) (367 mg, 4.58 mmol) in acetonitrile (2 mL) over a period of 8 h, and the mixture was stirred at this temperature for an additional 2 h. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 5:1 to 3:1) gave 144 mg (25%) of **7laz** [R_f = 0.42 (pentane/Et_2O, 5:1)] and 63 mg (11%) of **8laz** [R_f = 0.13 (pentane/Et_2O, 5:1)] as colorless oils. **7laz**: IR (film): $\tilde{\nu}$ = 2989 cm^{-1}, 2874 (C−H), 1636 (C=C), 1584, 1471, 1250, 1038, 918, 769. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.02 [s, 6 H, $Si(CH_3)_2$], 0.88 [s, 9 H, $SiC(CH_3)_3$], 1.13 (m_c, 2 H, 2′′-H), 1.37 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.51 (m_c, 1 H, 1′′-H), 1.86−2.12 (m, 3 H, 1′′-H, 2′-H), 2.18 [s, 6 H, $N(CH_3)_2$], 2.30 (m_c, 2 H, 1′-H), 3.57 (t, ^3J = 7.0 Hz, 2 H, 3′′-H), 3.86 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.69 (d, ^4J = 1.7 Hz, 1 H, 4-H), 4.95 (dd, ^2J = 1.7, ^3J = 10.1 Hz, 1 H, 4′-H), 5.04 (dd, ^4J = 1.7, ^3J = 17.1 Hz, 1 H, 4′-H), 5.74 (d, ^4J = 1.7 Hz, 1 H, 2-H), 5.85 (m_c, 1 H, 3′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.4 [+, $Si(CH_3)_2$], 14.4 (+, OCH_2CH_3), 18.2 [$C_{quat.}$, $SiC(CH_3)_3$], 25.9 [+, $SiC(CH_3)_3$], 26.0, 26.8 (−, C-2′,2′′), 30.5 × 2 (−, C-1′,1′′), 39.8 [+, $N(CH_3)_2$], 63.6, 64.4 (−, OCH_2CH_3, C-3′′), 76.2 ($C_{quat.}$, C-5), 94.8 (+, C-4), 114.7 (−, C-4′), 122.7 (+, C-2), 138.1 (+, C-3′), 155.1 ($C_{quat.}$, C-1), 160.2 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 379 (75) [M^+], 350 (83) [$M^+ - C_2H_5$], 338 (100), 206 (11), 174 (6), 89 (8), 73 (17) [$SiMe_3^+$]. HRMS (EI) calcd. for $C_{22}H_{41}NO_2Si$: 379.2906 (correct HRMS).

8laz: IR (film): $\tilde{\nu}$ = 2935 cm^{-1}, 2858 (C−H), 1640 (C=C), 1580, 1256, 834, 598. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.03 [s, 6 H, $Si(CH_3)_2$], 0.86 [s, 9 H, $SiC(CH_3)_3$], 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.51 (m_c, 4 H, 1′′,2′′-H), 1.70 (m_c, 2 H, 2′-H), 2.20 [s, 6 H, $N(CH_3)_2$], 2.21 (m_c, 2 H, 1′-H), 3.59 (t, ^3J = 7.0 Hz, 2 H, 3′′-H), 3.82 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.68 (d, ^5J = 1.7 Hz, 1 H, 4-H), 4.96 (dd, ^2J = 1.5, ^3J = 10.0 Hz, 1 H, 4′-H), 5.04 (dd, ^2J = 1.5, ^3J = 17.2 Hz, 1 H, 4′-H), 5.81 (d, ^5J = 1.7 Hz, 1 H, 1-H), 5.82 (m_c, 1 H, 3′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.3 [+, $Si(CH_3)_2$], 14.5 (+, OCH_2CH_3), 18.3 [$C_{quat.}$, $SiC(CH_3)_3$], 25.9 [+, $SiC(CH_3)_3$], 26.0, 28.6 (−, C-2′,2′′), 30.24 (−, C-1′), 32.1 (−, C-1′′), 40.3 [+, $N(CH_3)_2$], 63.8, 64.6 (−, OCH_2CH_3, C-3′′), 73.2 ($C_{quat.}$, C-5), 100.8 (+, C-4), 114.5 (−, C-4′), 134.4 (+, C-1), 138.5 (+, C-3′), 141.0 ($C_{quat.}$, C-2), 159.0 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 379 (11) [M^+], 350 (18) [$M^+ - C_2H_5$], 293 (100), 206 (38), 132 (17), 84 (91), 75 (100), 59 (21), 47 (19).

5-(3′-Bromobut-3′-enyl)-5-(dimethylamino)-3-ethoxy-1,2-dimethyl-1,3-cyclopentadiene (7naaa): According to GP2A, a solution of complex **3na** (200 mg, 0.44 mmol) in pyridine (10 mL) was treated with 2-butyne (**1aa**) (95.0 mg, 1.76 mmol), and the mixture was stirred at 70 °C for 3 days. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 2:1) gave 110 mg (79%) of **7naaa** [R_f = 0.27 (pentane/Et_2O, 2:1)] as a colorless oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.62 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.58−1.82 (m, 1 H, 1′-H), 1.84−2.04 (m, 3 H, 1′,2′-H), 2.15 [s, 6 H, $N(CH_3)_2$], 3.84 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.66 (s, 1 H, 4-H), 5.28 (s, 1 H, 4′-H), 5.31 (s, 1 H, 4′-H) ppm. ^{13}C NMR

(62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.7, 10.2 (+, CH_3), 14.5 (+, OCH_2CH_3), 32.7 (−, C-1′), 36.0 (−, C-2′), 39.9 [+, $N(CH_3)_2$], 64.5 (−, OCH_2CH_3), 74.2 ($C_{quat.}$, C-5), 93.0 (+, C-4), 115.8 (−, C-4′), 131.3 ($C_{quat.}$, C-2), 135.7 ($C_{quat.}$, C-3′), 141.6 ($C_{quat.}$, C-1), 161.3 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 315/313 (22/21) [M^+], 286/284 (67/65) [$M^+ - C_2H_5$], 234 (53) [M^+ − Br], 194 (63), 180 (70), 161 (100), 152 (62), 122 (42), 91 (27). HRMS (EI) calcd. for $C_{15}H_{24}BrNO$: 313.1041 (correct HRMS).

5-[4′-Bromo-2′,2′-bis(ethoxycarbonyl)-4′-pentenyl]-5-(dimethylamino)-3-ethoxy-1,2-dimethyl-1,3-cyclopentadiene (7oaaa): According to GP2A, a solution of complex **3oa** (1.00 g, 1.64 mmol) in pyridine (33 mL) was treated with 2-butyne (**1aa**) (352 mg, 6.51 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (50 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 5:1) gave 575 mg (74%) of **7oaaa** [R_f = 0.21 (pentane/Et_2O, 5:1)] as a colorless oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (m_c, 6 H, 2 × $CO_2CH_2CH_3$), 1.34 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.62 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 2.06 [s, 6 H, $N(CH_3)_2$], 2.30 (d, ^2J = 15.0 Hz, 1 H, 1′-H), 2.79 (s, 1 H, 3′-H), 2.82 (s, 1 H, 3′-H), 3.19 (d, ^2J = 15.0 Hz, 1 H, 1′-H), 3.79 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.21 (m_c, 4 H, 2 × $CO_2CH_2CH_3$), 4.54 (s, 1 H, 4-H), 5.46 (s, 1 H, 5′-H), 5.52 (s, 1 H, 5′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 9.0, 10.6 (+, 2 × CH_3), 13.7 (+, 2 × $CO_2CH_2CH_3$), 14.4 (+, OCH_2CH_3), 33.6 (−, C-1′), 39.6 [+, $N(CH_3)_2$], 43.72 (−, C-3′), 55.64 ($C_{quat.}$, C-2′), 61.2 (−, 2 × $CO_2CH_2CH_3$), 64.4 (−, OCH_2CH_3), 72.9 ($C_{quat.}$, C-5), 91.9 (+, C-4), 119.4 (−, C-5′), 128.8 ($C_{quat.}$, C-4′), 132.3 ($C_{quat.}$, C-2), 142.3 ($C_{quat.}$, C-1), 161.5 ($C_{quat.}$, C-3), 169.9, 170.3 ($C_{quat.}$, CO_2Et) ppm. MS (70 eV): *m/z* (%) = 473/471 (8/9) [M^+], 429/427 (17/18), 392 (55) [M^+ − Br], 347 (18), 194 (100), 152 (31), 44 (9). HRMS (EI) calcd. for $C_{22}H_{34}BrNO_5$: 471.1620 (correct HRMS). $C_{22}H_{34}BrNO_5$ (472.4): calcd. C 55.93, H 7.25; found C 55.74, H 7.38.

5-(Dimethylamino)-3-ethoxy-1-(trimethylsilyl)-5-(5′-(trimethylsilyl)-4′-pentynyl)-1,3-cyclopentadiene (7qag) and 5-(Dimethylamino)-3-ethoxy-2-(trimethylsilyl)-5-(5′-(trimethylsilyl)-4′-pentynyl)-1,3-cyclopentadiene (8qag): According to GP2A, a solution of complex **3qa** (550 mg, 1.20 mmol) in pyridine (24 mL) was treated with trimethylsilylethyne (**1g**) (471 mg, 4.80 mmol), and the mixture was stirred at 80 °C for 16 h. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 2:1) gave 210 mg (48%) of **7qag** [R_f = 0.71 (pentane/Et_2O, 5:1)] and 17 mg (4%) of **8qag** [R_f = 0.13 (pentane/Et_2O, 5:1)] as colorless oils. **7qag:** IR (film): $\tilde{\nu}$ = 2956 cm^{-1}, 2819, 2174 (C≡C), 1606 (C=C), 1322, 1248, 841, 760. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.12, 0.13 [s, 18 H, $Si(CH_3)_3$], 1.31 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.48−1.62 (m, 2 H, 2′-H), 1.64−1.78 (m, 2 H, 1′-H), 2.17 (t, ^3J = 7.2 Hz, 2 H, 3′-H), 2.26 [s, 6 H, $N(CH_3)_2$], 3.80 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.76 (d, ^4J = 2.2 Hz, 1 H, 4-H), 6.35 (d, ^4J = 2.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −1.3, 0.1 [+, $Si(CH_3)_3$], 14.5 (+, OCH_2CH_3), 20.4 (−, C-2′), 24.6 (−, C-1′), 33.9 (−, C-3′), 40.2 [+, $N(CH_3)_2$], 64.5 (−, OCH_2CH_3), 76.7 ($C_{quat.}$, C-5), 84.44 ($C_{quat.}$, C-4′), 99.3 (+, C-4), 107.54 ($C_{quat.}$, C-5′), 124.1 (+, C-2), 142.9 ($C_{quat.}$, C-1), 162.6 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 363 (17) [M^+], 334 (98) [$M^+ - C_2H_5$], 224 (58), 180 (19), 73 (100) [$SiMe_3^+$]. $C_{20}H_{37}NOSi_2$ (363.7): calcd. C 66.05, H 10.25; found C 67.01, H 10.42.

8qag: IR (film): $\tilde{\nu}$ = 2955 cm^{-1}, 2816, 2778 (C−H), 2174 (C≡C), 1618 (C=C), 1320, 1250, 1024, 736. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.03, 0.09 [s, 18 H, $Si(CH_3)_3$], 1.22 (m_c, 2 H, 2′-H), 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.69−2.08 (m, 2 H, 1′-H), 2.14 (m_c, 2 H, 3′-H), 2.18 [s, 6 H, $N(CH_3)_2$], 3.82 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.72 (d, ^5J = 1.6 Hz, 1 H, 4-H), 6.29 (d, ^5J = 1.6 Hz, 1 H, 1-H).

5-(Dimethylamino)-3-ethoxy-1,2-dimethyl-5-[5′-(trimethylsilyl)-4′-pentynyl]-1,3-cyclopenta-2,4-diene (7qaaa): According to GP2A, a solution of complex **3qa** (300 mg, 0.66 mmol) in pyridine (13 mL) was treated with 2-butyne (**1aa**) (142 mg, 2.62 mmol), and the mixture was stirred at 80 °C for 4 days. Chromatography on aluminum oxide (20 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1)] gave 97 mg (46%) of **7qaaa** [R_f = 0.38 (pentane/Et_2O, 5:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2955 cm^{-1}, 2173 (C≡C), 1653 (C=C), 1384, 1249, 843, 760. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.12 [s, 9 H, $Si(CH_3)_3$], 1.11 (m_c, 2 H, 2′-H), 1.34 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.61 (d, ^5J = 1.0 Hz, 3 H, CH_3), 1.62 (m_c, 2 H, 1′-H), 1.69 (d, ^5J = 1.0 Hz, 3 H, CH_3), 1.91 (m_c, 2 H, 3′-H), 2.15 [s, 6 H, $N(CH_3)_2$], 3.84 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.64 (s, 1 H, 4-H) ppm. ^{13}C NMR (62.9 MHz, plus DEPT, $CDCl_3$): δ = 0.1 [+, $Si(CH_3)_3$], 8.7, 10.2 (+, CH_3), 14.5 (+, OCH_2CH_3), 20.3 (−, C-2′), 22.7 (−, C-3′), 33.3 (−, C-1′), 39.8 [+, $N(CH_3)_2$], 64.4 (−, OCH_2CH_3), 74.5 ($C_{quat.}$, C-5), 84.4 ($C_{quat.}$, C-5′), 93.4 (+, C-4), 107.7 ($C_{quat.}$, C-4′), 130.8 ($C_{quat.}$, C-2), 142.1 ($C_{quat.}$, C-1), 161.0 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 319 (3) [M^+], 290 (38) [$M^+ - C_2H_5$], 274 (50) [$M^+ - OC_2H_5$], 246 (81) [M^+ − $SiMe_3$], 180 (51), 152 (100), 73 (48) [$SiMe_3^+$], 44 (9). HRMS (EI) calcd. for $C_{19}H_{33}NOSi$: 319.2331 (correct HRMS).

5-(Dimethylamino)-5-[2′-(1′′,3′′-dioxolan-2′′-yl)ethyl]-3-ethoxy-1-methyl-1,3-cyclopentadiene (7raa): According to GP2A, a solution of complex **3ra** (839 mg, 2.00 mmol) in pyridine (40 mL) was treated with propyne (**1a**) (1.19 mL, 20.0 mmol), and the mixture was stirred at 80 °C for 4 days. Chromatographic purification on aluminum oxide (60 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 0:1) gave 471 mg (88%) of **7raa** [R_f = 0.10 (pentane/Et_2O, 3:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2978 cm^{-1}, 2818, 2781 (C−H), 1640 (C=C), 1585, 1442, 1405, 1203, 1032, 743. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.13 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.52−1.67 (m, 2 H, 1′-H), 1.71 (s, 3 H, CH_3), 1.80−1.98 (m_c, 2 H, 2′-H), 2.23 [s, 6 H, $N(CH_3)_2$], 3.37−3.47 (m, 2 H, OCH_2CH_3), 3.49−3.67 (m, 4 H, OCH_2CH_2O), 4.67 (d, ^4J = 1.7 Hz, 1 H, 4-H), 4.85 (t, ^3J = 5.5 Hz, 1 H, 2′′-H), 5.63 (d, ^4J = 1.8 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 12.8 (+, CH_3), 14.5 (+, OCH_2CH_3), 28.3, 28.6 (−, C-1′,2′), 39.9 [+, $N(CH_3)_2$], 64.4, 64.8, 64.9 (−, OCH_2CH_2O, OCH_2CH_3), 76.0 ($C_{quat.}$, C-5), 94.7 (+, C-4), 105.1 (+, C-2′′), 124.8 (+, C-2), 152.0 ($C_{quat.}$, C-1), 161.0 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 267 (25) [M^+], 238 (100) [$M^+ - C_2H_5$], 229 (7), 166 (20), 150 (5), 138 (13), 136 (9), 108 (3), 99 (24), 84 (10). $C_{15}H_{25}NO_3$ (267.4): calcd. C 67.38, H 9.42; found C 67.22, H 9.31.

