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Three Molecules of an Arylalkyne Reacting with a β-Amino-Substituted α,β-Unsaturated Fischer Carbene Complex to Give Highly Substituted Spiro[4.4]nonatrienes

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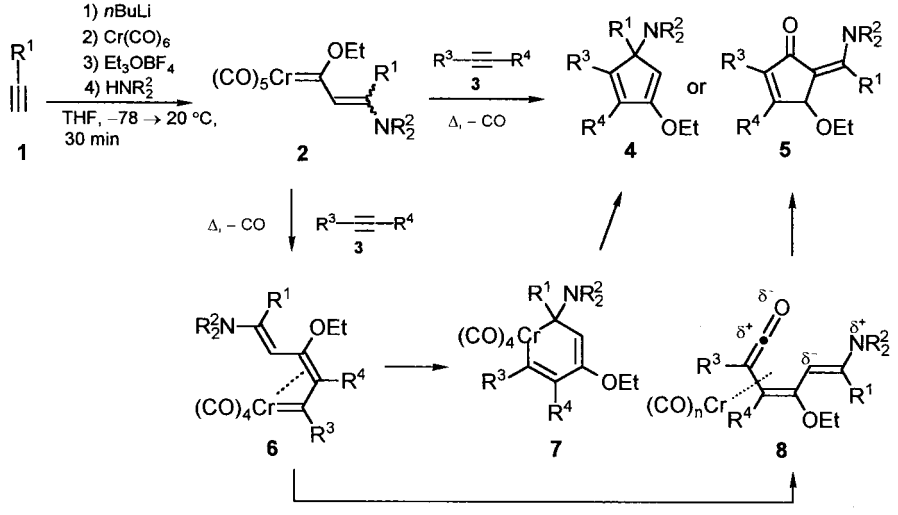
Abstract—A novel mode of reaction towards arylethynes is shown by the β-trimethylsilyl-substituted α,β-unsaturated Fischer carbene complex **10**. A mixture of the isomeric, highly substituted spiro[4.4]nonatrienes **12** and **13** (ratios 1.6:1 to 4.5:1) in yields ranging from 34 to 62% is formed by the formal insertion of three alkyne molecules and concomitant or subsequent cyclization. Such selective triple reactions of alkynes with ethenylcarbene complexes have not previously been observed. It is believed that this reaction proceeds via an unprecedented domino sequence of a formal [3+2] cycloaddition, carbene reformation, and formal [2+2+1] cycloaddition process which occur in conjunction with a number of other additional in situ transformations of transient chromium π-complexes. © 2000 Published by Elsevier Science Ltd.

Introduction

The chemistry of Fischer carbene, and transition metal carbene complexes in general, is a fascinating area both in terms of the variety of reaction types that can be attained and the possibility of achieving a number of these in domino type sequences.[1] Due to these versatile features, these reagents and reactive intermediates are playing an increasing role in the development of new multiple bond-forming reactions that lead to substantial increases in molecular complexity from simple substrates in a single operation.[2] An essential element in many of these processes is the



Scheme 1.

Keywords: Fischer carbene complex; metathesis-type reaction; metal-carbene.
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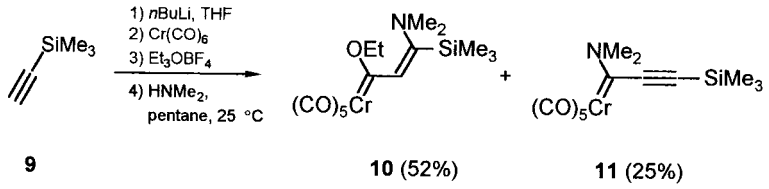


Scheme 2. Synthesis of **10** from trimethylsilylethyne **9** by the one-pot procedure.

ability of the metal-carbene to insert an alkyne via a metathesis-type reaction to give a new metal-carbene that can further react in any one of a number of ways.[1,3]

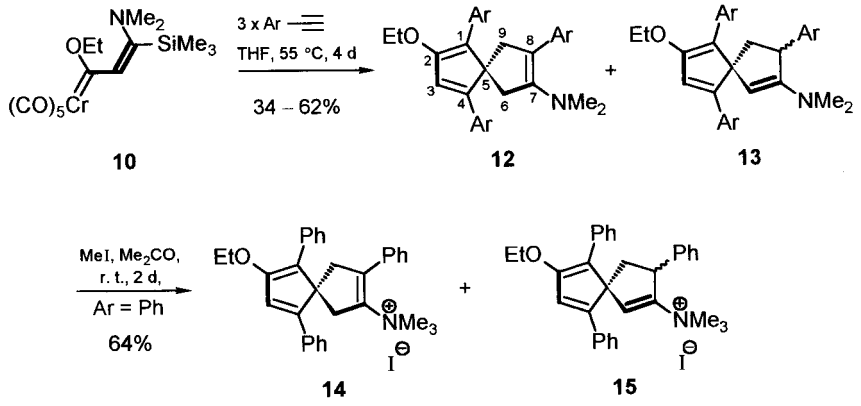
Work within our group has concentrated on the chemistry of β-aminoalkenylidenecarbene complexes **2** accessible from terminal alkynes **1** and secondary amines in a simple one-pot operation (Scheme 1).[4,5] In nearly all cases, these complexes react with alkynes **3** to give either cyclopentadienes **4** in a formal [3+2] cycloaddition or 5-(dialkylamino)alkylidenecyclopent-2-enones **5** in a formal [2+2+1] cycloaddition (Scheme 1).[6,7] Both processes involve initial insertion of the alkyne **3** to give **6**. Cyclization of **6** to **7** and reductive elimination of $Cr(CO)_4$ affords the cyclopentadiene-type product **4**.[5a,6] Alternatively, carbonyl insertion in **6** to give **8** with subsequent 1,5-cyclization and loss of $Cr(CO)_3$ leads eventually to product **5**.[7a] The nature of the product obtained can be controlled, in a highly selective fashion, simply by appropriate choice of the reaction conditions.[5a,7b] A variety of methods involving in situ transforming versions of **4** and **5** by interception of their corresponding $Cr(CO)_n$ π-complexes (not shown) has also been explored.[5a,8] In this work we describe a remarkable reaction of the silyl-substituted complex **10** with three equivalents of an arylethyne to produce 7-dimethylamino-2-ethoxy-1,4,8-triarylspiro[4.4]nonatrienes **12** and **13** (Scheme 2).

Results and Discussion

The (3-dimethylaminoalkenylidene)chromium complexes of type **2** with sterically demanding substituents on the alkenyl terminus, and therefore normally having a (*Z*) configuration, react preferentially by sequential insertion of two alkyne units and carbon monoxide to give cyclopenta[*b*]pyranes by a [3+2+2+1] cocyclization, frequently in high yields.[9] Although it also has a sterically demanding substituent and a (*Z*) configuration, the trimethylsilyl-substituted complex **10** reacts with formal insertion of three alkyne units in a manner not previously observed.[5c] Pentacarbonyl(3-dimethylamino-1-ethoxy-3-trimethylsilylallylidene)chromium (**10**) may be prepared by an improved method[5c,10] as a 2:1 mixture of **10** and the (1-dimethylaminoalkynylidene)chromium complex **11** in good yield (Scheme 2).

Upon heating complex **10** with six equivalents (optimized, twofold excess) of phenylethyne in THF at 55°C (complete conversion of **10** after 4 days according to thin-layer chromatography), a yellow solid which fluoresces strongly in solution was obtained after purification by chromatography (Scheme 3). ^1H and ^{13}C NMR spectra indicated that it was a mixture of three isomers (ratio 3.6:1:1), none of which contained a trimethylsilyl group. Assuming that the highest peak in the mass spectrum of the mixture at *m/z* 433 corresponded to the molecular ion peak, a compound had been formed in this reaction in 62% yield from the protiodesilylated carbene ligand and three molecules of phenylethyne without carbonyl insertion.

However, neither was it possible to separate the three isomers by repeated column chromatography, nor to assign the correct structures from the NMR spectra of the mixture. All attempts at crystallizing the major isomer failed since the mixture of compounds dissolved in only a small volume of pentane and decomposed rapidly during slow evaporation. To increase the polarity of all isomers at their dimethylamino groups the mixture was treated with iodomethane in acetone at room temperature. The mixture of the three isomeric quaternary ammonium iodides obtained in 64% yield after two days, was considerably more stable in



Scheme 3. Synthesis of **12** and **13** and their conversion (Ar=Ph) to the quaternary ammonium salts **14** and **15**. For details see Table 1.

Table 1. Formation of spiro[4.4]nonatrienes **12** and **13**

	Ar	Yield **12**+**13** (%)	Ratio **12**:**13**
a	C_6H_5	62	1.8:1
b	C_6H_4-4-C_6H_5	34	4.5:1
c	C_6H_4-4-OMe	37	2.5:1
d	C_6H_3-3,5-Me_2	48	1.6:1

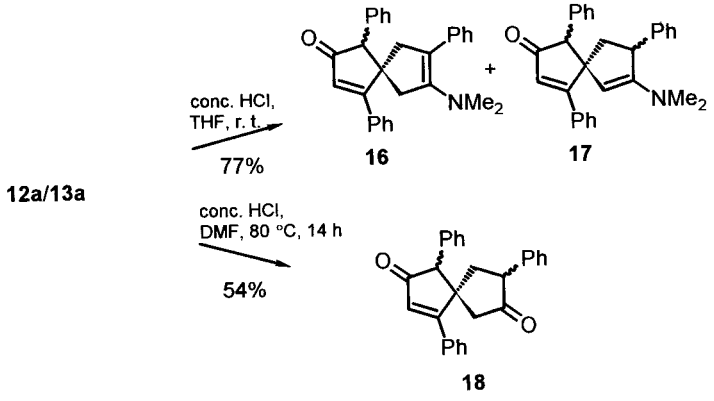
solution (Scheme 3). Slow evaporation of a solution of the mixture in ethanol/acetone allowed single crystals to be isolated. According to X-ray crystal structure analysis these consisted of the quaternary ammonium iodide **14** of 7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,7-triene (**12a**).[5c] An NMR spectrum of the single crystals showed that the product was the main isomer in the mixture of products.

A conclusive assignment of the other isomers obtained from **10** and phenylethyne was achieved by high-resolution 2D-NMR correlation experiments, according to which the two minor isomers were a 1:1 mixture of the two diastereomeric spiro[4.4]nona-1,3,6-trienes **13a**. An assumption that the isomers **12** and **13** existed in a dynamic equilibrium could not be confirmed. ^{1}H NMR spectra measured at different temperatures showed that there were no changes in the characteristic signal intensities.

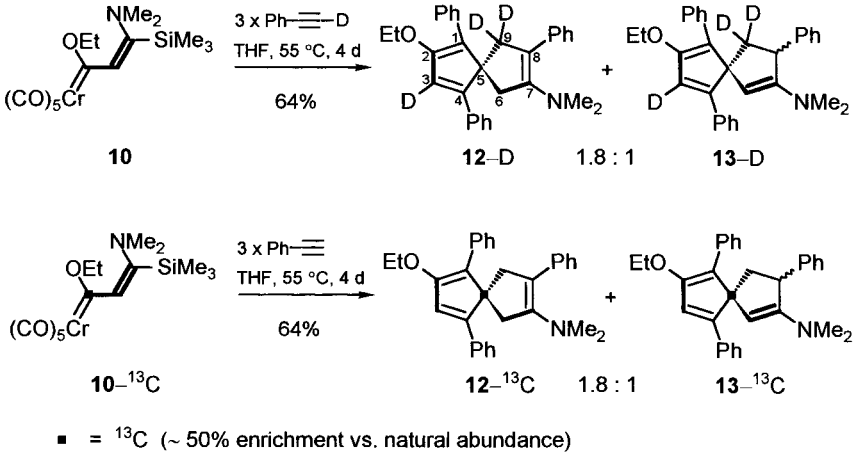
To elucidate the scope of this new reaction, **10** was allowed to react with a series of alkynes. This showed that only arylethynes yielded the spiro[4.4]nonatrienes **12** and **13**. The isomer ratio of the products thus obtained varied with the substituent types and the substitution pattern on the arylethyne employed (Table 1). Aliphatic terminal alkynes such as 1-pentyne and internal alkynes such as 2-butyne react in the previously known manner to give the respective substituted cyclopentadienes.[5a]