5-(Dimethylamino)-3-ethoxy-1-phenyl-5-propyl-1,3-cyclopentadiene (7bah): According to GP2B, to a solution of complex **3ba** (200 mg, 0.55 mmol) in acetonitrile (11 mL) at 80 °C was slowly added a solution of phenylethyne (**1h**) (113 mg, 1.11 mmol) in acetonitrile (2 mL) over a period of 15 h, and the mixture was stirred at this temperature for an additional 2 h. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (5:1) gave 119 mg (80%) of **7bah** [R_f = 0.54 (pentane/Et_2O, 5:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 3058 cm^{-1}, 2955, 2869 (C−H), 1622 (C=C), 1345, 1109, 769, 695. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.77 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.30 (m_c, 5 H, $CH_2CH_2CH_3$), 1.74−2.06 (m, 2 H, $CH_2CH_2CH_3$), 2.31 [s, 6 H, $N(CH_3)_2$], 4.00 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 5.05 (d, ^4J = 1.8 Hz, 1 H, 4-H), 6.47 (d, ^4J = 1.8 Hz, 1 H, 2-H), 7.24−7.48 (m, 3 H, Ph−H), 7.82−7.98 (m, 2 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.5, 14.7 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 16.6 (−,

$CH_2CH_2CH_3$), 37.2 (−, $CH_2CH_2CH_3$), 40.1 [+, $N(CH_3)_2$], 64.6 (−, OCH_2CH_3), 81.4 ($C_{quat.}$, C-5), 98.5 (+, C-4), 126.3, 127.20, 128.2 × 2 (+, C-2, Ph−C), 135.0 ($C_{quat.}$, Ph−C), 150.8 ($C_{quat.}$, C-1), 159.6 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 271 (1) [M^+], 242 (1) [$M^+ - C_2H_5$], 174 (18), 159 (100), 105 (12), 43 (9) [$C_3H_7^+$].

5-(Dimethylamino)-3-ethoxy-2-hexyl-5-isopropyl-1-phenyl-1,3-cyclopentadiene (7dahe) and 5-(Dimethylamino)-3-ethoxy-1-hexyl-5-isopropyl-2-phenyl-1,3-cyclopentadiene (8dahe): According to GP2A, a solution of complex **3da** (553 mg, 1.53 mmol) in pyridine (31 mL) was treated with 1-phenyloct-1-yne (**1he**) (295 mg, 1.58 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (40 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 1:1) gave 382 mg (70%) of **7dahe** and **8dahe** [R_f = 0.59, pentane/Et_2O (3:1); ratio 2.2:1] as a colorless oil. After identification of the mixture and chromatography again on aluminum oxide [40 g, activity grade II; elution with pentane/Et_2O (10:1)], **7dahe** was obtained. IR (film): $\tilde{\nu}$ = 2929 cm^{-1} (C−H), 2859, 2823, 1636 (C=C), 1601, 1586, 1457, 1373, 1192, 1139, 701. **7dahe:** (major stereoisomer): ^1H NMR (250 MHz, $CDCl_3$): δ = 0.76 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.83 (t, ^3J = 6.5 Hz, 3 H, 6′-H), 0.92 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.13−1.30 (m, 8 H, 2′,3′,4′,5′-H), 1.38 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.19 (t, ^3J = 7.7 Hz, 2 H, 1′-H), 2.25 [s, 6 H, $N(CH_3)_2$], 2.43 (sept, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 3.92 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.76 (s, 1 H, 4-H), 7.22−7.38 (m, 5 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0, 14.5 (+, OCH_2CH_3, C-6′), 17.1 (+, *i*Pr-C), 18.1 (+, *i*Pr-C), 22.5, 24.6, 29.0, 29.2 (−, C-2′,3′,4′,5′), 29.6 (+, *i*Pr-C), 31.4 (−, C-1′), 39.7 [+, $N(CH_3)_2$], 64.4 (−, OCH_2CH_3), 79.4 ($C_{quat.}$, C-5), 98.3 (+, C-4), 126.2, 127.8, 128.9 (+, Ph−C), 139.0, 140.0 ($C_{quat.}$, C-2, Ph−C), 142.8 ($C_{quat.}$, C-1), 159.8 ($C_{quat.}$, C-3). **8dahe:** (Minor stereoisomer). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.83 (t, ^3J = 6.5 Hz, 3 H, 6′-H), 0.98 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.02−1.25 (m, 11 H, 2′,3′,4′,5′-H, *i*Pr-H), 1.27 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.19 (t, ^3J = 7.7 Hz, 2 H, 1′-H), 2.37 [s, 6 H, $N(CH_3)_2$], 2.43 (sept, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 3.92 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.68 (s, 1 H, 4-H), 7.22−7.38 (m, 5 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0, 14.3 (+, OCH_2CH_3, C-6′), 17.3 (+, *i*Pr-C), 18.4 (+, *i*Pr-C), 22.5, 27.0, 28.0, 30.0 (−, C-2′,3′,4′,5′), 30.4 (+, *i*Pr-C), 31.2 (−, C-1′), 39.5 [+, $N(CH_3)_2$], 64.5 (−, OCH_2CH_3), 78.4 ($C_{quat.}$, C-5), 97.2 (+, C-4), 126.6, 127.6, 129.2 (+, Ph−C), 134.7, 137.2 ($C_{quat.}$, C-2, Ph−C), 149.4 ($C_{quat.}$, C-1), 158.9 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 355 (14) [M^+], 326 (13) [$M^+ - C_2H_5$], 312 (100) [$M^+ - C_3H_7$], 284 (10). HRMS (EI) calcd. for $C_{24}H_{37}NO$: 355.2875 (correct HRMS).

5-(Dimethylamino)-3-ethoxy-5-isopropyl-1-[(4′-ethoxycarbonyl)-phenyl]-2-phenyl-1,3-cyclopentadiene (7dahh[1]) and 5-(Dimethylamino)-3-ethoxy-5-isopropyl-2-[(4′-ethoxycarbonyl)-phenyl]-2-phenyl-1,3-cyclopentadiene (8dahh[1]): According to GP2A, a solution of complex **3da** (469 mg, 1.30 mmol) in pyridine (23 mL) was treated with 1-[(4′-ethoxycarbonyl)phenyl]-2-phenylethyne (**1hh[1]**) (325 mg, 1.30 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (40 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 194 mg (36%) of **7dahh[1]** and **8dahh[1]** [R_f = 0.53 (pentane/Et_2O, 3:1); ratio 1:1.3] as a yellow oil. IR (film): $\tilde{\nu}$ = 2976 cm^{-1} (C−H), 1717 (C=O), 1635 (C=C), 1457, 1368, 1321, 1196, 1106, 1021. **Major Stereoisomer:** ^1H NMR (250 MHz, $CDCl_3$): δ = 0.76 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.80 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.35 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.36 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.37 [s, 6 H, $N(CH_3)_2$], 2.40−2.60 (m, 1 H, *i*Pr-H), 3.97 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.33 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 5.00 (s, 1 H, 4-H), 7.11−7.27 (m, 5 H, Ph−H), 7.39 (d, ^3J = 8.4 Hz, 2 H, Ph−H), 7.83 (d, ^3J = 8.4 Hz, 2 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3, 14.4 (+, OCH_2CH_3), 16.9 (+, *i*Pr-C), 18.0 (+, *i*Pr-C), 30.0 (+, *i*Pr-C), 39.6 [+, $N(CH_3)_2$], 60.7 (−, OCH_2CH_3), 64.9 (−, OCH_2CH_3), 79.6 ($C_{quat.}$, C-5), 99.4 (+, C-4), 126.9, 128.0, 128.9, 129.7, 130.1 (+, Ph−C), 128.2, 133.2, 138.5, 143.2 ($C_{quat.}$, C-2, Ph−C), 144.7 ($C_{quat.}$, C-1), 158.2 ($C_{quat.}$, C-3), 166.6 ($C_{quat.}$, CO_2Et). **Minor Stereoisomer:** ^1H NMR (250 MHz, $CDCl_3$): δ = 0.94 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.98 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.35 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.36 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.36 [s, 6 H, $N(CH_3)_2$], 2.40−2.60 (m, 1 H, *i*Pr-H), 3.97 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.33 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.97 (s, 1 H, 4-H), 7.11−7.27 (m, 5 H, Ph−H), 7.39 (d, ^3J = 8.4 Hz, 2 H, Ph−H), 7.86 (d, ^3J = 8.2 Hz, 2 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3, 14.4 (+, OCH_2CH_3), 17.1 (+, *i*Pr-C), 17.8 (+, *i*Pr-C), 30.4 (+, *i*Pr-C), 39.8 [+, $N(CH_3)_2$], 60.7 (−, OCH_2CH_3), 64.9 (−, OCH_2CH_3), 79.6 ($C_{quat.}$, C-5), 99.8 (+, C-4), 127.1, 127.8, 129.0, 129.6, 130.0 (+, Ph−C), 128.5, 137.8, 137.9, 140.2 ($C_{quat.}$, C-2, Ph−C), 147.7 ($C_{quat.}$, C-1), 158.4 ($C_{quat.}$, C-3), 166.6 ($C_{quat.}$, CO_2Et) ppm. MS (70 eV): *m/z* (%) = 419 (20) [M^+], 390 (24) [$M^+ - C_2H_5$], 376 (100) [$M^+ - C_3H_7$], 348 (12), 347 (10), 250 (11), 211 (10). HRMS (EI) calcd. for $C_{27}H_{33}NO_3$: 419.2460 (correct HRMS).

5-(Dimethylamino)-3-ethoxy-5-isopropyl-1-[4′-(methoxycarbonyl)-phenyl]-2-(4′′-methoxyphenyl)-1,3-cyclopentadiene (7dah^{2}h^3) and 5-(Dimethylamino)-3-ethoxy-5-isopropyl-2-[(4′′-methoxycarbonyl)-phenyl]-1-(4′-methoxyphenyl)-1,3-cyclopentadiene (8dah^{2}h^3): According to GP2A, a solution of complex **3da** (723 mg, 2.00 mmol) in pyridine (40 mL) was treated with 4-(4′-methoxyphenylethynyl)-benzoic acid methyl ester (**1h^{2}h^3**) (586 mg, 2.20 mmol), and the mixture was stirred at 80 °C for 3 days. The alkyne **1h^{2}h^3** with very low solubility could not be completely removed. Two successive chromatographic separations on aluminum oxide (60 g, activity grade II) eluting with pentane/Et_2O (first time: from 20:1 to 3:1, second time: from 6:1 to 3:1) gave 548 mg of a yellow solid, which contained **1h^{2}h^3** (30%) and products [**7dah^{2}h^3** and **8dah^{2}h^3**; 70%; ratio 1:1.1; R_f = 0.59 (pentane/Et_2O, 3:1)]. The amount of products totaled 384 mg (44% from complex **3da**). **Major Stereoisomer:** ^1H NMR (250 MHz, $CDCl_3$): δ = 0.76 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.80 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.34 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.35 [s, 6 H, $N(CH_3)_2$], 2.40−2.60 (m, 1 H, *i*Pr-H), 3.75 (s, 3 H, CO_2CH_3), 3.87 (s, 3 H, OCH_3), 3.97 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.95 (s, 1 H, 4-H), 6.70 (d, ^3J = 8.8 Hz, 2 H, Ph−H), 7.17 (d, ^3J = 8.8 Hz, 2 H, Ph−H), 7.38 (d, ^3J = 8.4 Hz, 2 H, Ph−H), 7.85 (d, ^3J = 8.4 Hz, 2 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 17.1 (+, *i*Pr-C), 17.8 (+, *i*Pr-C), 30.4 (+, *i*Pr-C), 39.8 [+, $N(CH_3)_2$], 52.2, 55.3 (+, CO_2CH_3, OCH_3), 64.4 (−, OCH_2CH_3), 79.5 ($C_{quat.}$, C-5), 99.7 (+, C-4), 113.3 (+, Ph−C), 114.7, 125.4, 127.7 ($C_{quat.}$, C-2, Ph−C), 129.1, 129.8, 131.3 (+, Ph−C), 139.7, 143.6 ($C_{quat.}$, C-1, Ph−C), 158.5, 158.6 ($C_{quat.}$, C-3, Ph−C), 166.6 ($C_{quat.}$, CO_2Me). **Minor Stereoisomer:** ^1H NMR (250 MHz, $CDCl_3$): δ = 0.93 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.97 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.36 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.36 [s, 6 H, $N(CH_3)_2$], 2.40−2.60 (m, 1 H, *i*Pr-H), 3.75 (s, 3 H, CO_2CH_3), 3.87 (s, 3 H, OCH_3), 3.97 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.98 (s, 1 H, 4-H), 6.71 (d, ^3J = 8.8 Hz, 2 H, Ph−H), 7.05 (d, ^3J = 8.8 Hz, 2 H, Ph−H), 7.22 (d, ^3J = 8.4 Hz, 2 H, Ph−H), 7.83 (d, ^3J = 8.4 Hz, 2 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 16.8 (+, *i*Pr-C), 17.9 (+, *i*Pr-C), 30.1 (+, *i*Pr-C), 39.6 [+, $N(CH_3)_2$], 52.2, 55.3 (+, CO_2CH_3, OCH_3), 64.4 (−, OCH_2CH_3), 79.5 ($C_{quat.}$, C-5), 99.7 (+, C-4), 113.4 (+, Ph−C),

114.7, 125.4, 128.0 ($C_{quat.}$, C-2, Ph−C), 128.9, 130.1, 130.8 (+, Ph−C), 138.9, 143.6 ($C_{quat.}$, C-1, Ph−C), 158.3, 158.6 ($C_{quat.}$, C-3, Ph−C), 166.6 ($C_{quat.}$, CO_2Me) ppm. MS (70 eV): *m/z* (%) = 435 (28) [M^+], 406 (13) [$M^+ - C_2H_5$], 392 (60) [$M^+ - C_3H_7$], 266 (100) [M^+ of **1h²h³**]. HRMS (EI) calcd. for $C_{27}H_{33}NO_4$: 435.2410 (correct HRMS).

5-(Dimethylamino)-3-ethoxy-5-isopropyl-1,2-dimethyl-1,3-cyclopentadiene (7daaa) and **5-(Dimethylamino)-2-ethoxy-4-isopropyl-1,5-dimethyl-1,3-cyclopentadiene (17daaa):** According to GP2A, a solution of complex **3da** (903 mg, 2.50 mmol) in pyridine (50 mL) was treated with 2-butyne (**1aa**) (348 mg, 6.43 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 1:2) gave 218 mg (39%) of **17daaa** [R_f = 0.58 (pentane/Et_2O, 3:1)] and 212 mg (38%) of **7daaa** [R_f = 0.22 (pentane/Et_2O, 3:1)] as colorless oils. **7daaa:** IR (film): $\tilde{\nu}$ = 2945 cm^{-1} (C−H), 2819 (C−H), 2779 (C−H), 1643 (C=C), 1596 (C=C), 1462, 1382, 1323, 1201, 1043, 998. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.84 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.85 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.33 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.67 (s, 6 H, CH_3), 2.13 (sept, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 2.23 [s, 6 H, $N(CH_3)_2$], 3.85 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.55 (s, 1 H, 4-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.4 (+, CH_3), 13.0 (+, CH_3), 14.5 (+, OCH_2CH_3), 16.9 (+, *i*Pr-C), 18.1 (+, *i*Pr-C), 29.9 (+, *i*Pr-C), 39.5 [+, $N(CH_3)_2$], 65.3 (−, OCH_2CH_3), 77.0 ($C_{quat.}$, C-5), 96.2 (+, C-4), 131.4 ($C_{quat.}$, C-2), 141.5 ($C_{quat.}$, C-1), 160.3 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 223 (28) [M^+], 194 (17) [$M^+ - C_2H_5$], 180 (100) [$M^+ - C_3H_7$], 151 (75) [$M^+ - C_3H_7 - C_2H_5$], 136 (18), 123 (8), 107 (6), 91 (7), 77 (5), 58 (10).

17daaa: IR (film): $\tilde{\nu}$ = 2968 cm^{-1} (C−H), 2866 (C−H), 1654 (C=C), 1457, 1379, 1109, 976, 837. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.08 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.12 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.21 (s, 3 H, CH_3), 1.25 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.69 (s, 3 H, CH_3), 2.25 [s, 6 H, $N(CH_3)_2$], 2.55 (sept, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 3.90 (q, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 3.91 (q, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 5.95 (d, ^4J = 1.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 9.8 (+, CH_3), 15.4 (+, OCH_2CH_3), 20.9 (+, CH_3), 23.3 (+, *i*Pr-C), 24.8 (+, *i*Pr-C), 26.1 (+, *i*Pr-C), 39.5 [+, $N(CH_3)_2$], 65.0 (−, OCH_2CH_3), 72.7 ($C_{quat.}$, C-5), 117.9 (+, C-3), 118.6 ($C_{quat.}$, C-4), 150.9 ($C_{quat.}$, C-1), 162.1 ($C_{quat.}$, C-2) ppm. MS (70 eV): *m/z* (%) = 223 (23) [M^+], 194 (12) [$M^+ - C_2H_5$], 180 (100) [$M^+ - C_3H_7$], 152 (58), 136 (18), 121 (8), 107 (8), 77 (5).