The conspicuously intense fluorescence of these spiro[4.4]-nonatrienes must be attributed to the conjugated diaryl-cyclopentadiene moiety in **12** and **13**. The mixture of the (3,5-dimethylphenyl)-substituted isomers **12d/13d** showed an absorption maximum in the UV spectrum at λ_{max}= 237 nm (isooctane) with ϵ_{max}=480 (isooctane), and the relative fluorescence quantum yield was calculated to be 46%.[5c]

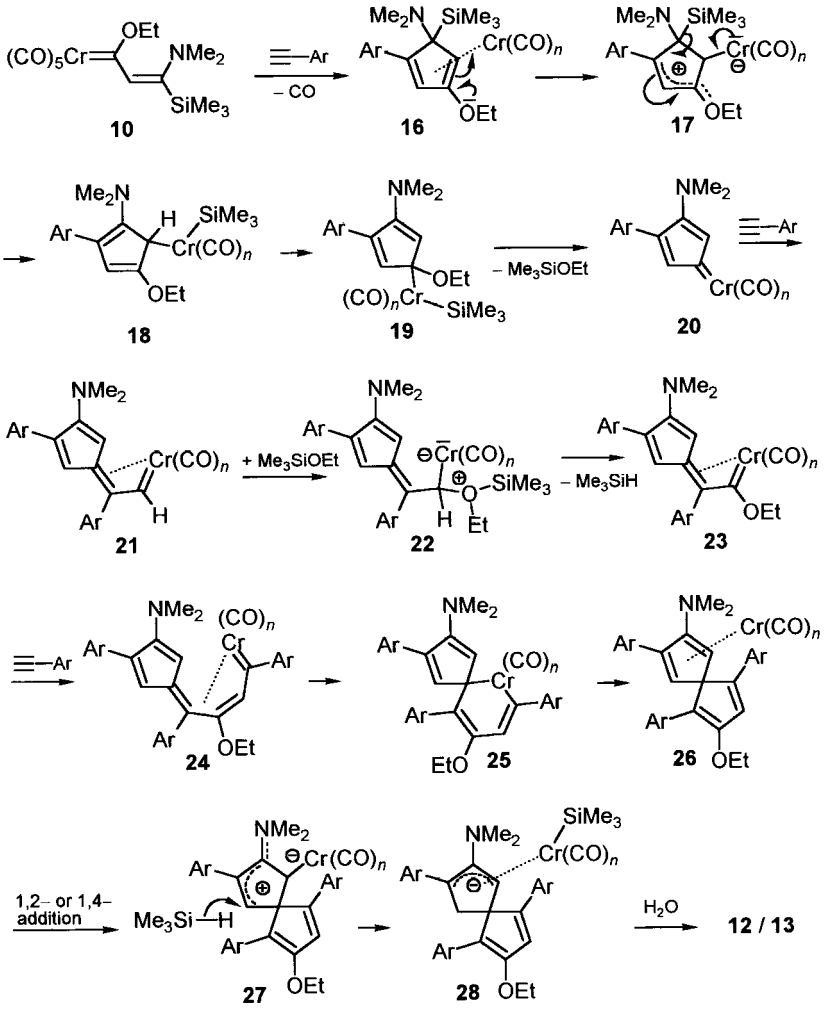
Hydrolysis of the enol ether and enamine functionalities in **12** and **13** should yield a spiro[4.4]nonenedione **18**. Unexpectedly, however, the enamine functionality was stable under strongly acidic conditions (concentrated HCl) at room temperature and only the enol ether moiety in **12a/13a** was hydrolyzed to yield the isomeric spiro[4.4]nona-dienones **16** and **17**. Yet, under more forcing conditions (concentrated HCl, 80°C), complete hydrolysis to the diketone **18** as a mixture of three diastereomers (ratio 3:3:1) was achieved (Scheme 4).



Scheme 4.



Scheme 5.



Scheme 6. Proposed mechanism for the formation of spiro[4.4]nonatrienes **12/13** from **10** and three molecules of an arylethyne.

Mechanistically, the reaction of **10** leading to **12/13** is very intriguing. It is particularly unusual that the original connectivity of the carbene ligand in **10** appears to be lost in the products **12** and **13**. In contrast, the original connectivity is maintained in all previously known products from β-dialkylamino-substituted α,β-unsaturated carbenechromium complexes.[1k] In order to derive a plausible mechanism, it was proved that both hydrogens at C9 in **12** and **13** originated from those initially at C2 of the arylethyne by letting **10** react with deuterophenylethyne (Scheme 5). The reaction of the ^{13}C-labelled carbenechromium complex **10**-^{13}C—prepared from trimethylsilylethyne and ^{13}C-labelled hexacarbonylchromium (approximately 50% enrichment versus natural abundance)—and phenylethyne yielded the spiro[4.4]nonatrienes **12**-^{13}C and **13**-^{13}C with the ^{13}C label clearly detectable only at the spiro-carbon C5 (Scheme 5).

On the basis of these results, it is proposed that arylalkynes initially react with **10** in the same manner as their aliphatic counterparts to give cyclopentadienes **16** (Scheme 6). The π-acidity of the transiently bound carbonylchromium unit induces formation of the zwitterionic isomer **17**. A similar rationalization has brought forward the in situ transformation of cyclopentadienes **4** under analogous conditions.[8] An aryl substituent at C1 of the cyclopentadiene due to its ability to stabilize an adjacent cationic center favors a zwitterionic species of type **17** more than an alkyl substituent. Subsequent migration of the trimethylsilyl group to chromium to give **18**, [1,5]-shift of the carbonylchromium unit and elimination of ethyl trimethylsilyl ether ($EtOSiMe_3$) would afford the cyclopentadienylidenechromium complex **20**. The latter must next insert another arylethyne molecule to give **21** with a regioselectivity opposite to what is normally observed.[3] Nucleophilic addition of $EtOSiMe_3$ would produce **22** and subsequent elimination of trimethylsilane[11] would generate the new fulvenylcarbene complex **23**. Regioselective insertion of another alkyne, cyclization and reductive elimination would than produce the spiro[4.4]nonatetraene complex **26**. The π-acidic carbonylchromium unit eventually attacks the dimethylaminocyclopentadiene moiety, and this may induce attack by trimethylsilane to produce the π-allylchromium complex **28**. Protiodemetalation upon work-up would finally give the observed products **12** and **13**.