5-(Dimethylamino)-3-ethoxy-5-isopropyl-1-(4′-trifluoromethylphenyl)-2-[2′′-(4′′′-trifluoromethylphenyl)ethynyl]-1,3-cyclopentadiene (7dah⁴z), 5-(Dimethylamino)-3-ethoxy-5-isopropyl-2-(4′-trifluoromethylphenyl)-1-[2′′-(4′′′-trifluoromethylphenyl)ethynyl]-1,3-cyclopentadiene (8dah⁴z) and 5-(Dimethylamino)-2-ethoxy-4-isopropyl-5-(4′-trifluoromethylphenyl)-1-[2′′-(4′′′-trifluoromethylphenyl)ethynyl]-1,3-cyclopentadiene (17dah⁴z): According to GP2A, a solution of complex **3da** (723 mg, 2.00 mmol) in pyridine (40 mL) was treated with 1,4-bis(*p*-trifluoromethylphenyl)butadiyne (**1h⁴h⁴**) (713 mg, 2.11 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (60 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 1:1) gave 172 mg (17%) of **17dah⁴z** [R_f = 0.89 (pentane/Et_2O, 3:1)], 68 mg (7%) of **7dah⁴z** [R_f = 0.84 (pentane/Et_2O, 3:1)] and 501 mg (49%) of **8dah⁴z** [R_f = 0.31 (pentane/Et_2O, 3:1)] as yellow oils. **7dah⁴z:** IR (film): $\tilde{\nu}$ = 2979 cm^{-1} (C−H), 2187 (C≡C), 1653 (C=C), 1616, 1559, 1457, 1323, 1126, 1062. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.75 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.81 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.47 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.33 [s, 6 H, $N(CH_3)_2$], 2.37 (sept, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 4.03 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.98 (s, 1 H, 4-H), 7.50−7.64 (m, 6 H, Ph−H), 8.15 (d, ^3J = 8.2 Hz, 2 H, 2′,6′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 17.0 (+, *i*Pr-C), 17.4 (+, *i*Pr-C), 31.4 (+, *i*Pr-C), 40.1 [+, $N(CH_3)_2$], 65.3 (−, OCH_2CH_3), 80.9 ($C_{quat.}$, C-5), 85.6, 94.0 ($C_{quat.}$, C≡C), 99.4 (+, C-4), 121.7 ($C_{quat.}$, Ph−C), 124.6, 125.2 (+, q, $^3J_{C,F}$ = 3.8 Hz, Ph−Ch), 126.9 ($C_{quat.}$, Ph−C), 129.5, 130.0 ($C_{quat.}$, q, $^2J_{C,F}$ = 32.3 Hz, C-4′,4′′′), 129.1, 131.8 (+, Ph−C), 140.4 ($C_{quat.}$, C-2), 153.4 ($C_{quat.}$, C-1), 156.5 ($C_{quat.}$, C-3) ppm. The signals of CF_3 were not detected. MS (70 eV): *m/z* (%) = 507 (80) [M^+], 478 (38), 464 (100) [$M^+ - C_3H_7$], 462 (75), 436 (12), 338 (10). HRMS (EI) calcd. for $C_{28}H_{27}F_6NO$: 507.1997 (correct HRMS).

8dah⁴z: IR (film): $\tilde{\nu}$ = 2981 cm^{-1} (C−H), 2873 (C−H), 2782 (C−H), 2187 (C≡C), 1653 (C=C), 1617, 1559, 1457, 1324, 1127, 1067. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.98 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.17 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.42 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.57 [s, 6 H, $N(CH_3)_2$], 2.62 (sept, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 4.03 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 5.01 (s, 1 H, 4-H), 7.49 (d, ^3J = 8.3 Hz, 2 H, Ph−H), 7.59 (d, ^3J = 8.3 Hz, 2 H, Ph−H), 7.70 (d, ^3J = 8.2 Hz, 2 H, Ph−H), 7.99 (d, ^3J = 8.0 Hz, 2 H, 2′,6′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3 (+, OCH_2CH_3), 16.8 (+, *i*Pr-C), 18.6 (+, *i*Pr-C), 30.5 (+, *i*Pr-C), 39.4 [+, $N(CH_3)_2$], 65.4 (−, OCH_2CH_3), 79.1 ($C_{quat.}$, C-5), 89.2, 99.1 ($C_{quat.}$, C≡C), 104.0 (+, C-4), 123.9, 124.2 ($C_{quat.}$, q, $^1J_{C,F}$ = 270.3 Hz, CF_3), 124.5, 125.3 (+, q, $^3J_{C,F}$ = 3.8 Hz, Ph−C), 127.2, ($C_{quat.}$, Ph−C), 129.4 (+, Ph−C), 129.9 × 2 ($C_{quat.}$, q, $^2J_{C,F}$ = 32.5 Hz, C-4′,4′′′), 130.1 ($C_{quat.}$, Ph−C), 131.2 (+, Ph−C), 132.5 ($C_{quat.}$, C-2), 144.7 ($C_{quat.}$, C-1), 157.3 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m/z* (%) = 507 (8) [M^+], 478 (7), 465 (26), 464 (100) [$M^+ - C_3H_7$], 436 (17). $C_{28}H_{27}F_6NO$ (507.5): calcd. C 66.27, H 5.36; found C 66.05, H 5.15.

17dah⁴z: IR (film): $\tilde{\nu}$ = 2968 cm^{-1} (C−H), 2183 (C≡C), 1653 (C=C), 1616, 1559, 1457, 1323, 1125, 1068. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.33 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.15 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.25 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.45 (sept, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 2.48 [s, 6 H, $N(CH_3)_2$], 4.67 (q, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 4.69 (q, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 5.83 (s, 1 H, 3-H), 7.27 (d, ^3J = 8.0 Hz, 2 H, Ph−H), 7.46 (d, ^3J = 8.3 Hz, 2 H, Ph−H), 7.58 (d, ^3J = 8.3 Hz, 2 H, Ph−H), 7.76 (d, ^3J = 8.0 Hz, 2 H, 2′,6′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.5 (+, OCH_2CH_3), 22.6 (+, *i*Pr-C), 24.7 (+, *i*Pr-C), 25.9 (+, *i*Pr-C), 40.3 [+, $N(CH_3)_2$], 66.4 (−, OCH_2CH_3), 83.0 ($C_{quat.}$, C-5), 90.1, 94.7, 95.2 ($C_{quat.}$, C-1, C≡C), 120.5 (+, C-3), 124.0, 124.3 ($C_{quat.}$, q, $^1J_{C,F}$ = 271.9 Hz, CF_3), 125.1 (+, q, $^3J_{C,F}$ = 3.8 Hz, Ph−C), 125.2 (+, q, $^3J_{C,F}$ = 3.8 Hz, Ph−C), 125.2 (+, Ph−C), 128.46 ($C_{quat.}$, Ph−C), 128.54, 129.4 ($C_{quat.}$, q, $^2J_{C,F}$ = 32.5 Hz, C-4′,4′′′), 130.1 (+, Ph−C), 144.3 ($C_{quat.}$, Ph−C), 165.6 ($C_{quat.}$, C-4), 167.4 ($C_{quat.}$, C-2) ppm. MS (70 eV): *m/z* (%) = 507 (88) [M^+], 478 (40), 464 (100) [$M^+ - C_3H_7$], 436 (10), 342 (42), 340 (18), 237 (26), 185 (18), 159 (15). $C_{28}H_{27}F_6NO$ (507.5): calcd. C 66.27, H 5.36; found C 66.58, H 5.68.

5-(Dimethylamino)-3-ethoxy-5-isopropyl-1-phenyl-2-(phenylethynyl)-1,3-cyclopentadiene (7dahz¹), 5-(Dimethylamino)-3-ethoxy-5-isopropyl-2-phenyl-1-(phenylethynyl)-1,3-cyclopentadiene (8dahz¹) and 5-(Dimethylamino)-2-ethoxy-4-isopropyl-5-phenyl-1-(phenylethynyl)-1,3-cyclopentadiene (17dahz¹): According to GP2A, a solution of complex **3da** (723 mg, 2.00 mmol) in pyridine (40 mL) was treated with 1,4-diphenylbutadiyne (**1hz¹**) (607 mg, 3.00 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (60 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 1:1) gave 67 mg (9%) of **17dahz¹** [R_f = 0.81 (pentane/Et_2O,

3:1)] as a yellow solid, 163 mg (22%) of **7dahz[1]** [R_f = 0.67 (pentane/Et_2O, 3:1)] as a yellow solid and 278 mg (37%) of **8dahz[1]** [R_f = 0.31 (pentane/Et_2O, 3:1)] as a yellow oil. The structures of all three compounds were assigned on the basis of HH COSY, HH NOESY and CH COSY spectra.

7dahz[1]: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.84 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 0.90 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.51 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.38 [s, 6 H, $N(CH_3)_2$], 2.43 (sept, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 4.05 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.94 (s, 1 H, 4-H), 7.30−7.51 (m, 8 H, Ph−H), 8.06 (dd, ^3J = 7.0, ^4J = 1.5 Hz, 2 H, 2′,6′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 16.8 (+, *i*Pr-C), 17.5 (+, *i*Pr-C), 31.1 (+, *i*Pr-C), 40.0 [+, $N(CH_3)_2$], 65.0 (−, OCH_2CH_3), 80.5 ($C_{quat.}$, C-5), 83.9, 94.6 ($C_{quat.}$, C≡C), 98.2 (+, C-4), 120.5, 123.4 ($C_{quat.}$, Ph−C), 127.5, 127.6, 128.0, 128.1, 128.9, 131.6 (+, Ph−C), 137.2 ($C_{quat.}$, C-2), 154.1 ($C_{quat.}$, C-1), 156.8 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 371 (100) [M^+], 356 (12), 342 (59), 328 (78) [$M^+ - C_3H_7$], 326 (90), 299 (16), 284 (17), 202 (13). HRMS (EI) calcd. for $C_{26}H_{29}NO$: 371.2349 (correct HRMS).

8dahz[1]: IR (film): $\tilde{\nu}$ = 2978 cm^{-1} (C−H), 2870 (C−H), 2185 (C≡C), 1617 (C=C), 1576, 1485, 1443, 1211, 1054, 755. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.22 (d, ^3J = 6.7 Hz, 3 H, *i*Pr-H), 1.44 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.63 [s, 6 H, $N(CH_3)_2$], 2.67 (sept, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 4.06 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.97 (s, 1 H, 4-H), 7.30−7.51 (m, 8 H, Ph−H), 7.95 (dd, ^3J = 7.0, ^4J = 1.5 Hz, 2 H, 2‴,6‴-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 16.9 (+, *i*Pr-C), 18.7 (+, *i*Pr-C), 30.3 (+, *i*Pr-C), 39.3 [+, $N(CH_3)_2$], 65.0 (−, OCH_2CH_3), 78.3 ($C_{quat.}$, C-5), 87.6, 99.7 ($C_{quat.}$, C≡C), 102.8 (+, C-4), 123.5, 128.2 ($C_{quat.}$, Ph−C), 127.6, 127.9 × 2, 128.6, 129.0, 130.9 (+, Ph−C), 132.5 ($C_{quat.}$, C-2), 144.6 ($C_{quat.}$, C-1), 157.9 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 371 (17) [M^+], 342 (13), 328 (100) [$M^+ - C_3H_7$], 300 (17). HRMS (EI) calcd. for $C_{26}H_{29}NO$: 371.2349 (correct HRMS).

17dahz[1]: IR (film): $\tilde{\nu}$ = 2964 cm^{-1} (C−H), 2868 (C−H), 2183 (C≡C), 1626 (C=C), 1569, 1488, 1333, 1070, 1030, 753. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.32 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.13 (d, ^3J = 6.8 Hz, 3 H, *i*Pr-H), 1.48 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.48 (sept, ^3J = 6.8 Hz, 1 H, *i*Pr-H), 2.50 [s, 6 H, $N(CH_3)_2$], 4.67 (q, ^3J = 7.1 Hz, 1 H, OCH_2CH_3), 4.68 (q, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 5.75 (d, ^4J = 0.7 Hz, 1 H, 3-H), 7.17−7.34 (m, 8 H, Ph−H), 7.61−7.66 (m, 2 H, 2‴,6‴-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.6 (+, OCH_2CH_3), 22.6 (+, *i*Pr-C), 24.7 (+, *i*Pr-C), 25.7 (+, *i*Pr-C), 40.3 [+, $N(CH_3)_2$], 66.1 (−, OCH_2CH_3), 83.2 ($C_{quat.}$, C-5), 87.4, 95.5, 95.8 ($C_{quat.}$, C-1, C≡C), 119.9 (+, C-3), 124.9 ($C_{quat.}$, Ph−C), 126.8, 126.9, 127.8, 128.1, 128.2, 130.1 (+, Ph−C), 139.9 ($C_{quat.}$, Ph−C), 164.0 ($C_{quat.}$, C-4), 167.0 ($C_{quat.}$, C-2) ppm. MS (70 eV): *m*/*z* (%) = 371 (100) [M^+], 356 (12), 342 (52), 328 (80) [$M^+ - C_3H_7$], 326 (92), 299 (14), 284 (13), 202 (13). HRMS (EI) calcd. for $C_{26}H_{29}NO$: 371.2349 (correct HRMS).

(4*R*,2′*S*)- and (4*S*,2′*S*)-3-*tert*-Butyl-4-[2′-(methoxymethyl)pyrrolidino]-4-propyl-2-cyclopentenone (21bef): According to GP2B, to a solution of complex **3be** (146 mg, 0.34 mmol) in acetonitrile (7 mL) at 80 °C was slowly added a solution of 3,3-dimethylbutyne (**1f**) (83.4 mg, 1.02 mmol) in acetonitrile (2 mL) over a period of 8 h, and the mixture was stirred at this temperature for an additional 16 h. Chromatography on aluminum oxide (10 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 1:2) gave 11 mg (11%) of **1st stereoisomer** [R_f = 0.28 (pentane)] and 43 mg (43%) of **2nd stereoisomer** [R_f = 0.20 (pentane)] as colorless oils. **1st Stereoisomer:** IR (film): $\tilde{\nu}$ = 2926 cm^{-1} (C−H), 1734, 1700 (C=O), 1653 (C=C), 1550, 1457, 1096, 804, 668, 641. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 7.5 Hz, 3 H, $CH_2CH_2CH_3$), 0.95−1.25 (m, 2 H, 4′-H), 1.25 [s, 9 H, $C(CH_3)_3$], 1.65−2.08 (m, 6 H, 3′-H, $CH_2CH_2CH_3$), 2.17 (AB, d, ^2J = 18.0 Hz, 1 H, 5-H), 2.48−2.58 (m, 1 H, 5′-H), 2.60−2.70 (m, 1 H, 5′-H), 2.65 (AB, d, ^2J = 18.0 Hz, 1 H, 5-H), 3.12 (dd, ^2J = 9.0, ^3J = 6.0 Hz, 1 H, CH_2OCH_3), 3.26 (dd, ^2J = 9.0, ^3J = 6.0 Hz, 1 H, CH_2OCH_3), 3.28 (s, 3 H, OCH_3), 3.52 (m_c, 1 H, 2′-H), 6.05 (s, 1 H, 2-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, plus APT): δ = 14.3 (+, $CH_2CH_2CH_3$), 18.1 (−, $CH_2CH_2CH_3$), 21.8 (−, C-4′), 27.6 (−, C-3′), 31.2 [+, $C(CH_3)_3$], 36.3 [−, $C(CH_3)_3$], 38.3 (−, $CH_2CH_2CH_3$), 43.9 (−, C-5), 44.9 (−, C-5′), 55.9, 59.1 (+, C-2′, OCH_3), 70.5 (−, C-4), 77.2 (−, CH_2OCH_3), 132.3 (+, C-2), 192.3 (−, C-3), 207.1 (−, C-1) ppm. MS (70 eV): *m*/*z* (%) = 239 (1) [M^+], 278 (1), 248 (72), 179 (19), 153 (18), 84 (35), 70 (100) [$C_4H_8N^+$]. HRMS (EI) calcd. for $C_{18}H_{31}NO_2$: 293.2354 (correct HRMS).

2nd Stereoisomer: IR (film): $\tilde{\nu}$ = 2957 cm^{-1} (C−H), 1996, 1696 (C=O), 1582, 1462, 1066, 882, 641. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 7.0 Hz, 3 H, $CH_2CH_2CH_3$), 0.97−1.22 (m, 2 H, 4′-H), 1.29 [s, 9 H, $C(CH_3)_3$], 1.60−2.03 (m, 6 H, 3′-H, $CH_2CH_2CH_3$), 2.28−2.43 (m, 1 H, 5′-H), 2.31 (AB, d, ^2J = 17.4 Hz, 1 H, 5-H), 2.41 (AB, d, ^2J = 18.0 Hz, 1 H, 5-H), 2.58−2.65 (m, 1 H, 5′-H), 2.96−3.15 (m, 2 H, 2′-H, CH_2OCH_3), 3.33−3.38 (m, 1 H, CH_2OCH_3), 3.34 (s, 3 H, OCH_3), 6.08 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.2 (+, $CH_2CH_2CH_3$), 18.0 (−, $CH_2CH_2CH_3$), 23.6 (−, C-4′), 29.1 (−, C-3′), 31.4 [+, $C(CH_3)_3$], 36.1 [$C_{quat.}$, $C(CH_3)_3$], 40.1 (−, $CH_2CH_2CH_3$), 42.4 (−, C-5), 49.8 (−, C-5′), 58.3, 59.0 (+, C-2′, OCH_3), 73.3 ($C_{quat.}$, C-4), 77.8 (−, CH_2OCH_3), 133.4 (+, C-2), 191.3 ($C_{quat.}$, C-3), 206.7 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 239 (1) [M^+], 278 (1), 248 (54), 179 (19), 138 (12), 123 (17), 84 (14), 70 (100) [$C_4H_8N^+$]. $C_{18}H_{31}NO_2$: calcd. C 73.67, H 10.65, N 4.77; found C 73.70, H 10.68, N 4.82.

(4*R*,2′*S*)- and (4*S*,2′*S*)-4-[2′-(Methoxymethyl)pyrrolidino]-2,3-dimethyl-4-propyl-2-cyclopentenone (21beaa): According to GP2A, a solution of complex **3be** (179 mg, 0.42 mmol) in pyridine (8 mL) was treated with 2-butyne (**1aa**) (67.3 mg, 1.24 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (10 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 1:2) gave 108 mg (98%) of **21beaa** [R_f = 0.10 (pentane/Et_2O, 3:1); *dr* 1.9:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2926 cm^{-1} (C−H), 1700 (C=O), 1653 (C=C), 1457, 1383, 1321, 1197, 1112, 971, 923, 734, 666. **Major Stereoisomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.70−0.98 (m, 2 H, 4′-H), 0.84 (t, ^3J = 3.8 Hz, 3 H, $CH_2CH_2CH_3$), 1.50−2.05 (m, 6 H, 3′-H, $CH_2CH_2CH_3$), 1.64 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3), 2.10−2.57 (m, 2 H, 5′-H), 2.21 (AB, d, ^2J = 18.7 Hz, 1 H, 5-H), 2.30 (AB, d, ^2J = 18.7 Hz, 1 H, 5-H), 3.00 (m_c, 2 H, CH_2OCH_3), 3.28 (m_c, 1 H, 2′-H), 3.21 (s, 3 H, OCH_3) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.8, 12.4 (+, CH_3), 14.5 (+, $CH_2CH_2CH_3$), 17.6 (−, $CH_2CH_2CH_3$), 23.3 (−, C-4′), 29.0 (−, C-3′), 39.9 (−, $CH_2CH_2CH_3$), 40.7 (−, C-5), 48.8 (−, C-5′), 58.2, 58.9 (+, C-2′, OCH_3), 69.0 ($C_{quat.}$, C-4), 77.9 (−, CH_2OCH_3), 138.6 ($C_{quat.}$, C-2), 172.2 ($C_{quat.}$, C-3), 206.9 ($C_{quat.}$, C-1). **Minor Stereoisomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.70−0.98 (m, 2 H, 4′-H), 0.84 (t, ^3J = 3.8 Hz, 3 H, $CH_2CH_2CH_3$), 1.50−2.05 (m, 6 H, 3′-H, $CH_2CH_2CH_3$), 1.66 (s, 3 H, CH_3), 1.92 (s, 3 H, CH_3), 2.10−2.57 (m, 2 H, 5′-H), 2.18 (AB, d, ^2J = 18.8 Hz, 1 H, 5-H), 2.32 (AB, d, ^2J = 18.8 Hz, 1 H, 5-H), 3.00 (m_c, 2 H, CH_2OCH_3), 3.21 (s, 3 H, OCH_3), 3.28 (m_c, 1 H, 2′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.8, 13.2 (+, CH_3), 14.5 (+, $CH_2CH_2CH_3$), 17.4 (−, $CH_2CH_2CH_3$), 23.6 (−, C-4′),

29.0 (−, C-3′), 39.1 (−, *C*H$_2$CH$_2$CH$_3$), 40.3 (−, C-5), 49.9 (−, C-5′), 56.7, 58.7 (+, C-2′, OCH$_3$), 68.7 (C$_{quat.}$, C-4), 75.9 (−, *C*H$_2$OCH$_3$), 138.6 (C$_{quat.}$, C-2), 172.2 (C$_{quat.}$, C-3), 206.9 (C$_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 222 (5) [M$^+$], 278 (1), 248 (54), 179 (19), 138 (12), 123 (17), 84 (14), 70 (100) [C$_4$H$_8$N$^+$]. C$_{16}$H$_{27}$NO$_2$ (265.4): calcd. C 72.41, H 10.25; found C 71.52, H 10.10.

(4*R*,2′*S*)- and (4*S*,2′*S*)-3-*tert*-Butyl-4-[2′-(methoxycarbonyl)pyrrolidino]-4-propyl-2-cyclopentenone (21bff): According to GP2B, to a solution of complex **3bf** (197 mg, 0.44 mmol) in acetonitrile (9 mL) at 80 °C was slowly added a solution of 3,3-dimethylbutyne (**1f**) (109 mg, 1.33 mmol) in acetonitrile (2 mL) over a period of 8 h, and the mixture was stirred at this temperature for an additional 12 h. Chromatography on aluminum oxide (10 g, activity grade II) eluting with pentane/Et$_2$O (from 20:1 to 1:2) gave 98 mg (72%) of **21bff** [R_f = 0.12 (pentane/Et$_2$O, 1:1); *dr* 2.3:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2995 cm^{-1} (C−H), 2873, 1740, 1700 (C=O), 1653 (C=C), 1559, 1457, 1009, 732, 667. **Major Stereoisomer:** ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.83 (t, ^3J = 7.0 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 0.95−1.09 (m, 2 H, CH$_2$C*H*$_2$CH$_3$), 1.33 [s, 9 H, C(CH$_3$)$_3$], 1.45−2.12 (m, 6 H, 3′,4′-H, C*H*$_2$CH$_2$CH$_3$), 2.08 (AB, d, ^2J = 18.9 Hz, 1 H, 5-H), 2.38−2.55 (m, 1 H, 5′-H), 2.73−2.86 (m, 1 H, 5′-H), 2.93 (AB, d, ^2J = 18.9 Hz, 1 H, 5-H), 3.53 (dd, ^3J = 9.2, ^3J = 4.3 Hz, 1 H, 2′-H), 3.69 (s, 3 H, CO$_2$CH$_3$), 6.07 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 14.0 (+, CH$_2$CH$_2$*C*H$_3$), 18.0 (−, CH$_2$*C*H$_2$CH$_3$), 24.6 (−, C-4′), 31.3 [+, C(*C*H$_3$)$_3$], 31.5 (−, C-3′), 36.1 [C$_{quat.}$, *C*(CH$_3$)$_3$], 39.2 (−, *C*H$_2$CH$_2$CH$_3$), 42.0 (−, C-5), 49.6 (−, C-5′), 51.7, 61.3 (+, C-2′, OCH$_3$), 72.8 (C$_{quat.}$, C-4), 133.1 (+, C-2), 176.8 (C$_{quat.}$, *C*O$_2$CH$_3$), 191.2 (C$_{quat.}$, C-3), 206.0 (C$_{quat.}$, C-1). **Minor Stereoisomer:** ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.83 (t, ^3J = 7.0 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 0.95−1.09 (m, 2 H, CH$_2$C*H*$_2$CH$_3$), 1.23 [s, 9 H, C(CH$_3$)$_3$], 1.45−2.12 (m, 6 H, 3′,4′-H, C*H*$_2$CH$_2$CH$_3$), 2.26 (AB, d, ^2J = 18.5 Hz, 1 H, 5-H), 2.37 (AB, d, ^2J = 18.5 Hz, 1 H, 5-H), 2.57−2.70 (m, 1 H, 5′-H), 2.89−3.01 (m, 1 H, 5′-H), 3.53 (dd, ^3J = 9.2, ^3J = 4.3 Hz, 1 H, 2′-H), 3.65 (s, 3 H, CO$_2$CH$_3$), 6.06 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 14.1 (+, CH$_2$CH$_2$*C*H$_3$), 18.2 (−, CH$_2$*C*H$_2$CH$_3$), 22.1 (−, C-4′), 29.4 (−, C-3′), 31.0 [+, C(*C*H$_3$)$_3$], 36.1 [C$_{quat.}$, *C*(CH$_3$)$_3$], 38.7 (−, *C*H$_2$CH$_2$CH$_3$), 43.0 (−, C-5), 45.2 (−, C-5′), 51.4, 58.7 (+, C-2′, OCH$_3$), 70.4 (C$_{quat.}$, C-4), 132.3 (+, C-2), 176.4 (C$_{quat.}$, *C*O$_2$CH$_3$), 190.5 (C$_{quat.}$, C-3), 206.6 (C$_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 307 (2) [M$^+$], 292 (4) [M$^+$ − CH$_3$], 264 (4) [M$^+$ − C$_3$H$_7$], 250 (7) [M$^+$ − C$_4$H$_9$], 248 (18) [M$^+$ − OCOCH$_3$], 179 (12), 135 (10), 97 (12), 70 (100) [C$_4$H$_8$N$^+$], 59 (14) [OCOCH$_3^+$], 57 (9) [C$_4$H$_9^+$], 43 (10) [C$_3$H$_7^+$]. C$_{18}$H$_{29}$NO$_3$ (307.4): calcd. C 70.32, H 9.51, N 4.56; found C 70.15, H 9.61, N 4.54.

(4*R*,2′*S*)- and (4*S*,2′*S*)-4-[2′-(Methoxycarbonyl)pyrrolidino]-2,3-dimethyl-4-propyl-2-cyclopentenone (21bfaa): According to GP2A, a solution of complex **3bf** (191 mg, 0.43 mmol) in pyridine (9 mL) was treated with 2-butyne (**1aa**) (69.6 mg, 1.29 mmol), and the mixture was stirred at 72 °C for 3.5 days. Chromatography on aluminum oxide (10 g, activity grade II) eluting with pentane/Et$_2$O (from 20:1 to 1:4) gave 94 mg (78%) of **21bfaa** [R_f = 0.71 (Et$_2$O); *dr* 1.6:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2926 cm^{-1} (C−H), 1700 (C=O), 1653 (C=C), 1457, 1383, 1321, 1197, 1112, 971, 923, 734, 666. **Major Stereoisomer:** ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.62−0.95 (m, 2 H, 4′-H), 0.76 (t, ^3J = 3.5 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 1.47−1.98 (m, 6 H, 3′-H, C*H*$_2$C*H*$_2$CH$_3$), 1.62 (s, 3 H, CH$_3$), 1.90 (s, 3 H, CH$_3$), 2.14 (AB, d, ^2J = 17.3 Hz, 1 H, 5-H), 2.27 (AB, d, ^2J = 17.3 Hz, 1 H, 5-H), 2.17−2.32 (m, 1 H, 5′-H), 2.57−2.69 (m, 1 H, 5′-H), 3.42 (dd, ^3J = 9.2, ^3J = 2.9 Hz, 1 H, 2′-H), 3.63 (s, 3 H, CO$_2$CH$_3$) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 7.7, 12.4 (+, CH$_3$), 14.2 (+, CH$_2$CH$_2$*C*H$_3$), 17.4 (−, CH$_2$*C*H$_2$CH$_3$), 24.2 (−, C-4′), 31.3 (−, C-3′), 39.0, 39.6 (−, *C*H$_2$CH$_2$CH$_3$, C-5), 48.4 (−, C-5′), 51.7, 60.7 (+, C-2′, OCH$_3$), 68.6 (C$_{quat.}$, C-4), 138.3 (C$_{quat.}$, C-2), 172.1 (C$_{quat.}$, C-3), 176.8 (C$_{quat.}$, *C*O$_2$CH$_3$), 206.3 (C$_{quat.}$, C-1). **Minor Stereoisomer:** ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.62−0.95 (m, 2 H, CH$_2$C*H*$_2$CH$_3$), 0.81 (t, ^3J = 3.5 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 1.47−1.98 (m, 6 H, 3′,4′-H, C*H*$_2$CH$_2$CH$_3$), 1.60 (s, 3 H, CH$_3$), 1.74 (s, 3 H, CH$_3$), 2.13 (AB, d, ^2J = 18.7 Hz, 1 H, 5-H), 2.27 (AB, d, ^2J = 18.7 Hz, 1 H, 5-H), 2.35−2.52 (m, 1 H, 5′-H), 3.05−3.16 (m, 1 H, 5′-H), 3.30 (dd, ^3J = 6.5, ^3J = 1.6 Hz, 1 H, 2′-H), 3.56 (s, 3 H, CO$_2$CH$_3$) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 7.7, 12.3 (+, CH$_3$), 14.3 (+, CH$_2$CH$_2$*C*H$_3$), 17.4 (−, CH$_2$*C*H$_2$CH$_3$), 23.9 (−, C-4′), 30.9 (−, C-3′), 39.2, 39.3 (−, *C*H$_2$CH$_2$CH$_3$, C-5), 48.8 (−, C-5′), 51.2, 59.3 (+, C-2′, OCH$_3$), 68.2 (C$_{quat.}$, C-4), 138.8 (C$_{quat.}$, C-2), 172.2 (C$_{quat.}$, C-3), 175.9 (C$_{quat.}$, *C*O$_2$CH$_3$), 206.5 (C$_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 279 (5) [M$^+$], 250 (1), 236 (100) [M$^+$ − C$_3$H$_7$], 220 (48), 151 (28), 109 (27), 84 (51), 70 (85) [C$_4$H$_8$N$^+$]. C$_{16}$H$_{25}$NO$_3$ (279.4): calcd. C 68.79, H 9.02; found C 67.72, H 9.18.