Although purely speculative, this rationalization brings together one molecule of the starting complex **10**, and three molecules of the alkyne in the right order to give the observed product skeleton. It implies that the connectivity of the carbene ligand in **10** is not lost in the process, but the

ethoxy substituent has migrated from its original position in **10** to a center two carbons away in the second inserted alkyne moiety.

Experimental

General

^{1}H and ^{13}C NMR: Varian VXR 500 (500 and 125.7 MHz), Bruker AW 250 (250 and 62.9 MHz). Chemical shifts in $CDCl_3$ or [D_6] benzene are reported as δ values with chloroform (δ=7.26 ppm) or benzene (δ=7.15 ppm) as internal reference unless stated otherwise. IR: Bruker IFS 66 (FT-IR). Low-resolution EI MS: Varian MAT CH 7 with Aerograph 1740, ionizing voltage 70 eV. High-resolution MS VG-70-250S. Melting points were determined with a Büchi melting point apparatus and are uncorrected. Solvents for extraction and chromatography were of technical grade and freshly distilled before use. Chromatography: Merck silica gel 60 (230–400 mesh) or ICN neutral alumina (Super I, Activity II according to Brockmann). The concentrations of organolithium compounds were determined by titration according to the method of Suffert.[12] All reactions were carried out under nitrogen or argon in oven- and/or flame-dried glassware. Unless specified otherwise, solutions of NH_4Cl, $NaHCO_3$ and NaCl were saturated aqueous solutions. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl.

General procedure for the preparation of spiro[4.4]-nonatrienes (GP 1)

A screw-cap Pyrex bottle was charged with a 0.05 M solution of a Fischer carbene complex **2** in anhydrous tetrahydrofuran and 6 equiv. of an arylalkyne. Dry nitrogen was bubbled through the solution for 5 min. The bottle was sealed with the screw cap and heated at 55°C for 2 to 4 days. The solvent was removed under reduced pressure and diethyl ether was added to the residue. The mixture was exposed to air for 2 h. After filtration of the solution through Celite, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel.

7-Dimethylamino-2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,7-triene (12a) and 7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,6-triene (13a). Pentacarbonyl[(2*Z*)-3-dimethylamino-1-ethoxy-3-trimethylsilylpropenylidene]chromium (**10**) (392 mg, 1.00 mmol) in 20 ml of THF was treated with phenylethyne (613 mg, 6.00 mmol) and heated at 55°C for 4 days according to GP 1. After column chromatography on silica gel (pentane/diethyl ether, 10:1, column 2×20 cm) 269 mg (62%) of a 1.8:1 mixture of **12a** and **13a** (R_f=0.45, pentane/diethyl ether 5:1) was obtained as yellow crystals, mp 45–47°C. IR (KBr): ν=3053 cm^{-1} (C–H), 2976 (C–H), 2850 (C–H), 2790, 1609 (C=C), 1595 (C=C), 1494, 1442, 1375, 1191, 1142, 1047, 999, 910, 846, 771, 697. **12a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.47 (t, ^3J=6.9 Hz, 3H, OCH_2CH_3), 2.65 [s, 6H, $N(CH_3)_2$], 2.96 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 6-H), 3.03 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 6-H), 3.09 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 9-H), 3.18 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 9-H), 4.24 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 4.25 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 6.95 (s, 1H, 3-H), 7.28–7.34 (m, 9H, Ph–H), 7.42 (dd, ^3J=7.6, ^4J=0.7 Hz, 2H, Ph–H), 7.66 (dd, ^3J=7.6, ^4J=0.7 Hz, 2H, Ph–H), 7.90 (dd, ^3J=7.6, ^4J=0.7 Hz, 2H, Ph–H). ^{13}C NMR (125.7 MHz, $CDCl_3$, plus DEPT): δ=15.59 (+, OCH_2CH_3), 42.30 (−, C-6), 42.57 [+, $N(CH_3)_2$], 44.55 (−, C-9), 53.11 (C_{quat}, C-5), 65.97 (−, OCH_2CH_3), 112.59 (C_{quat}, C-4), 119.46 (+, C-3), 124.70, 125.20, 125.59, 125.97, 127.20, 127.74, 127.98, 128.32, 128.69 (+, Ph–C), 134.01, 134.83, 138.97 (C_{quat}, Ph–C), 144.89 (C_{quat}, C-8), 147.04 (C_{quat}, C-1), 154.48 (C_{quat}, C-7), 156.37 (C_{quat}, C-2). **13a** (1:1diastereomeric mixture): ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.23 and 1.25 (t, ^3J=6.9 Hz, 3H, OCH_2CH_3), 2.09 and 2.12 (dd, ^2J=13.5, ^3J=8.5 Hz, 1H, 9H), 2.37 and 2.38 (dd, ^2J=13.5, ^3J=8.5 Hz, 1H, 9H), 2.48 and 2.52 [s, 6H, $N(CH_3)_2$], 3.40 and 3.61 (dt, ^3J=8.5, ^4J=1.4 Hz, 1H, 8H) 3.92 and 4.04 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 3.93 and 4.05 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 4.48 and 4.49 (d, ^4J=1.4 Hz, 1H, 6H), 6.43 and 6.59 (s, 1H, 3H), 6.92 and 7.02 (d, ^3J=7.6 Hz, 2H, Ph–H), 7.14–7.26 (m, 9H, Ph–H), 7.56 and 7.58 (d, ^3J=7.6 Hz, 2H, Ph–H), 7.74 and 7.79 (d, ^3J=7.6 Hz, 2H, Ph–H). ^{13}C NMR (125.7 MHz, $CDCl_3$, plus DEPT): δ=15.47 and 15.52 (+, OCH_2CH_3), 40.87 and 40.88 [+, $N(CH_3)_2$], 41.58 and 42.81 (−, C-9), 50.96 (+, C-8), 65.78 and 65.91 (−, OCH_2CH_3), 66.23 (C_{quat}, C-5), 102.62 and 102.86 (+, C-6), 121.75 and 122.97 (+, C-3), 123.72 (C_{quat}, C-4), 125.38, 125.89, 127.03, 127.16, 127.34, 127.40, 127.42, 127.59, 127.62, 127.77, 127.80, 128.02, 128.09, 128.29, 128.30, 128.89, 129.55 (+, Ph–C), 135.73, 136.16, 136.17, 136.41, 136.48 (C_{quat}, Ph–C), 152.25 and 153.03 (C_{quat}, C-1), 153.79 and 155.09 (C_{quat}, C-7), 155.34 (C_{quat}, C-2). The assignments were verified with 2D correlation experiments. MS (70 eV), *m/z* (%): 433 (81) [M^+], 404 (100) [$M^+-C_2H_5$], 398 (17), 356 (13), 202 (6), 103 (5). $C_{31}H_{31}NO$ (433.6): 433.2405 (correct HRMS).