(5*R*,2′*R*)- and (5*S*,2′*R*)-5-[2′-(Diethylaminocarbonyl)pyrrolidino]-3-ethoxy-1,2-dimethyl-5-propyl-1,3-cyclopentadiene (7bgaa): According to GP2A, a solution of complex **3bg** (201 mg, 0.41 mmol) in pyridine (8 mL) was treated with 2-butyne (**1aa**) (67.3 mg, 1.24 mmol), and the mixture was stirred at 82 °C for 3 days. Chromatography on aluminum oxide (10 g, activity grade II) eluting with pentane/Et$_2$O (from 20:1 to 1:2) gave 50 mg (35%) of **1st stereoisomer** [R_f = 0.16 (pentane/Et$_2$O, 1:3)] and 55 mg (39%) of **2nd stereoisomer** [R_f = 0.09 (pentane/Et$_2$O, 1:3)] as colorless oils. **1st Stereoisomer:** IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 2872 (C−H), 1700 (C=O), 1653 (C=C), 1457, 1258, 1132, 795. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.87 (t, ^3J = 7.1 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 0.72−1.38 (m, 4 H, C*H*$_2$C*H*$_2$CH$_3$), 1.09 (t, ^3J = 7.0 Hz, 3 H, NCH$_2$C*H*$_3$), 1.13 (t, ^3J = 7.1 Hz, 3 H, NCH$_2$C*H*$_3$), 1.31 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.40−2.10 (m, 4 H, 3′,4′-H), 1.67 (s, 6 H, CH$_3$), 2.50−2.62 (m, 1 H, 5′-H), 2.82−2.90 (m$_c$, 1 H, 5′-H), 3.15−3.71 [m$_c$, 5 H, 2′-H, N(C*H*$_2$CH$_3$)$_2$], 3.79 (q, ^3J = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.70 (s, 1 H, 4-H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 8.6 (+, CH$_3$), 11.0 (+, CH$_3$), 12.5, 14.4, 14.5, 14.6 [+, CH$_2$CH$_2$*C*H$_3$, N(CH$_2$*C*H$_3$)$_2$, OCH$_2$*C*H$_3$], 16.7 (−, CH$_2$*C*H$_2$CH$_3$), 24.5 (−, C-4′), 31.4 (−, C-3′), 37.3 (−, *C*H$_2$CH$_2$CH$_3$), 40.4, 40.8 [−, N(*C*H$_2$CH$_3$)$_2$], 47.7 (−, C-5′), 61.0 (+, C-2′), 64.4 (−, O*C*H$_2$CH$_3$), 74.3 (C$_{quat.}$, C-5), 97.4 (+, C-4), 130.3 (C$_{quat.}$, C-2), 142.8 (C$_{quat.}$, C-1), 160.1 (C$_{quat.}$, C-3), 175.9 (C$_{quat.}$, NCO) ppm. MS (70 eV): *m*/*z* (%) = 348 (7) [M$^+$], 319 (6), 248 (7), 220 (31), 179 (65), 151 (19), 109 (15), 84 (45), 70 (100) [C$_4$H$_8$N$^+$]. HRMS (EI) calcd. for C$_{21}$H$_{36}$N$_2$O$_2$: 348.2276 (correct HRMS).

2nd Stereoisomer: IR (film): $\tilde{\nu}$ = 2961 cm^{-1}, 2872 (C−H), 1699 (C=O), 1646 (C=C), 1456, 1256, 1131, 731. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.74 (t, ^3J = 7.0 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 0.65−1.10 (m, 4 H, C*H*$_2$C*H*$_2$CH$_3$), 0.96 (t, ^3J = 7.1 Hz, 3 H, NCH$_2$C*H*$_3$), 1.00 (t, ^3J = 6.9 Hz, 3 H, NCH$_2$C*H*$_3$), 1.30 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 1.40−2.20 (m, 4 H, 3′,4′-H), 1.49 (s, 3 H, CH$_3$), 1.60 (s, 3 H, CH$_3$), 2.49−3.70 [m, 7 H, 2′,5′-H, N(C*H*$_2$CH$_3$)$_2$], 3.84 (q, ^3J = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.78 (s, 1 H, 4-H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 8.7 (+, CH$_3$), 10.3 (+, CH$_3$), 13.0, 14.3, 14.47, 14.52 [+, CH$_2$CH$_2$*C*H$_3$, N(CH$_2$*C*H$_3$)$_2$, OCH$_2$*C*H$_3$], 16.2 (−, CH$_2$*C*H$_2$CH$_3$), 24.8 (−, C-4′), 32.5 (−, C-3′), 37.2 (−, *C*H$_2$CH$_2$CH$_3$), 40.6, 41.1 [−, N(*C*H$_2$CH$_3$)$_2$], 50.8 (−, C-5′), 55.3 (+, C-2′), 64.4 (−, O*C*H$_2$CH$_3$), 74.9 (C$_{quat.}$, C-5), 94.5 (+, C-4), 130.2 (C$_{quat.}$, C-2), 144.2 (C$_{quat.}$, C-1), 161.4 (C$_{quat.}$, C-3), 175.2 (C$_{quat.}$, NCO) ppm. MS (70 eV): *m*/*z* (%) = 348 (2) [M$^+$],

319 (2), 248 (2), 179 (100), 151 (11), 70 (43) [$C_4H_8N^+$]. HRMS (EI) calcd. for $C_{21}H_{36}N_2O_2$: 348.2276 (correct HRMS).

(4*R*,2′*R*,5′*R*)- and (4*S*,2′*R*,5′*R*)-4-(2′,5′-Dimethylpyrrolidino)-2,3-dimethyl-4-propyl-2-cyclopentenone (21bhaa): According to GP2A, a solution of complex **3bh** (168 mg, 0.40 mmol) in pyridine (8 mL) was treated with 2-butyne (**1aa**) (65.6 mg, 1.21 mmol), and the mixture was stirred at 80 °C for 4 days. The ^{1}H NMR spectrum of the crude product showed two diastereomers in a ratio of 3:1. Chromatography on aluminum oxide (10 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 1:2) gave 22 mg (22%) of **21bhaa** [R_f = 0.45 (pentane/Et_2O, 3:1); *dr* 3:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 2872 (C−H), 1700 (C=O), 1653 (C=C), 1457, 1375, 1074. ^{1}H NMR (250 MHz, $CDCl_3$): **Major Product:** δ = 0.81−1.01 (m, 3 H, $CH_2CH_2CH_3$), 0.86 (d, ^3J = 6.2 Hz, 6 H, CH_3), 1.08−1.40 (m, 4 H, $CH_2CH_2CH_3$), 1.43−2.05 (m, 4 H, 3′,4′-H), 1.66, 1.69 (s, 6 H, CH_3), 2.17 (AB, d, ^2J = 19.2 Hz, 1 H, 5-H), 2.32 (AB, d, ^2J = 19.2 Hz, 1 H, 5-H), 3.10−3.34 (m, 2 H, 2′,5′-H). **Minor Product:** δ = 0.81−1.01 (m, 3 H, $CH_2CH_2CH_3$), 0.90 (d, ^3J = 9.8 Hz, 6 H, CH_3), 1.08−1.40 (m, 4 H, $CH_2CH_2CH_3$), 1.43−2.05 (m, 4 H, 3′,4′-H), 1.64, 1.91 (s, 6 H, CH_3), 2.48 (AB, d, ^2J = 19.7 Hz, 1 H, 5-H), 2.63 (AB, d, ^2J = 19.7 Hz, 1 H, 5-H), 3.10−3.34 (m, 2 H, 2′,5′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): **Major Product:** δ = 7.9, 13.7 (+, CH_3), 14.6 (+, $CH_2CH_2CH_3$), 17.3 (−, $CH_2CH_2CH_3$), 31.2 × 2 (+, 2′,5′-CH_3), 31.9 × 2 (−, C-3′,4′), 39.0 (−, $CH_2CH_2CH_3$), 41.5 (−, C-5), 52.9, 55.2 (+, C-2′,5′), 65.9 ($C_{quat.}$, C-4), 137.2 ($C_{quat.}$, C-2), 175.4 ($C_{quat.}$, C-3), 206.9 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 249 (9) [M^+], 206 (100) [$M^+ - C_3H_7$], 151 (37), [$M^+ - C_6H_{12}N$], 109 (16), 84 (46). HRMS (EI) calcd. for $C_{16}H_{27}NO$: 249.2092 (correct HRMS).

1-*tert*-Butyl-5-(dimethylamino)-3-ethoxy-5-(1′-methoxyethyl)-1,3-cyclopentadiene (7iaf). Variation A: According to GP2A, a solution of complex **3ia** (400 mg, 1.06 mmol) in pyridine (20 mL) was treated with 3,3-dimethylbutyne (**1f**) (261 mg, 3.18 mmol), and the mixture was stirred at 80 °C for 24 h. The ^{1}H NMR spectrum of the crude product showed two diastereomers in a ratio of 7.1:1. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 83 mg (29%) of diastereomerically pure **7iaf** [R_f = 0.62 (pentane/Et_2O, 3:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2977 cm^{-1} (C−H), 2784 (C−H), 1628 (C=C), 1572, 1457, 1372, 1271, 1084, 969, 851. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 [d, ^3J = 6.0 Hz, 3 H, 2′-H), 1.18 [s, 9 H, $C(CH_3)_3$], 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.23 [s, 6 H, $N(CH_3)_2$], 3.28 (s, 3 H, OCH_3), 3.75 (q, ^3J = 6.0 Hz, 1 H, 1′-H), 3.84 (pq, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 3.91 (pq, ^3J = 7.0 Hz, 1 H, OCH_2CH_3), 4.87 (d, ^4J = 1.9 Hz, 1 H, 4-H), 5.84 (d, ^4J = 1.9 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.2, 14.5 (+, C-2′, OCH_2CH_3), 31.0 [+, $C(CH_3)_3$], 34.4 [$C_{quat.}$, $C(CH_3)_3$], 41.5 [+, $N(CH_3)_2$], 55.8 (+, OCH_3), 64.3 (−, OCH_2CH_3), 79.5 (+, C-1′), 82.7 ($C_{quat.}$, C-5), 94.8 (+, C-4), 125.0 (+, C-2), 159.1 ($C_{quat.}$, C-1), 162.0 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 267 (18) [M^+], 252 (4), 236 (3), 222 (9) [$M^+ - OC_2H_5$], 210 (37), 208 (100), 193 (11), 180 (10), 59 (19). $C_{16}H_{29}NO_2$ (267.4): calcd. C 71.87, H 10.93; found C 71.94, H 11.10.

Variation B: According to GP2A, a solution of complex **3ia** (300 mg, 0.80 mmol) in pyridine (16 mL) was treated with 3,3-dimethylbutyne (**1f**) (196 mg, 2.39 mmol), and the mixture was stirred at 60 °C for 42 h. The ^{1}H NMR spectrum of the crude product showed two diastereomers in a ratio of 8.5:1. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 70 mg (33%) of diastereomerically pure **7iaf**.

Variation C: According to GP2A, a solution of complex **3ia** (313 mg, 0.83 mmol) in pyridine (12 mL) was treated with 3,3-dimethylbutyne (**1f**) (204 mg, 2.48 mmol), and the mixture was stirred at 40 °C for 528 h. The ^{1}H NMR spectrum of the crude product showed two diastereomers in a ratio of 15:1. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 47 mg (21%) of diastereomerically pure **7iaf**.

Variation D: According to GP2A, a solution of complex **3ia** (350 mg, 0.93 mmol) in pyridine (19 mL) was treated with 3,3-dimethylbutyne (**1f**) (228 mg, 2.78 mmol), and the mixture was stirred at 20 °C for 336 h. The ^{1}H NMR spectrum of the crude product showed two diastereomers in a ratio of 15:1. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 41 mg (17%) of diastereomerically pure **7iaf**.

5-(Dimethylamino)-3-ethoxy-5-(1′-methoxyethyl)-1-phenyl-1,3-cyclopentadiene (7iah): According to GP2A, a solution of complex **3ia** (333 mg, 0.88 mmol) in pyridine (18 mL) was treated with phenylethyne (**1h**) (271 mg, 2.65 mmol), and the mixture was stirred at 80 °C for 42 h. The ^{1}H NMR spectrum of the crude product showed two diastereomers in a ratio of 30:1. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 54 mg (21%) of diastereomerically pure **7iah** [R_f = 0.62 (pentane/Et_2O, 3:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2977 cm^{-1} (C−H), 2822 (C−H), 2782 (C−H), 1622, 1577 (C=C), 1446, 1372, 1135, 962, 854. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.72 [d, ^3J = 6.2 Hz, 3 H, 2′-H), 1.48 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.28 [s, 6 H, $N(CH_3)_2$], 3.31 (s, 3 H, OCH_3), 3.74 (q, ^3J = 6.2 Hz, 1 H, 1′-H), 3.96 (m, 2 H, OCH_2CH_3), 5.19 (d, ^4J = 1.9 Hz, 1 H, 4-H), 6.38 (d, ^4J = 1.9 Hz, 1 H, 2-H), 7.15−7.38 (m, 3 H, Ph−H), 7.70−7.90 (m, 2 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.8, 14.5 (+, C-2′, OCH_2CH_3), 41.6 [+, $N(CH_3)_2$], 56.3 (+, OCH_3), 64.7 (−, OCH_2CH_3), 80.8 (+, C-1′), 82.7 ($C_{quat.}$, C-5), 95.8 (+, C-4), 125.3 (+, C-2), 126.2, 127.4, 128.4 (+, Ph−C), 135.1 ($C_{quat.}$, Ph−C), 150.4 ($C_{quat.}$, C-1), 160.5 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 287 (13) [M^+], 272 (4), 258 (3), [$M^+ - C_2H_5$], 228 (9), 200 (25). $C_{18}H_{25}NO_2$ (287.4): calcd. C 75.22, H 8.77; found C 75.13, H 8.88.

5-(Dimethylamino)-3-ethoxy-1-phenyl-5-(2′-trimethylsiloxypropyl)-1,3-cyclopentadiene (7jah): According to GP2A, a solution of complex **3ja** (358 mg, 0.80 mmol) in pyridine (16 mL) was treated with phenylethyne (**1h**) (245 mg, 2.40 mmol), and the mixture was stirred at 80 °C for 4 days. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 137 mg (48%) of **7jah** [R_f = 0.88 (pentane/Et_2O, 3:1); *dr* 1.9:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2975 cm^{-1} (C−H), 2823 (C−H), 2782 (C−H), 1622, 1576 (C=C), 1445, 1371, 1248, 1106, 977, 839. **Major Stereoisomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.01 [s, 9 H, $Si(CH_3)_3$], 0.72 [d, ^3J = 6.4 Hz, 3 H, 3′-H), 1.39 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.92 (dd, ^2J = 12.8, ^3J = 6.4 Hz, 1 H, 1′-H), 2.19 [s, 6 H, $N(CH_3)_2$], 2.35 (dd, ^2J = 12.8, ^3J = 6.4 Hz, 1 H, 1′-H), 3.30 (m_c, 1 H, 2′-H), 3.92 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 5.06 (d, ^4J = 1.6 Hz, 1 H, 4-H), 6.97 (d, ^4J = 1.9 Hz, 1 H, 2-H), 7.10−7.35 (m, 4 H, Ph−H), 7.75−7.90 (m, 1 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 0.37 [+, $Si(CH_3)_3$], 14.5 (+, OCH_2CH_3), 25.6 (+, C-3′), 40.0 [+, $N(CH_3)_2$], 45.3 (−, C-1′), 64.5 (−, OCH_2CH_3), 66.0 (+, C-2′), 76.3 ($C_{quat.}$, C-5), 99.2 (+, C-4), 124.7 (+, C-2), 126.2, 126.6, 127.5 (+, Ph−C), 134.7 ($C_{quat.}$, Ph−C), 149.9 ($C_{quat.}$, C-1), 158.9 ($C_{quat.}$, C-3). **Minor Stereoisomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.31 [s, 9 H, $Si(CH_3)_3$], 0.94 [d, ^3J = 6.4 Hz, 3 H, 3′-H), 1.39 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.92 (dd, ^2J = 12.8, ^3J = 6.4 Hz, 1 H, 1′-H), 2.19 [s, 6 H, $N(CH_3)_2$], 2.35 (dd, ^2J = 12.8, ^3J = 6.4 Hz, 1 H, 1′-H), 3.30 (m_c, 1 H, 2′-H), 3.92 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.96 (d, ^4J = 1.6 Hz, 1 H, 4-H), 6.89 (d, ^4J = 1.9 Hz, 1 H, 2-H),

7.10−7.35 (m, 4 H, Ph−H), 7.75−7.90 (m, 1 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −0.3 [+, $Si(CH_3)_3$], 15.6 (+, OCH_2CH_3), 25.6 (+, C-3′), 39.8 [+, $N(CH_3)_2$], 45.6 (−, C-1′), 64.7 (−, OCH_2CH_3), 65.6 (+, C-2′), 75.3 ($C_{quat.}$, C-5), 98.9 (+, C-4), 124.9 (+, C-2), 126.6, 127.5, 128.3 (+, Ph−C), 134.7 ($C_{quat.}$, Ph−C), 150.1 ($C_{quat.}$, C-1), 159.1 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 359 (45) [M^+], 330 (35) [$M^+ - C_2H_5$], 242 (61), 199 (28), 159 (26), 131 (100), 117 (31), 73 (60), 52 (88). $C_{21}H_{33}NO_2Si$ (359.6): calcd. C 70.15, H 9.25; found C 70.43, H 9.20.