3,9,9-Trideutero-7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,7-triene (12-D) and 3,9,9-trideutero-7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,6-triene (13-D). Pentacarbonyl[(2*Z*)-3-dimethylamino-1-ethoxy-3-trimethylsilylpropenylidene]-chromium (**10**) (392 mg, 1.00 mmol) in 20 ml of THF was treated with deuterophenylethyne (750 mg, 7.28 mmol) and heated at 55°C for 4 days according to GP 1. After column chromatography on silica gel (pentane/diethyl ether, 10:1, column 2×20 cm) 281 mg (64%) of a 1.8:1 mixture of **12-D** and **13-D** (R_f=0.45, pentane/diethyl ether 5:1) was obtained as yellow crystals, mp 47–49°C. IR (KBr): ν=3052 cm^{-1} (C–H), 2976 (C–H), 2875 (C–H), 2799, 1617 (C=C), 1594 (C=C), 1495, 1442, 1372, 1352, 1126, 1057, 1031, 978, 875, 758, 697. **12-D**: ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.48 (t, ^3J=6.9 Hz, 3H, OCH_2CH_3), 2.65 [s, 6H, $N(CH_3)_2$], 2.96 (AB, d, ^2J=17.1 Hz, 1H, 6-H), 3.03 (AB, d, ^2J=17.1 Hz, 1H, 6-H), 4.24 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 4.25 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 7.28–7.34 (m, 9H, Ph–H), 7.42 (dd, ^3J=7.6, ^4J=0.7 Hz, 2H, Ph–H), 7.67 (dd, ^3J=7.6, ^4J=0.7 Hz, 2H, Ph–H), 7.91 (dd, ^3J=7.6, ^4J=0.7 Hz, 2H, Ph–H). ^{13}C NMR (125.7 MHz, $CDCl_3$, plus DEPT): δ=15.51 (+, OCH_2CH_3), 42.22 (−, C-6), 42.49 [+, $N(CH_3)_2$], 52.82 (C_{quat}, C-5), 65.88 (−, OCH_2CH_3), 112.38 (C_{quat}, C-4), 119.37 (+, t, J_{D-C}=32.2 Hz, C-3), 124.61, 125.12, 125.49, 125.86, 127.12, 127.67, 127.88, 128.25, 128.63 (+, Ph–C), 133.90, 134.76, 138.87 (C_{quat}, Ph–C), 144.78 (C_{quat}, C-8), 147.06 (C_{quat}, C-1), 154.38

(C_{quat}, C-7), 156.17 (C_{quat}, C-2). **13-D** (1:1-diastereomeric mixture): ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.26 and 1.33 (t, ^3J=6.9 Hz, 3H, OCH_2CH_3), 2.47 and 2.53 [s, 6H, $N(CH_3)_2$], 3.41 and 3.61 (bs, 1H, 8-H) 3.94 and 4.04 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 3.95 and 4.05 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 4.48 and 4.49 (d, ^4J=1.4 Hz, 1H, 6-H), 6.92 and 7.01 (d, ^3J=7.6 Hz, 2H, Ph–H), 7.14–7.26 (m, 9H, Ph–H), 7.57–7.61 (m, 2H, Ph–H), 7.75 and 7.81 (d, ^3J=7.6 Hz, 2H, Ph–H). ^{13}C NMR (125.7 MHz, $CDCl_3$, plus DEPT): δ=15.40 and 15.45 (+, OCH_2CH_3), 40.80 and 40.81 [+, $N(CH_3)_2$], 50.71 and 50.72 (+, C-8), 65.69 and 65.82 (−, OCH_2CH_3), 65.97 and 66.04 (C_{quat}, C-5), 102.55 and 102.80 (+, C-6), 123.57 (C_{quat}, C-4), 125.29, 125.82, 125.89, 126.96, 127.09, 127.20, 127.31, 127.35, 127.48, 127.55, 127.72, 127.81, 127.95, 128.22, 128.79, 129.43 (+, Ph–C), 135.66, 136.06, 136.33, 137.37 (C_{quat}, Ph–C), 152.16 and 152.84 (C_{quat}, C-1), 154.41 and 155.02 (C_{quat}, C-7), 155.13 and 155.27 (C_{quat}, C-2). MS (70 eV), *m/z* (%): 436 (83) [M^+], 407 (100) [$M^+-C_2H_5$], 392 (15) [$M^+-N(CH_3)_2$], 359 (15), 204 (6), 146 (4), 105 (4) 72 (2).

7-Dimethylamino-1,4,8-tris(3,5-dimethylphenyl)-2-ethoxyspiro[4.4]nona-1,3,7-triene (12d) and 7-dimethylamino-1,4,8-tris(3,5-dimethylphenyl)-2-ethoxyspiro[4.4]nona-1,3,6-triene (13d). Pentacarbonyl[(2*Z*)-3-dimethylamino-1-ethoxy-3-trimethylsilylpropenylidene]chromium (**10**) (392 mg, 1.00 mmol) in 20 ml of THF was treated with 1-ethynyl-3,5-dimethylbenzene (781 mg, 6.00 mmol) and heated at 55°C for 2 days according to GP 1. After column chromatography on silica gel (pentane/diethyl ether, 10:1, column 2×20 cm) 248 mg (48%) of a 1.6:1 mixture of **12d** and **13d** (R_f=0.45, pentane/diethyl ether 10:1) was obtained as yellow crystals, mp 56–58°C. IR (KBr): ν=2975 cm^{-1} (C–H), 2915 (C–H), 1596 (C=C), 1457, 1371, 1356, 1141, 1070, 845, 679. UV (Isooctane): λ_{max} (log ϵ)= 237 nm (4.475), 291 (4.133), 309 (4.204), 330 (4.143), 373 (3.929). 12d: ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.46 (t, ^3J=6.9 Hz, 3H, OCH_2CH_3), 2.14 (bs, 18H, CH_3), 2.67 [s, 6H, $N(CH_3)_2$], 2.94 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 6-H), 3.00 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 6-H), 3.02 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 9-H), 3.13 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 9-H), 4.24 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 4.25 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 6.78 (s, 2H, Ph–H), 6.88 (s, 1H, Ph–H), 6.93 (s, 1H, 3-H), 7.01 (s, 2H, Ph–H), 7.36 (s, 2H, Ph–H), 7.63 (s, 2H, Ph–H). ^{13}C NMR (125.7 MHz, $CDCl_3$, plus APT): δ=15.50 (+, OCH_2CH_3), 21.38, 21.49, 21.73 (+, CH_3), 42.53 [+, $N(CH_3)_2$], 42.85 (−, C-6), 45.31 (−, C-9), 53.04 (−, C-5), 65.82 (−, OCH_2CH_3), 112.41 (−, C-4), 119.08 (+, C-3), 123.24, 123.63, 125.89, 126.14, 126.37 (+, Ph–C), 129.26 (−, C-1), 128.49 (+, Ph–C), 133.88, 134.47, 136.45, 137.21, 137.28, 138.00 (−, Ph–C), 139.52 (−, C-8), 146.10 (−, C-7), 155.88 (−, C-2). 13d (1:1-diastereomeric mixture): ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.24 and 1.32 (t, ^3J=6.9 Hz, 3H, OCH_2CH_3), 2.07–2.15 (m, 1H, 9-H), 2.17 and 2.19 (s, 6H, CH_3), 2.30–2.39 (m, 13H, CH_3, 9-H), 2.51 and 2.56 [s, 6H, $N(CH_3)_2$], 3.36 and 3.58 (dt, ^3J=8.5, ^4J=1.4 Hz, 1H, 8-H) 3.95 and 4.03 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 3.97 and 4.05 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 4.46 and 4.50 (d, ^4J=1.4 Hz, 1H, 6-H), 6.40 and 6.57 (s, 1H, 3-H), 6.56 and 6.65 (s, 2H, Ph–H), 6.72 and 6.81 (s, 1H, Ph–H), 6.89 and 6.94 (s, 2H, Ph–H), 7.20 and 7.28 (s, 2H, Ph–H), 7.41 and 7.47 (s, 2H, Ph–H). ^{13}C NMR (125.7 MHz, $CDCl_3$, plus APT): δ=15.43 and 15.46 (+, OCH_2CH_3), 21.20, 21.26, 21.42, 21.61 (+, CH_3), 40.87 [+, $N(CH_3)_2$], 41.66 (−, C-9), 50.89 (+, C-8), 65.60 and 65.70 (−, OCH_2CH_3), 66.01 (−, C-5), 102.99 and 103.43 (+, C-6), 121.44 and 122.54 (+, C-3), 124.13 (−, C-4), 125.16, 125.20, 125.66, 125.75, 126.26, 126.48, 128.11, 128.23 (+, Ph–C), 135.77, 135.98, 136.21, 136.89, 137.01 (−, Ph–C), 145.02 (−, C-1), 151.75 and 152.43 (−, C-7), 154.88 and 155.01 (−, C-2). MS (70 eV), *m/z*(%): 517 (84) [M^+], 488 (100) [$M^+-C_2H_5$], 473 (16), 356 (13), 412 (11), 330 (7), 258 (8), 245 (8), 172 (4), 159 (6), 131 (7), 119 (9), 105 (3), 58 (2). $C_{37}H_{43}NO$ (517.6): 517.3344 (correct HRMS).