1-*tert*-Butyl-5-(2′-*tert*-butyldimethylsiloxy)propyl-5-(dimethylamino)-3-ethoxy-1,3-cyclopentadiene (7kaf): According to GP2A, a solution of complex **3ka** (500 mg, 1.02 mmol) in pyridine (20 mL) was treated with 3,3-dimethylbutyne (**1f**) (250 mg, 3.04 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 169 mg (43%) of **7kaf** [R_f = 0.08 (pentane); *dr* 2.6:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2957 cm^{-1} (C−H), 2780 (C−H), 1702, 1629 (C=C), 1463, 1362, 1254, 1050, 907, 835. **Major Stereoisomer**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.22 (s, 3 H, $SiCH_3$), 0.00 (s, 3 H, $SiCH_3$), 0.82 [s, 9 H, $SiC(CH_3)_3$], 1.10 (d, ^3J = 6.1 Hz, 3 H, 3′-H), 1.21 [s, 9 H, $C(CH_3)_3$], 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.85−2.35 (m, 2 H, 1′-H), 2.17 [s, 6 H, $N(CH_3)_2$], 3.40 (m_c, 1 H, 2′-H), 3.82 (m_c, 2 H, OCH_2CH_3), 4.74 (d, ^4J = 1.6 Hz, 1 H, 4-H), 5.85 (d, ^4J = 1.6 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −4.4, −3.8 (+, $SiCH_3$), 14.5 (+, OCH_2CH_3), 18.0 [$C_{quat.}$, $SiC(CH_3)_3$], 25.98 (+, C-3′), 26.04 [+, $SiC(CH_3)_3$], 31.5 [+, $C(CH_3)_3$], 34.5 [$C_{quat.}$, $C(CH_3)_3$], 40.8 [+, $N(CH_3)_2$], 44.8 (−, C-1′), 64.2 (−, OCH_2CH_3), 67.0 (+, C-2′), 78.1 ($C_{quat.}$, C-5), 96.5 (+, C-4), 125.1 (+, C-2), 157.5 ($C_{quat.}$, C-1), 162.2 ($C_{quat.}$, C-3). **Minor Stereoisomer**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, $SiCH_3$), 0.06 (s, 3 H, $SiCH_3$), 0.84 [s, 9 H, $SiC(CH_3)_3$], 1.02 (d, ^3J = 5.6 Hz, 3 H, 3′-H), 1.24 [s, 9 H, $C(CH_3)_3$], 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.85−2.35 (m, 2 H, 1′-H), 2.17 [s, 6 H, $N(CH_3)_2$], 3.55 (m_c, 1 H, 2′-H), 3.82 (m_c, 2 H, OCH_2CH_3), 4.63 (d, ^4J = 1.6 Hz, 1 H, 4-H), 5.84 (d, ^4J = 1.6 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −4.4, −3.4 (+, $SiCH_3$), 14.6 (+, OCH_2CH_3), 17.9 [$C_{quat.}$, $SiC(CH_3)_3$], 26.0 [+, $SiC(CH_3)_3$], 26.6 (+, C-3′), 31.5 [+, $C(CH_3)_3$], 34.7 [$C_{quat.}$, $C(CH_3)_3$], 40.6 [+, $N(CH_3)_2$], 45.1 (−, C-1′), 64.3 (−, OCH_2CH_3), 67.0 (+, C-2′), 77.3 ($C_{quat.}$, C-5), 96.8 (+, C-4), 125.1 (+, C-2), 157.6 ($C_{quat.}$, C-1), 161.8 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 381 (90) [M^+], 336 (28), 324 (38) [$M^+ - C_4H_9$], 222 (100), 209 (22), 179 (43), 159 (43), 151 (21), 115 (24), 103 (20), 73 (78). $C_{22}H_{43}NO_2Si$ (381.7): calcd. C 69.23, H 11.36; found C 69.42, H 11.45.

5-(2′-*tert*-Butyldimethylsiloxy)propyl-5-(dimethylamino)-3-ethoxy-1-phenyl-1,3-cyclopentadiene (7kah): According to GP2A, a solution of complex **3ka** (560 mg, 1.14 mmol) in pyridine (20 mL) was treated with phenylethyne (**1h**) (356 mg, 3.49 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 3:1) gave 287 mg (63%) of **7kah** [R_f = 0.95 (pentane/Et_2O, 5:1); *dr* 1.8:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2928 cm^{-1} (C−H), 2823 (C−H), 2782 (C−H), 1622, 1577 (C=C), 1471, 1372, 1253, 1047, 937, 835. **Major Stereoisomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.05 (s, 3 H, $SiCH_3$), −0.03 (s, 3 H, $SiCH_3$), 0.69 (d, ^3J = 6.1 Hz, 3 H, 3′-H), 0.82 [s, 9 H, $SiC(CH_3)_3$], 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.90−2.45 (m, 2 H, 1′-H), 2.20 [s, 6 H, $N(CH_3)_2$], 3.28 (m_c, 1 H, 2′-H), 3.95 (m, 2 H, OCH_2CH_3), 5.18 (br. s, 1 H, 4-H), 6.48 (br. s, 1 H, 2-H), 7.05−7.80 (m, 5 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −4.6, −4.2 (+, $SiCH_3$), 14.6 (+, OCH_2CH_3), 18.0 [$C_{quat.}$, $SiC(CH_3)_3$], 25.7 [+, $SiC(CH_3)_3$], 25.9 (+, C-3′), 40.0 [+, $N(CH_3)_2$], 45.6 (−, C-1′), 64.6 (−, OCH_2CH_3), 66.0 (+, C-2′), 76.3 ($C_{quat.}$, C-5), 98.8 (+, C-4), 124.8 (+, C-2), 126.2, 127.3, 128.3 (+, Ph−C), 134.8 ($C_{quat.}$, Ph−C), 150.5 ($C_{quat.}$, C-1), 159.4 ($C_{quat.}$, C-3). **Minor Stereoisomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.05 (s, 3 H, $SiCH_3$), −0.03 (s, 3 H, $SiCH_3$), 0.65 (d, ^3J = 6.1 Hz, 3 H, 3′-H), 0.95 [s, 9 H, $SiC(CH_3)_3$], 1.32 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.90−2.45 (m, 2 H, 1′-H), 2.20 [s, 6 H, $N(CH_3)_2$], 3.28 (m_c, 1 H, 2′-H), 3.95 (m, 2 H, OCH_2CH_3), 4.99 (br. s, 1 H, 4-H), 6.41 (br. s, 1 H, 2-H), 7.05−7.80 (m, 5 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.3, −5.2 (s, 3 H, $SiCH_3$), 14.6 (+, OCH_2CH_3), 17.9 [$C_{quat.}$, $SiC(CH_3)_3$], 25.6 [+, $SiC(CH_3)_3$], 26.6 (+, C-3′), 39.9 [+, $N(CH_3)_2$], 45.6 (−, C-1′), 64.7 (−, OCH_2CH_3), 66.0 (+, C-2′), 72.3 ($C_{quat.}$, C-5), 99.0 (+, C-4), 124.8 (+, C-2), 126.4, 127.5, 128.4 (+, Ph−C), 134.8 ($C_{quat.}$, Ph−C), 150.3 ($C_{quat.}$, C-1), 159.3 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 401 (100) [M^+], 372 (49) [$M^+ - C_2H_5$], 356 (12), 271 (14), 242 (87), 199 (35), 171 (11), 159 (22), 131 (45), 115 (14), 73 (52), 52 (28). $C_{24}H_{39}NO_2Si$ (401.7): calcd. C 71.77, H 9.79; found C 71.69, H 9.88.

5-(2′-*tert*-Butyldimethylsiloxy)propyl-5-(dimethylamino)-3-ethoxy-1,2-dimethyl-1,3-cyclopentadiene (7kaaa): According to GP2A, a solution of complex **3ka** (404 mg, 0.82 mmol) in pyridine (20 mL) was treated with 2-butyne (**1aa**) (197 μL, 2.51 mmol), and the mixture was stirred at 80 °C for 3 days. Chromatography on aluminum oxide (30 g, activity grade II) eluting with pentane/Et_2O (from 20:1 to 0:1) gave 79 mg (27%) of **7kaaa** [R_f = 0.08 (pentane/Et_2O, 1:1); *dr* = 2.1:1] as a colorless oil. IR (film): $\tilde{\nu}$ = 2929 cm^{-1} (C−H), 2856 (C−H), 2779 (C−H), 1665, 1592 (C=C), 1472, 1378, 1253, 1042, 915, 835. **Major Stereoisomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.03 [s, 6 H, $Si(CH_3)_2$], 0.83 [s, 9 H, $SiC(CH_3)_3$], 0.97 (d, ^3J = 6.1 Hz, 3 H, 3′-H), 1.34 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.62 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.80−2.30 (m, 2 H, 1′-H), 2.12 [s, 6 H, $N(CH_3)_2$], 3.32 (m, 1 H, 2′-H), 3.84 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.69 (s, 1 H, 4-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −4.7, −4.2 (+, $SiCH_3$), 8.8, 10.9 (+, CH_3), 14.5 (+, OCH_2CH_3), 18.0 [$C_{quat.}$, $SiC(CH_3)_3$], 25.6 (+, C-3′), 25.9 [+, $SiC(CH_3)_3$], 39.7 [+, $N(CH_3)_2$], 44.7 (−, C-1′), 64.4 (−, OCH_2CH_3), 66.0 (+, C-2′), 73.8 ($C_{quat.}$, C-5), 93.9 (+, C-4), 131.3 ($C_{quat.}$, C-2), 142.1 ($C_{quat.}$, C-1), 160.7 ($C_{quat.}$, C-3). **Minor Stereoisomer:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.03 [s, 6 H, $Si(CH_3)_2$], 0.82 [s, 9 H, $SiC(CH_3)_3$], 0.97 (d, ^3J = 6.1 Hz, 3 H, 3′-H), 1.34 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.68 (s, 6 H, 2 × CH_3), 1.80−2.30 (m, 2 H, 1′-H), 2.10 [s, 6 H, $N(CH_3)_2$], 3.21 (m_c, 1 H, 2′-H), 3.84 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.62 (s, 1 H, 4-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −4.7, −4.3 (+, $SiCH_3$), 8.8, 10.7 (+, CH_3), 14.5 (+, OCH_2CH_3), 18.0 [$C_{quat.}$, $SiC(CH_3)_3$], 25.9 [+, $SiC(CH_3)_3$], 26.6 (+, C-3′), 39.6 [+, $N(CH_3)_2$], 45.0 (−, C-1′), 64.4 (−, OCH_2CH_3), 66.0 (+, C-2′), 73.1 ($C_{quat.}$, C-5), 94.0 (+, C-4), 131.1 ($C_{quat.}$, C-2), 141.8 ($C_{quat.}$, C-1), 160.5 ($C_{quat.}$, C-3) ppm. MS (70 eV): *m*/*z* (%) = 353 (40) [M^+], 324 (63) [$M^+ - C_2H_5$], 308 (13), 194 (100), 159 (46), 151 (29), 115 (22), 73 (58). $C_{20}H_{39}NO_2Si$ (353.6): calcd. C 67.93, H 11.12; found C 68.08, H 11.11.

4-(Dimethylamino)-2,3,4-trimethyl-2-cyclopentenone (21aaaa): According to GP3, a solution of **7aaaa** (756 mg, 3.87 mmol) in THF (5 mL) was treated with two drops of 2 N hydrochloric acid. Chromatography on silica gel (30 g) eluting with Et_2O gave 635 mg (98%) of **21aaaa** [R_f = 0.18 (Et_2O)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2968 cm^{-1} (C−H), 2824 (C−H), 2780 (C−H), 1700 (C=O), 1653 (C=C), 1456, 1382, 1323, 1288, 1261, 1228, 1189, 1158, 1083, 977, 840. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.21 (s, 3 H, CH_3), 1.55 (s, 3 H, CH_3), 1.76 (AB, d, ^2J = 18.4 Hz, 1 H, 5-H), 1.84 (s, 3 H,

CH_3), 1.98 [s, 6 H, $N(CH_3)_2$], 2.46 (AB, d, ^2J = 18.4 Hz, 1 H, 5-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.7 (+, CH_3), 11.7 (+, CH_3), 25.3 (+, CH_3), 37.3 (−, C-5), 39.2 [+, $N(CH_3)_2$], 65.6 ($C_{quat.}$, C-4), 135.9 ($C_{quat.}$, C-2), 174.0 ($C_{quat.}$, C-3), 206.5 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m/z* (%) = 167 (25) [M^+], 152 (38) [$M^+ - CH_3$], 123 (100) [$M^+ - N(CH_3)_2$], 112 (5), 95 (25), 79 (8), 67 (8), 55 (7), 44 (10) [$N(CH_3)_2^+$]. $C_{10}H_{17}NO$ (167.2): calcd. C 71.81, H 10.25; found C 71.94, H 10.28.

4-(Dimethylamino)-4-methyl-2,3-diphenyl-2-cyclopentenone (21aahh): According to GP2A, a solution of complex **3aa** (1.25 g, 3.75 mmol) in pyridine (80 mL) was treated with diphenylethyne (**1hh**) (1.33 g, 7.46 mmol), and the mixture was stirred at 80 °C for 4 days. After evaporation of the solvent, the residue was dissolved in THF (10 mL), to which 2 N hydrochloric acid was added (2 mL). Chromatography on silica gel (30 g) eluting with pentane/Et_2O (from 5:1 to 0:1) gave 550 mg (50%) of **21aahh** [R_f = 0.61 (Et_2O)] as colorless crystals, m.p. 115 °C. IR (KBr): $\tilde{\nu}$ = 3048 cm^{-1} (C−H), 2971 (C−H), 2938 (C−H), 2821 (C−H), 2776 (C−H), 1702 (C=O), 1624 (C=C), 1485, 1441, 1362, 1340, 1280, 1232, 1175, 1116, 1068, 1033, 971, 930, 797, 774, 695, 635, 522, 481. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.41 (s, 3 H, CH_3), 2.22 (AB, d, ^2J = 19.3 Hz, 1 H, 5-H), 2.35 [s, 6 H, $N(CH_3)_2$], 2.98 (AB, d, ^2J = 19.3 Hz, 1 H, 5-H), 7.18−7.27 (m, 8 H, Ph−H), 7.54 (d, ^3J = 7.2 Hz, 2 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 25.9 (+, CH_3), 39.3 (−, C-5), 39.6 [+, $N(CH_3)_2$], 66.3 ($C_{quat.}$, C-4), 127.8, 127.9, 128.1, 128.9, 129.65, 129.72 (+, Ph−C), 131.5, 134.4 ($C_{quat.}$, Ph−C), 140.0 ($C_{quat.}$, C-2), 172.5 ($C_{quat.}$, C-3), 205.4 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m/z* (%) = 291 (52) [M^+], 276 (31) [$M^+ - CH_3$], 247 (100) [$M^+ - N(CH_3)_2$], 204 (11), 178 (12), 112 (55), 85 (19), 70 (20), 44 (6) [$N(CH_3)_2^+$]. $C_{20}H_{21}NO$ (291.4): calcd. C 82.44, H 7.26; found C 82.63, H 7.14.

3-[3′-(*tert*-Butyldimethylsilyloxy)propyl]-4-(dimethylamino)-4-propyl-2-cyclopentenone (21bal): According to GP3, a solution of **7bal** (1.12 g, 3.05 mmol) in THF (5 mL) was treated with 2 drops of 2 N hydrochloric acid. Chromatography on silica gel (40 g) eluting with pentane/Et_2O (3:1) gave 963 mg (93%) of **21bal** [R_f = 0.18 (pentane/Et_2O, 1:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2929 cm^{-1}, 2855 (C−H), 1700 (C=O), 1617 (C=C), 1463, 1384, 1102, 963, 776. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.02 [s, 6 H, $Si(CH_3)_2$], 0.85 [s, 9 H, $SiC(CH_3)_3$], 0.86−0.90 (m, 5 H, $CH_2CH_2CH_3$), 1.55 (m_c, 1 H, $CH_2CH_2CH_3$), 1.70−1.84 (m, 3 H, $CH_2CH_2CH_3$, 1′-H), 1.90 (AB, d, ^2J = 18.6 Hz, 1 H, 5-H), 2.11 [s, 6 H, $N(CH_3)_2$], 2.33 (m, 2 H, 2′-H), 2.52 (AB, d, ^2J = 18.6 Hz, 1 H, 5-H), 3.66 (t, ^3J = 6.7 Hz, 2 H, 3′-H), 5.94 (s, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.4 [+, $Si(CH_3)_2$], 15.0 (+, $CH_2CH_2CH_3$), 17.9 (−, $CH_2CH_2CH_3$), 18.2 [$C_{quat.}$, $SiC(CH_3)_3$], 24.5 (−, $CH_2CH_2CH_3$), 25.8 [+, $SiC(CH_3)_3$], 29.9 (−, C-2′), 36.8 (−, C-1′), 39.2 (−, C-5), 39.3 [+, $N(CH_3)_2$], 62.2 (−, C-3′), 70.9 ($C_{quat.}$, C-4), 130.0 (+, C-2), 184.9 ($C_{quat.}$, C-3), 206.4 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m/z* (%) = 339 (8) [M^+], 295 (100) [$M^+ - N(CH_3)_2$], 282 (10), 237 (18), 181 (12), 138 (46), 73 (12).

4-(Dimethylamino)-3-(3′-hydroxypropyl)-4-propyl-2-cyclopentenone (21bal′): A solution of **21bal** (152 mg, 0.45 mmol) in acetonitrile (5 mL) was treated with 40% hydrofluoric acid (100 μL, 2.05 mmol) and the mixture was stirred at room temperature for 1 h. After addition of saturated K_2CO_3 solution (10 mL), the mixture was extracted with CH_2Cl_2 (5 × 20 mL), and the combined organic extracts were dried with $MgSO_4$. The solvent was removed under reduced pressure. The residue was dissolved in pentane/Et_2O (1:1) and crystallized at 0 °C. 68 mg (67%) of **21bal′** was obtained as colorless crystals, m.p. 74 °C. IR (film): $\tilde{\nu}$ = 3258 cm^{-1} (OH), 1695 (C=O), 1610 (C=C), 1461, 1331, 1123, 929, 751. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.79−0.92 (m, 5 H, $CH_2CH_2CH_3$), 1.53 (m_c, 1 H, $CH_2CH_2CH_3$), 1.69−1.85 (m, 3 H, $CH_2CH_2CH_3$, 1′-H), 1.90 (AB, d, ^2J = 18.6 Hz, 1 H, 5-H), 2.12 [s, 6 H, $N(CH_3)_2$], 2.31 (m, 2 H, 2′-H), 2.48 (AB, d, ^2J = 18.6 Hz, 1 H, 5-H), 2.85 (br. s, 1 H, OH), 3.67 (t, ^3J = 6.3 Hz, 2 H, 3′-H), 5.94 (t, ^4J = 1.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.5 (+, $CH_2CH_2CH_3$), 17.9 (−, $CH_2CH_2CH_3$), 24.6, 29.5 (−, C-2′, $CH_2CH_2CH_3$), 36.7 (−, C-1′), 38.9 (−, C-5), 39.3 [+, $N(CH_3)_2$], 62.0 (−, C-3′), 71.0 ($C_{quat.}$, C-4), 130.2 (+, C-2), 184.6 ($C_{quat.}$, C-3), 206.5 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m/z* (%) = 225 (2) [M^+], 181 (100) [$M^+ - N(CH_3)_2$], 138 (23), 108 (12), 91 (13), 77 (16), 55 (14), 44 (21) [$N(CH_3)_2^+$]. $C_{13}H_{23}NO_2$ (225.3): calcd. C 69.29, H 10.29, N 6.22; found C 69.55, H 10.20, N 6.15.

4-Cyclopropyl-4-(dimethylamino)-2,3-dimethyl-2-cyclopentenone (21caaa): According to GP3, a solution of **7caaa** (434 mg, 1.96 mmol) in THF (5 mL) was treated with two drops of 2 N hydrochloric acid. Chromatography on silica gel (30 g) eluting with pentane/Et_2O (1:1) gave 360 mg (95%) of **21caaa** [R_f = 0.14 (Et_2O)] as a colorless oil. IR (film): $\tilde{\nu}$ = 3021 cm^{-1} (C−H), 2934 (C−H), 2780 (C−H), 1699 (C=O), 1653 (C=C), 1456, 1237, 1084, 1050, 780. ^1H NMR (250 MHz, $CDCl_3$): δ = −0.35 (m_c, 1 H, *c*Pr-H), 0.38−0.47 (m, 2 H, *c*Pr-H), 0.72 (m_c, 1 H, *c*Pr-H), 1.10 (m_c, 1 H, *c*Pr-H), 1.21 (AB, d, ^2J = 18.8 Hz, 1 H, 5-H), 1.68 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 2.11 (AB, d, ^2J = 18.8 Hz, 1 H, 5-H), 2.18 [s, 6 H, $N(CH_3)_2$]. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −0.4 (−, *c*Pr-C), 6.0 (−, *c*Pr-C), 7.7 (+, CH_3), 12.0 (+, CH_3), 16.3 (+, *c*Pr-C), 29.2 (−, C-5), 39.7 [+, $N(CH_3)_2$], 69.4 ($C_{quat.}$, C-4), 135.6 ($C_{quat.}$, C-2), 173.8 ($C_{quat.}$, C-3), 206.7 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m/z* (%) = 193 (8) [M^+], 178 (3) [$M^+ - CH_3$], 152 (19) [$M^+ - C_3H_5$], 149 (100) [$M^+ - N(CH_3)_2$], 121 (95), 107 (55), 93 (72), 79 (32), 65 (11), 55 (13), 44 (13) [$N(CH_3)_2^+$], 41 (15) [$C_3H_5^+$]. $C_{12}H_{19}NO$ (193.3): calcd. C 74.56, H 9.91; found C 74.30, H 10.29.

4-(Dimethylamino)-4-(3′-hydroxypropyl)-2,3-dimethyl-2-cyclopentenone (21laaa): A solution of **7laaa** (393 mg, 1.11 mmol) in acetonitrile (12 mL) was treated with 40% hydrofluoric acid (220 μL, 4.44 mmol), and the mixture was stirred at room temperature for 1 h. After addition of saturated K_2CO_3 solution (10 mL), the mixture was extracted with CH_2Cl_2 (5 × 20 mL) and the combined organic extracts were dried with $MgSO_4$. The solvent was removed under reduced pressure. The residue was dissolved in pentane/Et_2O (1:1) and crystallized at 0 °C. 190 mg (81%) of **21laaa** was obtained as colorless crystals, m.p. 76 °C. IR (film): $\tilde{\nu}$ = 3177 cm^{-1} (OH), 1704 (C=O), 1652 (C=C), 1460, 1341, 1163, 914, 840. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.09 (m_c, 2 H, 2′-H), 1.64 (s, 3 H, CH_3), 1.66 (m_c, 1 H, 1′-H), 1.85 (AB, d, ^2J = 18.6 Hz, 1 H, 5-H), 1.87 (s, 3 H, CH_3), 1.89 (m_c, 1 H, 1′-H), 2.07 [s, 6 H, $N(CH_3)_2$], 2.45 (AB, d, ^2J = 18.6 Hz, 1 H, 5-H), 2.85 (br. s, 1 H, OH), 3.53 (t, ^3J = 6.3 Hz, 2 H, 3′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 7.7, 12.4 (+, CH_3), 27.9, 33.0, 35.8 (−, C-5,1′,2′), 39.3 [+, $N(CH_3)_2$], 62.4 (−, C-3′), 69.0 ($C_{quat.}$, C-4), 138.4 ($C_{quat.}$, C-3), 172.1 ($C_{quat.}$, C-2), 206.4 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m/z* (%) = 211 (8) [M^+], 167 (12) [$M^+ - N(CH_3)_2$], 152 (100), 149 (10). $C_{12}H_{21}NO_2$ (211.3): calcd. C 68.21, H 10.02; found C 68.68, H 10.00.

(1,2,3-Trimethyl-4-oxo-2-cyclopentenyl)trimethylammonium Iodide (24aaaa). Variation A: According to GP4A, 4-(dimethylamino)-2,3,4-trimethyl-2-cyclopentenone (**21aaaa**) (102 mg, 0.61 mmol) and methyl iodide (796 mg, 5.61 mmol) in acetone (8 mL) were stirred under 10 kbar for 20 h. After filtration and washing with Et_2O (3 × 20 mL), 175 mg (93%) of **24aaaa** was isolated as a colorless solid, m.p. 156 °C. IR (KBr): $\tilde{\nu}$ = 3027 cm^{-1} (C−H), 3007 (C−H), 2917 (C−H), 1717 (C=O), 1637 (C=C), 1470, 1387, 1327,

1288. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 0.83 (s, 3 H, CH$_3$), 0.85 (s, 3 H, CH$_3$), 1.34 (s, 3 H, CH$_3$), 1.67 (AB, d, ^2J = 19.0 Hz, 1 H, 5-H), 2.19 [s, 9 H, N(CH$_3$)$_3^+$], 2.47 (AB, d, ^2J = 19.0 Hz, 1 H, 5-H) ppm. ^{13}C NMR (62.9 MHz, [D$_6$]DMSO, plus DEPT): δ = 8.5 (+, CH$_3$), 14.9 (+, CH$_3$), 19.6 (+, CH$_3$), 43.9 (−, C-5), 50.4 [+, N(CH$_3$)$_3^+$], 78.9 (C$_{quat.}$, C-4), 143.4 (C$_{quat.}$, C-2), 162.5 (C$_{quat.}$, C-3), 201.3 (C$_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 263 (18), 253 (17), 122 (88) [M$^+$ − HN(CH$_3$)$_3$I], 108 (21), 95 (22), 79 (95), 59 (100) [N(CH$_3$)$_3^+$], 44 (87) [N(CH$_3$)$_2^+$]. C$_{11}$H$_{20}$INO (309.2): calcd. C 42.73, H 6.52; found C 42.53, H 6.44.

Variation B: According to GP4B, **21aaaa** (263 mg, 1.57 mmol) and methyl iodide (1.40 g, 9.86 mmol) in acetone (30 mL) were stirred at ambient pressure for 3 days. After filtration and washing with Et$_2$O (3 × 20 mL), 342 mg (70%) of **24aaaa** was isolated.

(4-Methyl-2,3-diphenyl-2-cyclopentenon-4-yl)trimethylammonium Iodide (24aahh). Variation A: According to GP4A, 4-(dimethylamino)-4-methyl-2,3-diphenyl-2-cyclopentenone (**21aahh**) (166 mg, 0.57 mmol) and methyl iodide (518 mg, 3.65 mmol) in acetone (8 mL) were stirred under 10 kbar for 3 days. After filtration and washing with Et$_2$O (3 × 20 mL), 236 mg (96%) of **24aahh** was isolated as a colorless solid, m.p. 159 °C. IR (KBr): $\tilde{\nu}$ = 3014 cm^{-1} (C−H), 2737 (C−H), 1699 (C=O), 1621 (C=C), 1473, 1444, 1416, 1377, 1344, 1253. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 1.45 (s, 3 H, CH$_3$), 2.72−2.78 [m, 10 H, N(CH$_3$)$_3^+$, 5-H], 3.78 (AB, d, ^2J = 19.0 Hz, 1 H, 5-H), 7.10−7.41 (m, 10 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, [D$_6$]DMSO, plus DEPT): δ = 21.0 (+, CH$_3$), 44.3 [+, N(CH$_3$)$_3^+$], 44.6 (−, C-5), 78.9 (C$_{quat.}$, C-4), 127.7, 128.0, 128.2, 128.3, 128.7, 128.9 (+, Ph−C), 133.7, 133.8 (C$_{quat.}$, Ph−C), 146.8 (C$_{quat.}$, C-2), 162.9 (C$_{quat.}$, C-3), 204.6 (C$_{quat.}$, C-1).

Variation B: According to GP4B, 4-(dimethylamino)-4-methyl-2,3-diphenyl-2-cyclopentenone (**21aahh**) (137 mg, 0.47 mmol) and methyl iodide (456 mg, 3.21 mmol) in acetone (20 mL) were stirred at ambient pressure for 3 days. After filtration and washing with Et$_2$O (3 × 20 mL), 142 mg (70%) of **24aahh** was isolated.

2,3-Dimethyl-4-methylene-2-cyclopentenone (25aa): A high-pressure-resistant bottle was charged with 4-(dimethylamino)-2,3,4-trimethyl-2-cyclopentenone (**21aaaa**) (393 mg, 2.35 mmol), acetone (30 mL) and methyl iodide (2.07 g, 14.6 mmol), sealed and the mixture stirred at 100 °C for 2 h. After dilution with Et$_2$O (50 mL), filtration and washing with Et$_2$O (3 × 20 mL), the white solid (434 mg) was identified as tetramethylammonium iodide. The solvent of the filtrate was removed under reduced pressure. Chromatography on silica gel (30 g) eluting with pentane/Et$_2$O (5:1) gave 158 mg (55%) of **25aa** [R_f = 0.39 (pentane/Et$_2$O, 3:1)] as a yellow oil. IR (film): $\tilde{\nu}$ = 2920 cm^{-1} (C−H), 2785 (C−H), 1700 (C=O), 1652 (C=C), 1616 (C=C), 1558, 1540, 1506, 1394, 1071, 887. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.75 (s, 3 H, CH$_3$), 2.02 (s, 3 H, CH$_3$), 2.89 (s, 2 H, 5-H), 5.06 (s, 1 H, =CH$_2$), 5.24 (s, 1 H, =CH$_2$) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 8.4 (+, CH$_3$), 11.4 (+, CH$_3$), 39.1 (−, C-5), 107.3 (−, =CH$_2$), 140.8 (C$_{quat.}$, C-2), 144.3 (C$_{quat.}$, C-4), 162.2 (C$_{quat.}$, C-3), 204.9 (C$_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 122 (92) [M$^+$], 107 (18) [M$^+$ − CH$_3$], 93 (20) [M$^+$ − CH$_3$ − CH$_2$], 79 (100), 53 (8), 41 (4).

4-(3′-Iodopropylidene)-2,3-dimethyl-2-cyclopentenone (26aa): According to GP4B, 4-cyclopropyl-4-(dimethylamino)-2,3-dimethyl-2-cyclopentenone (**21caaa**) (341 mg, 1.76 mmol) and methyl iodide (1.53 mg, 10.8 mmol) in acetone (30 mL) were stirred at ambient pressure for 3 days. After filtration and washing with Et$_2$O (3 × 20 mL), the white solid (268 mg) was identified as tetramethylammonium iodide. The solvent of the filtrate was removed under reduced pressure. Chromatography on silica gel (30 g) eluting with pentane/Et$_2$O (5:1) gave 347 mg (71%) of **26aa** [R_f = 0.18 (pentane/Et$_2$O, 3:1] as colorless crystals: m.p. 41 °C. IR (KBr): $\tilde{\nu}$ = 3025 cm^{-1} (C−H), 2913 (C−H), 2832 (C−H), 1706 (C=O), 1645 (C=C), 1607 (C=C), 1448, 1428, 1328, 920. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.76 (s, 3 H, CH$_3$), 2.06 (s, 3 H, CH$_3$), 2.73 (dt, ^3J = 7.1, ^3J = 7.1 Hz, 2 H, 2′-H), 2.87 (s, 2 H, 5-H), 3.20 (t, ^3J = 7.1 Hz, 2 H, 3′-H), 5.61 (t, ^3J = 7.1 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 4.5 (−, C-3′), 8.4 (+, CH$_3$), 11.8 (+, CH$_3$), 33.5 (−, C-2′), 36.9 (−, C-5), 121.9 (+, C-1′), 139.2, 139.9 (C$_{quat.}$, C-2, C-4), 162.6 (C$_{quat.}$, C-3), 204.2 (C$_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 276 (58) [M$^+$], 149 (100) [M$^+$ − I], 122 (95) [M$^+$ − C$_2$H$_3$I], 105 (19), 91 (23), 77 (17), 65 (9), 41 (10) [C$_3$H$_5^+$]. C$_{10}$H$_{13}$IO (276.1): calcd. C 43.50, H 4.75; found C 44.45, H 4.90.