1,4,8-Tris(biphenyl)-7-dimethylamino-2-ethoxyspiro[4.4]-nona-1,3,7-triene (12b) and 1,4,8-tris(biphenyl)-7-dimethylamino-2-ethoxyspiro[4.4]nona-1,3,6-triene (13b). Pentacarbonyl[(2*Z*)-3-dimethylamino-1-ethoxy-3-trimethylsilylpropenylidene]chromium (**10**) (135 mg, 0.35 mmol) in 20 ml of THF was treated with biphenylethyne (330 mg, 1.85 mmol) and heated at 55°C for 4 days according to GP 1. After column chromatography on silica gel (pentane/diethyl ether, 10:1, column 2×20 cm) 79 mg (34%) of a 4.5:1 mixture of **12b** and **13b** (R_f=0.24, pentane/diethyl ether 8:1) was obtained as yellow crystals, mp 101–104°C. IR (KBr): ν=3027 cm^{-1} (C–H), 2892 (C–H), 1598 (C=C), 1520 (C=C), 1486, 1447, 1200, 1049, 1007, 841, 766, 734, 697. UV (Isooctane): λ_{max} (log ϵ)= 254 nm (4.282), 340 (3.986), 363 (3.956), 377 (3.985), 401 (4.002), 505 (2.398), 524 (2.081). **12b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.52 (t, ^3J=6.9 Hz, 3H, OCH_2CH_3), 2.73 [s, 6H, $N(CH_3)_2$], 3.06 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 6-H), 3.12 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 6-H), 3.20 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 9-H), 3.30 (dd, ^2J=17.1, ^4J=2.4 Hz, 1H, 9-H), 4.32 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 4.33 (q, ^3J=6.9 Hz, 1H, OCH_2CH_3), 6.06 (s, 1H, 3-H), 7.29–7.64 (m, 23H, Ph–H), 7.79 (dd, ^3J=7.6, ^4J=0.7 Hz, 2H, Ph–H), 8.02 (dd, ^3J=7.6, ^4J=0.7 Hz, 2H, Ph–H). ^{13}C NMR (125.7 MHz, $CDCl_3$, plus APT): δ=15.57 (+, OCH_2CH_3), 42.48 (−, C-6), 42.63 [(+, $N(CH_3)_2$], 44.38 (−, C-9), 52.83 (−, C-5), 66.00 (−, OCH_2CH_3), 112.26 (−, C-4), 119.41 (+, C-3), 125.86, 126.12, 126.39, 126.64, 126.76, 126.79, 126.86, 126.88, 127.29, 128.16, 128.61, 128.64, 128.75 (+, Ph–C), 133.23, 124.00, 136.91, 137.78, 139.72, 140.35, 140.99 (−, Ph–C, C-8), 147.26 (−, C-1), 155.01 (−, C-7), 156.22 (−, C-2). **13b** (1:1-diastereomeric mixture): ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.32 and 1.38 (t, ^3J=6.9 Hz, 3H, OCH_2CH_3), 2.22 and 2.52 (m_c, 2H, 9-H), 2.59 and 2.62 [s, 6H, $N(CH_3)_2$], 3.70 and 3.82 (m_c, 1H, 8-H), 4.04–4.11 (m, 2H, OCH_2CH_3), 4.47 and 4.48 (d, ^4J=1.4 Hz, 1H, 6-H), 6.55 and 6.69 (s, 1H, 3-H), 7.10–7.91 (m, 27H, Ph–H). MS (70 eV), *m/z* (%): 661 (21) [M^+], 632 (49) [$M^+-C_2H_5$], 45 (100).

7-Dimethylamino-2-ethoxy-1,4,8-tris(4-methoxyphenyl)-spiro[4.4]nona-1,3,7-triene (12c) and 7-dimethylamino-2-ethoxy-1,4,8-tris(4-methoxyphenyl)spiro[4.4]nona-1,3,6-triene (13c). Pentacarbonyl[(2*Z*)-3-dimethylamino-1-ethoxy-3-trimethylsilylpropenylidene]chromium (**10**) (392 mg, 1.00 mmol) in 20 ml of THF was treated with 1-ethynyl-4-methoxybenzene (793 mg, 6.00 mmol) and heated at 55°C for 1 day according to GP 1. After column chromatography on silica gel (pentane/diethyl ether, 10:1, column 2×20 cm) 194 mg (37%) of a 2.5:1 mixture of **12c** and **13c** (R_f=0.30,

pentane/diethyl ether 3:1) was obtained as yellow crystals, mp 65–66°C. IR (KBr): ν=3053 cm^{-1} (C–H), 2931 (C–H), 2767 (C–H), 1652 (C=C), 1616 (C=C), 1506, 1456, 1437, 1373, 1245, 1197, 1033, 829, 667. **12c**: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.49 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 2.68 [s, 6H, $N(CH_3)_2$], 2.99 (bs, 2H, 6-H), 3.08 (dd, ^2J=17.0, ^4J=2.4 Hz, 1H, 9-H), 3.16 (dd, ^2J=17.0, ^4J=2.4 Hz, 1H, 9-H), 3.87 (bs, 9H, OCH_3), 4.25 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.83–6.94 (m, 7H, Ph–H, 3-H), 7.48 (d, ^3J=8.8 Hz, 2H, Ph–H), 7.62 (d, ^3J=8.8 Hz, 2H, Ph–H), 7.89 (d, ^3J=8.8 Hz, 2H, Ph–H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=15.53 (+, OCH_2CH_3), 41.96 (−, C-6), 42.45 [(+, $N(CH_3)_2$], 44.49 (−, C-9), 52.63 (C_{quat}, C-5), 55.08, 55.12, 55.17 (+, OCH_3), 65.70 (−, OCH_2CH_3), 113.12, 113.59 (+, Ph–C), 113.74 (C_{quat}, C-4), 113.98 (+, Ph–C), 117.54 (+, C-3), 126.24 (C_{quat}, Ph–C), 126.60, 126.95 (+, Ph–C), 127.90 (C_{quat}, Ph–C), 128.82 (+, Ph–C), 131.17 (C_{quat}, Ph–C), 146.10 (C_{quat}, C-8), 152.95 (C_{quat}, C-1), 155.02 (C_{quat}, C-7), 156.55 (C_{quat}, C-2), 157.21, 157.25, 158.60 (C_{quat}, Ph–C). 13b (1:1-diastereomeric mixture): ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.29 and 1.31 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 2.10 and 2.39 (m_c, 2H, 9-H), 2.53 and 2.58 [s, 6H, $N(CH_3)_2$], 3.46 and 3.69 (m_c, 1H, 8-H), 3.84–3.92 (m, 9H, OCH_3), 3.94–4.06 (m, 2H, OCH_2CH_3), 4.52 (bs, 1H, 6-H), 6.42 and 6.55 (s, 1H, 3-H), 6.70–7.75 (m, 12H, Ph–H). MS (70 eV), *m/z*(%): 523 (84) [M^+], 494 (100) [$M^+-C_2H_5$], 479 (8), 416 (5), 334 (5), 261 (5), 135 (8), 122 (7), 44 (3) [$N(CH_3)_2^+$].