Dimethyl (2,3,4-Trimethyl-2-cyclopentenon-4-yl)malonate (27aaa-Me) and 2,3,4,7,8,9-Hexamethyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene-5,10-dione (29aaa): According to GP5, (2,3,4-trimethyl-2-cyclopentenon-4-yl)trimethylammonium iodide (**24aaaa**) (59 mg, 0.19 mmol) in THF (5 mL) was treated with a solution of sodium dimethylmalonate (0.40 mmol) in THF (5 mL) and the mixture was stirred at ambient temperature for 6 h. Chromatography on silica gel (10 g) eluting with pentane/Et$_2$O (3:1) gave 13 mg (56%) of **29aaa** [R_f = 0.42 (pentane/Et$_2$O, 2:1)] as colorless crystals, m.p. 76 °C and 16 mg (33%) of **27aaa**-Me [R_f = 0.15 (pentane/Et$_2$O, 2:1)] as a colorless oil, respectively. **27aaa**-Me: IR (film): $\tilde{\nu}$ = 2955 cm^{-1} (C−H), 1734 (C=O), 1700 (C=O), 1653 (C=C), 1436, 1386, 1326, 1241, 1195. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.30 (s, 3 H, CH$_3$), 1.66 (s, 3 H, CH$_3$), 1.96 (s, 3 H, CH$_3$), 2.23 (AB, d, ^2J = 19.1 Hz, 1 H, 5-H), 3.14 (AB, d, ^2J = 19.1 Hz, 1 H, 5-H), 3.58 (s, 3 H, CO$_2$CH$_3$), 3.61 [s, 1 H, C*H*(CO$_2$CH$_3$)$_2$], 3.75 (s, 3 H, CO$_2$CH$_3$) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 8.1 (+, CH$_3$), 12.22 (+, CH$_3$), 25.06 (+, CH$_3$), 45.2 (−, C-5), 46.1 (C$_{quat.}$, C-4), 52.4 (+, CO$_2$*C*H$_3$), 52.5 (+, CO$_2$*C*H$_3$), 56.8 [+, *C*H(CO$_2$CH$_3$)$_2$], 137.1 (C$_{quat.}$, C-2), 167.4 [C$_{quat.}$, CH(*C*O$_2$CH$_3$)$_2$], 168.0 [C$_{quat.}$, CH(*C*O$_2$CH$_3$)$_2$], 171.2 (C$_{quat.}$, C-3), 207.0 (C$_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 254 (10) [M$^+$], 223 (8) [M$^+$ − OCH$_3$], 195 (4), 163 (5), 133 (5), 122 (100) [M$^+$ − CH$_2$(CO$_2$CH$_3$)$_2$], 95 (20), 79 (4). HRMS (EI) calcd. for C$_{13}$H$_{18}$O$_5$: 254.1154 (correct HMRS).

29aaa: IR (KBr): $\tilde{\nu}$ = 2967 cm^{-1} (C−H), 2937 (C−H), 2843 (C−H), 1772 (C=O), 1686 (C=O), 1639 (C=C), 1436, 1383. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.29 (s, 3 H, CH$_3$), 1.37 (s, 3 H, CH$_3$), 1.53 (s, 3 H, CH$_3$), 1.58 (s, 3 H, CH$_3$), 1.65 (d, ^4J = 1.1 Hz, 3 H, CH$_3$), 1.95 (s, 3 H, CH$_3$), 1.98 (s, 1 H, 6-H), 2.62 (s, 1 H, 1-H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ = 6.2 (+, CH$_3$), 10.6 (+, CH$_3$), 10.8 (+, CH$_3$), 13.7 (+, CH$_3$), 13.7 (+, CH$_3$), 20.4 (+, CH$_3$), 49.9 (C$_{quat.}$, C-2), 57.2 (+, C-6), 57.4 (C$_{quat.}$, C-7), 60.5 (+, C-1), 131.6, 134.0 (C$_{quat.}$, C-4, C-9), 141.9 (C$_{quat.}$, C-8), 168.9 (C$_{quat.}$, C-3), 201.7 (C$_{quat.}$, C-10), 205.3 (C$_{quat.}$, C-5). C$_{16}$H$_{20}$O$_2$ (244.3): calcd. C 78.65, H 8.25; found C 77.80, H 8.45.

Diethyl (2,3,4-Trimethyl-2-cyclopentenon-4-yl)malonate (27aaa-Et): According to GP5, (2,3,4-trimethyl-2-cyclopentenon-4-yl)trimethylammonium iodide (**24aaaa**) (120 mg, 0.39 mmol) in THF (10 mL) was treated with a solution of sodium diethylmalonate (0.80 mmol) in THF (5 mL) and the mixture was stirred at ambient temperature for 2 h. Chromatography on silica gel (10 g) eluting with pentane/Et$_2$O (1:1) gave 82 mg (74%) of **27aaa**-Et [R_f = 0.10 (pentane/Et$_2$O, 3:1)] as a colorless oil, which later became a colorless crystal, m.p. 54 °C. IR (KBr): $\tilde{\nu}$ = 2993 cm^{-1} (C−H), 2924 (C−H), 2876 (C−H), 1725 (C=O), 1695 (C=O), 1645 (C=C), 1475, 1454, 1388. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.10 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.24 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.27 (s, 3 H, CH$_3$), 1.62 (s, 3 H, CH$_3$), 1.94 (s, 3 H, CH$_3$), 2.20 (AB,

d, ^2J = 19.2 Hz, 1 H, 5-H), 3.14 (AB, d, ^2J = 19.2 Hz, 1 H, 5-H), 3.61 [s, 1 H, C*H*($CO_2CH_2CH_3$)$_2$], 4.00 (q, ^3J = 7.1 Hz, 1 H, OC*H*$_2$CH$_3$), 4.01 (q, ^3J = 7.1 Hz, 1 H, OC*H*$_2$CH$_3$), 4.17 (q, ^3J = 7.1 Hz, 1 H, OC*H*$_2$CH$_3$), 4.18 (q, ^3J = 7.1 Hz, 1 H, OC*H*$_2$CH$_3$) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.0 (+, CH_3), 12.3 (+, CH_3), 13.8 (+, OCH$_2$*C*H$_3$), 14.0 (+, OCH$_2$*C*H$_3$), 25.1 (+, CH_3), 45.2 (−, C-5), 45.9 ($C_{quat.}$, C-4), 57.1 [+, *C*H(CO_2Et)$_2$], 61.4 (−, O*C*H$_2$CH$_3$), 61.4 (−, O*C*H$_2$CH$_3$), 136.9 ($C_{quat.}$, C-2), 166.9, 167.5 [$C_{quat.}$, CH(*C*O$_2$Et)$_2$], 171.6 ($C_{quat.}$, C-3), 207.2 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 282 (10) [M$^+$], 237 (5) [M$^+$ − OCH$_2$CH$_3$], 209 (4), 161 (9), 122 (100) [M$^+$ − CH$_2$($CO_2CH_2CH_3$)$_2$], 107 (5), 95 (9), 79 (4), 67 (4), 43 (4). $C_{15}H_{22}O_5$ (282.3): calcd. C 63.81, H 7.85; found C 63.94, H 7.84.

Diethyl (4-Methyl-2,3-diphenyl-2-cyclopentenon-4-yl)malonate (27ahh-Et): According to GP5, (4-methyl-2,3-diphenyl-2-cyclopentenon-4-yl)trimethylammonium iodide (**24aahh**) (74 mg, 0.17 mmol) in THF (10 mL) was treated with a solution of sodium diethylmalonate (0.60 mmol) in THF (5 mL) and the mixture was stirred at ambient temperature for 1 h. Chromatography on silica gel (10 g) eluting with pentane/Et_2O (3:1) gave 52 mg (75%) of **27ahh**-Et [R_f = 0.30 (pentane/Et_2O, 2:1)] as colorless crystals, m.p. 64 °C. IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1} (C−H), 2975 (C−H), 2934 (C−H), 1750 (C=O), 1728 (C=O), 1704 (C=O), 1620 (C=C), 1570, 1488, 1462. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.17 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.28 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.47 (s, 3 H, CH_3), 2.52 (AB, d, ^2J = 19.2 Hz, 1 H, 5-H), 3.58 (AB, d, ^2J = 19.2 Hz, 1 H, 5-H), 3.63 [s, 1 H, C*H*($CO_2CH_2CH_3$)$_2$], 4.12 (q, ^3J = 7.1 Hz, 2 H, OC*H*$_2$CH$_3$), 4.21 (q, ^3J = 7.1 Hz, 1 H, OC*H*$_2$CH$_3$), 4.22 (q, ^3J = 7.1 Hz, 1 H, OC*H*$_2$CH$_3$), 7.11−7.34 (m, 10 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, OCH$_2$*C*H$_3$), 14.0 (+, OCH$_2$*C*H$_3$), 26.1 (+, CH_3), 46.2 (−, C-5), 46.8 ($C_{quat.}$, C-4), 56.9 [+, *C*H(CO_2Et)$_2$], 61.6 (−, 2 × O*C*H$_2$CH$_3$), 127.6, 127.8, 128.3, 128.4, 128.5, 129.4 (+, Ph−C), 130.9, 134.5 ($C_{quat.}$, Ph−C), 141.1 ($C_{quat.}$, C-2), 167.1, 167.7 [$C_{quat.}$, CH(*C*O$_2$Et)$_2$], 171.3 ($C_{quat.}$, C-3), 205.6 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 406 (65) [M$^+$], 361 (5) [M$^+$ − OCH$_2$CH$_3$], 247 (100) [M$^+$ − CH($CO_2CH_2CH_3$)$_2$], 219 (20), 204 (16), 178 (10), 141 (4), 91 (7). $C_{25}H_{26}O_5$ (406.5): calcd. C 73.87, H 6.45; found C 73.59, H 6.68.

Di-*tert*-butyl (4-Methyl-2,3-diphenyl-2-cyclopentenon-4-yl)malonate (27ahh-*t*Bu) and 1,2-Dimethyl-3,4,9,10-tetraphenyltricyclo[5.3.0.0^{2,6}]deca-3,9-diene-5,8-dione (31ahh): According to GP5, (4-methyl-2,3-diphenyl-2-cyclopentenon-4-yl)trimethylammonium iodide (24aahh) (61 mg, 0.14 mmol) in THF (10 mL) was treated with a solution of sodium di(*tert*-butyl)malonate (0.60 mmol) in THF (5 mL) and the mixture was stirred at ambient temperature for 1 h. Chromatography on silica gel (10 g) eluting with pentane/Et_2O (4:1) gave 29 mg (45%) of **27ahh**-*t*Bu [R_f = 0.45 (pentane/Et_2O, 2:1)] as colorless crystals, m.p. 174 °C and 16 mg (46%) of **31ahh** [R_f = 0.21 (pentane/Et_2O, 2:1)] as colorless crystals, m.p. 124 °C. **27ahh**-*t*Bu: IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (C−H), 2978 (C−H), 2931 (C−H), 1752 (C=O), 1707 (C=O), 1594 (C=C), 1489, 1445, 1394, 1371. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.38 [s, 9 H, C(CH_3)$_3$], 1.43 (s, 3 H, CH_3), 1.48 [s, 9 H, C(CH_3)$_3$], 2.47 (AB, d, ^2J = 19.2 Hz, 1 H, 5-H), 3.45 [s, 1 H, C*H*(CO_2tBu)$_2$], 3.56 (AB, d, ^2J = 19.2 Hz, 1 H, 5-H), 7.15−7.32 (m, 10 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 26.2 (+, CH_3), 27.7 [+, C(*C*H$_3$)$_3$], 27.9 [+, C(*C*H$_3$)$_3$], 46.1 ($C_{quat.}$, C-4), 47.0 (−, C-5), 58.8 [+, *C*H(CO_2tBu)$_2$], 82.2 [$C_{quat.}$, CO_2C(CH$_3$)$_3$], 82.4 [$C_{quat.}$, CO_2C(CH$_3$)$_3$], 127.6, 127.8, 128.3, 128.4, 129.6, 129.6 (+, Ph−C), 131.0, 134.8 ($C_{quat.}$, Ph−C), 140.8 ($C_{quat.}$, C-2), 166.5, 166.9 [$C_{quat.}$, CH(*C*O$_2t$Bu)$_2$], 174.4 ($C_{quat.}$, C-3), 206.3 ($C_{quat.}$, C-1) ppm. MS (70 eV): *m*/*z* (%) = 462 (15) [M$^+$], 405 (8) [M$^+$ − C(CH$_3$)$_3$], 350 (100) [M$^+$ − 2C$_4$H$_8$], 233 (17), 261 (10), 247 (30) [M$^+$ − CH(CO$_2t$Bu)$_2$], 234 (9), 178 (17), 57 (44) [C(CH$_3$)$_3^+$]. $C_{29}H_{34}O_5$ (462.6): calcd. C 75.29, H 7.41; found C 75.09, H 7.91.

31ahh: IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1} (C−H), 2967 (C−H), 2912 (C−H), 1700 (C=O), 1488, 1444, 1345, 1159, 1031. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.54 (s, 6 H, CH_3), 2.69 (s, 2 H, 6-H, 7-H), 7.09−7.32 (m, 20 H, Ph−H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 20.6 (+, CH_3), 48.5 (+, C-6, C-7), 55.8 ($C_{quat.}$, C-1, C-2), 128.1, 128.29 128.32, 129.2, 129.3, 129.6 (+, Ph−C), 131.4, 134.2 ($C_{quat.}$, Ph−C), 143.9 ($C_{quat.}$, C-4, C-9), 171.6 ($C_{quat.}$, C-3, C-10), 204.8 ($C_{quat.}$, C-5, C-8) ppm. MS (70 eV): *m*/*z* (%) = 492 (35) [M$^+$], 246 (100) [$C_{18}H_{14}O^+$], 218 (15), 178 (16), 116 (18).

5-Methyl-4,6-dimethylenebicyclo[3.3.0]oct-1-en-3-one (32): A solution of 5-(3′-bromobut-3′-enyl)-5-(dimethylamino)-3-ethoxy-1,2-dimethyl-1,3-cyclopentadiene (**7naaa**) (90 mg, 0.29 mmol) in THF/MeOH (5:1, 5 mL) was treated with a small amount of silica gel and the mixture was stirred for 24 h. After filtration through silica gel and removal of the solvent, the residue was dissolved in DMF (10 mL) and transferred to a Pyrex bottle. Palladium acetate (7.0 mg, 11 mol %), triphenylphosphane (15 mg, 20 mol %) and triethylamine (500 mg, 4.94 mmol) were added to the solution. Dry nitrogen was bubbled through the solution for 5 min, and the mixture was stirred at 100 °C for an additional 20 h. The reaction mixture was diluted with H_2O and extracted with pentane (3 × 50 mL). The organic extract was dried with $MgSO_4$ and the solvent was removed under reduced pressure. Chromatography on flash silica gel (20 g) eluting with pentane/Et_2O (10:1) gave 17 mg (37%) of **32** [R_f = 0.21 (pentane/Et_2O, 10:1)] as a colorless oil. IR (film): $\tilde{\nu}$ = 2963 cm^{-1}, 2925, 2853 (C−H), 1703 (C=O), 1655, 1623 (C=C), 1451, 1126, 876. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.38 (s, 3 H, CH_3), 2.57 (m_c, 1 H, 8-H), 2.70−2.83 (m, 2 H, 7-H, 8-H), 2.84−3.05 (m, 1 H, 7-H), 4.78 (d, ^2J = 1.7 Hz, 1 H, 6-CH$_2$), 5.31 (d, ^2J = 1.7 Hz, 1 H, 6-CH$_2$), 5.49 (s, 1 H, 2-H), 6.54 (s, 1 H, 4-CH$_2$), 6.93 (s, 1 H, 4-CH$_2$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 25.1 (CH_3), 27.2 (C-6), 31.2 (C-7), 55.1 (C-5), 106.4 (6-CH$_2$), 114.7 (C-6), 124.8 (4-CH$_2$), 150.06 (C-4), 150.10 (C-2), 185.7 (C-1), 197.0 (C-3) ppm. MS (70 eV): *m*/*z* (%) = 160 (95) [M$^+$], 145 (100) [M$^+$ − CH$_3$], 132 (38) [M$^+$ − CO], 117 (61), 91 (53), 77 (18), 51 (19). HRMS (EI) calcd. for $C_{11}H_{12}O$: 160.0888 (correct HMRS).

Supporting Information (see also the footnote on the first page of this article): For the following compounds experimental details are available: **3la**, **3ra**, **3sa**, **7raf**, (**7rag**, **8rag**), **7saf** and **7dacc**.

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