(2-Ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,7-trien-7-yl)-trimethylammonium iodide (14) and (2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,6-trien-7-yl)trimethylammonium iodide (15). To a solution of a mixture of 7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,7-triene (**12a**) and 7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro-[4.4]nona-1,3,6-triene (**13a**) (1.8:1) (151 mg, 0.35 mmol) in 20 ml of acetone was added methyliodide (500 mg, 3.52 mmol). The solution was stirred at room temp. for 3 days and 50 ml of diethyl ether was added. After filtration the ammonium salt was washed with diethyl ether and dried in vacuo to yield 129 mg (64%) of a mixture of **14** and **15** (3:1) as yellow crystals, mp 106–108°C. IR (KBr): ν= 3048 cm^{-1} (C–H), 2976 (C–H), 2899 (C–H), 1630 (C=C), 1595 (C=C), 1492, 1442, 1375, 1288, 1275, 1202, 1077, 1045, 944, 865, 773, 705. **14**: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.38 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 3.21 (bs, 2H, 6-H), 3.26 (bs, 2H, 9-H), 3.42 [s, 9H, $N(CH_3)_3^+$], 4.11 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.84 (s, 1H, 3-H), 7.11 (dd, ^3J=7.5, ^4J=1.2 Hz, 2H, Ph–H), 7.28–7.56 (m, 11H, Ph–H), 7.62 (dd, ^3J=7.5, ^4J=1.2 Hz, 2H, Ph–H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=15.39 (+, OCH_2CH_3), 39.09 (−, C-9), 48.61 (−, C-6), 53.79 (C_{quat}, C-5), 56.79 [+, $N(CH_3)_3^+$], 66.31 (−, OCH_2CH_3), 122.60 (+, C-3), 123.58 (C_{quat}, C-4), 126.08, 126.48, 126.60, 127.52, 128.28, 128.72, 128.91, 129.29, 129.56 (+, Ph–C), 133.37, 134.23, 134.37 (C_{quat}, Ph–C), 138.61 (C_{quat}, C-8), 139.53 (C_{quat}, C-1), 152.17 (C_{quat}, C-7), 154.53 (C_{quat}, C-2). **15** (1:1-diastereomeric mixture): ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.19 and 1.24 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 2.35 and 2.72 (m_c, 2H, 9-H), 3.30 and 3.35 [s, 9H, $N(CH_3)_3^+$], 3.64 and 3.70 (m_c, 1H, 8-H) 3.82–3.94 (m, 2H, OCH_2CH_3), 6.36 and 6.38 (bs, 1H, 6-H), 6.57 and 6.59 (s, 1H, 3-H), 6.85–7.70 (m, 15H, Ph–H).

7-Dimethylamino-1,4,8-triphenylspiro[4.4]nona-3,7-dien-2-one (16) and 7-dimethylamino-1,4,8-triphenylspiro-[4.4]nona-3,6-dien-2-one (17). To a solution of a mixture of 7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,7-triene (**12a**) and 7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,6-triene (**13a**) (1.8:1) (200 mg, 0.46 mmol) in 20 ml of dimethoxyethane was added 3 equiv. of concentrated HCl. The solution was stirred at room temp. for 5 min. After neutralization with 1 N KOH, the mixture was poured into diethyl ether (20 ml) and water (20 ml), and the aqueous layer was extracted with three portions (10 ml) of diethyl ether. The combined organic layers were dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. After column chromatography of the residue on silica gel (pentane/diethyl ether, 5:1, column 2×12 cm) 144 mg (77%) of a diastereomeric mixture of 16 and 17 (R_f=0.35, pentane/diethyl ether 2:1) was obtained as colorless crystals, mp 55–56°C. IR (KBr): ν=3059 cm^{-1} (C–H), 2941 (C–H), 1698 (C=O), 1619 (C=C), 1493, 1445, 1368, 1154, 1076, 1030, 771, 670. MS (70 eV), *m/z* (%): 405 (100) [M^+], 377 (28), 314 (22), 286 (9), 247 (13), 215 (10), 202 (8), 141 (5), 115 (11), 91 (12), 77 (5) [$C_6H_5^+$].

1,4,8-Triphenylspiro[4.4]nona-3-en-2,7-dione(18). To a solution of a mixture of 7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,7-triene (**12a**) and 7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro-[4.4]nona-1,3,6-triene (**13a**) (1.8:1) (200 mg, 0.46 mmol) in 20 ml of dimethoxyethane was added 10 equiv. of concentrated HCl. The solution was stirred at 80°C for 14 h. After neutralization with 1 N KOH, the mixture was poured into diethyl ether (20 ml) and water (20 ml), and the aqueous layer was extracted with three portions (10 ml) of diethyl ether. The combined organic layers were dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. After column chromatography of the residue on silica gel (pentane/diethyl ether, 2:1, column 2×12 cm) 94 mg (54%) of a diastereomeric mixture of **18** (3:3:1) (R_f=0.61, diethyl ether) was obtained as colorless crystals, mp 61–62°C. IR (KBr): ν=3059 cm^{-1} (C–H), 2926 (C–H), 1743 (C=O), 1704 (C=O), 1591 (C=C), 1496, 1452, 1401, 1263, 1160, 1076, 1030, 889, 765, 699, 646. Two major isomers from **18**: ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.28–3.19 (m, 4H, 6-H, 9-H), 3.67 and 3.69 (t, ^3J=7.2 Hz, 1H, 8-H), 4.06 and 4.12 (s, 1H, 1-H), 6.50 and 6.53 (s, 1H, 3-H), 6.71–7.59 (m, 15H, Ph–H). ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=38.78 and 44.03 (−, C-9), 45.36 and 49.65 (−, C-6), 53.29 and 53.79 (C_{quat}, C-5), 53.34 and 54.16 (+, C-8), 65.13 and 65.89 (+, C-1), 127.05, 127.22, 127.29, 127.44, 127.50, 127.68, 127.76, 127.94, 128.13, 128.56, 128.68, 128.92, 129.02, 129.17, 129.26, 129.64, 129.76, 129.90 (+, Ph–C), 131.73 and 132.35 (+, C-3), 132.98, 133.06, 135.89, 136.81, 137.25, 137.48 (C_{quat}, Ph–C), 178.49 and 180.14 (C_{quat}, C-4), 205.32 and 206.30 (C_{quat}, C-2), 213.17 and 214.23 (C_{quat}, C-7). MS (70 eV), *m/z* (%): 378 (100) [M^+], 348 (4), 335 (7), 287 (6), 274 (23), 247 (85), 215 (20), 204 (17), 165 (4), 115 (9), 91 (7), 77 (5) [$C_6H_5^+$].

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