Highly Regio- and Diastereoselective Chromium(0)-Catalysed Cyclopropanation of 1-Alkoxy-1,3-dienes with Diazo Compounds[‡]

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Keywords: Cyclopropanation / Vinylcyclopropanes / Chromium / Catalysis / Carbenes / Diazo compounds

Pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) is an efficient catalyst for diazo decomposition and selective [2+1]-cycloaddition reactions of the resulting carbene intermediates with electron-rich dienes. The cyclopropanation of 1-alkoxy-1,3-butadienes **4**–**8** with 9-diazo-9*H*-fluorene (**2**) yields vinylspirocyclopropanes **9**–**13** in good to excellent yields, as single regioisomers arising from carbene transfer to the less substituted C=C bond. The pentacarbonylchromium-catalysed cyclopropanation with ethyl α-diazophenylacetate (**3**) gives the corresponding vinylcyclopropanecarboxylates **16**–**20** in very good yields and with exceptionally high *trans* stereoselectivities (> 95%).

Introduction

Since the early research results of Loose[1] and Wolff,[2] who observed that the decomposition temperatures of diazo ketones and diazoacetic esters were significantly lowered by the presence of copper powder, cupric sulfate or silver salts, the catalytic decomposition of diazo compounds to form reactive carbenes has become a standard method in organic synthesis. For example, it is used in CH insertions, OH insertions, the cyclopropanation of olefins and the Buchner reaction.[3] In particular, the opportunity to synthesise cyclopropanes by the reaction of diazo compounds with alkenes, catalysed by copper, rhodium, platinum or ruthenium complexes, has become a powerful tool for the stereoselective construction of three-membered ring systems.[4] The mechanisms of these reactions are assumed to proceed via metal−carbene complex intermediates of type **A** (Figure 1).

Cyclopropanes have proved to be very useful building blocks in synthetic chemistry.[5] In particular, vinylcyclopropanes represent a structural key feature in a wide range of bioactive natural and non-natural molecules,[6] and have therefore been the focus of recent research. Vinylcyclopropanes are important intermediates, as shown, for example, in the [4+1]-annulation strategy, based on an intra-/intermolecular cyclopropanation of dienes followed by rearrangement of the resulting vinylcyclopropanes.[7] This approach has been used in the elegant synthesis of several fused cyclopentanoid terpenes, such as retigeranic acid.[8] One important method to generate vinylcyclopropanes in a selective fashion is the [2+1]-cycloaddition reaction of diazo compounds and dienes, catalysed by metal complexes (Figure 2).

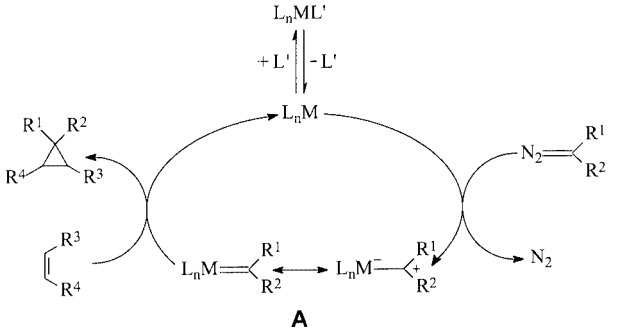

Figure 1. Proposed mechanism for the metal-catalysed cyclopropanation of olefins with diazo compounds[9b]

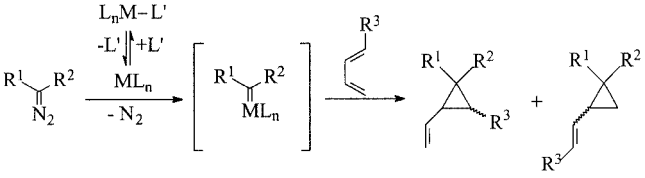

Figure 2. Metal complex catalysed [2+1]-cycloaddition reaction of diazo compounds with dienes

The reaction of electron-rich olefins with 9-diazo-9*H*-fluorene (**2**) catalysed by the pentacarbonylchromium(0) frag-

[‡] Reactions of Complex Ligands, 97. Part 96: Ref.[25]

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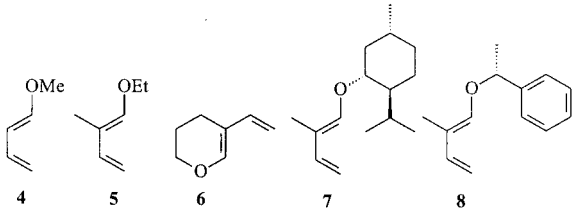
ment, and a proposed mechanism, have been described previously by our group.[9] We now present the first chromium complex catalysed reaction of 1-alkoxy-1,3-butadiene with diazo compounds to generate vinylcyclopropanes in an efficient, direct and stereoselective way.

Results and Discussion

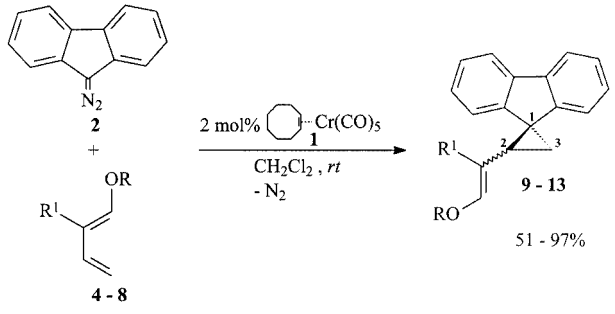
Cyclopropanations with 9-Diazo-9*H*-fluorene (2)

The present study aims to extend the scope of the chromium-catalysed cyclopropanation reaction from olefins to electron-rich dienes. The dienes **4**−**6**, which differ in their steric and electronic properties, were used to study the regioselectivity of the reaction. Of further interest was the extent to which a bulky chiral auxiliary like (−)-menthol or (1*R*)-1-phenylethanol (used in **7** and **8**) affects the regioselectivity, and also the diastereoselectivity, of the reaction.



Scheme 1. 1-Alkoxy-1,3-butadienes **4**−**8** applied to cyclopropanation

A solution of 9-diazo-9*H*-fluorene (**2**)[10] in dichloromethane was added at room temp. over a period of 8 h to a solution of 1-alkoxy-1,3-butadiene (molar ratio **2**/diene = 1:1) and 2 mol % pentacarbonyl(η²-*cis*-cyclooctene)chromium(0) (**1**)[11] in dichloromethane, and the reaction mixture was stirred for a further 8 h. The spiro-vinylcyclopropanes **9**−**13** were obtained in 51−97% yield after chromatographic work-up (Scheme 2, Table 1).



Scheme 2. Synthesis of spiro-vinylcyclopropanes **9**−**13**

Table 1. Cyclopropanation of 1-alkoxy-1,3-dienes with 9-diazo-9*H*-fluorene (**2**) catalysed by chromium complex **1**

Vinylcyclopropane	R	R¹	Yield [%]	*de* [%]
9	Me	H	97	
10	Et	Me	62	
11	−CH_2−CH_2−CH_2−		51	
12	(−)-menthyl	Me	83	0
13	(1*R*)-Ph(Me)CH	Me	76	0

The less electron-rich aryl-substituted 1,3-butadienes (e.g. 1-phenyl-1,3-butadiene and 1,4-diphenyl-1,3-butadiene) and 1-acetoxy-1,3-butadiene did not produce the desired cyclopropanation products under these conditions. 9,9′-Bifluorenylidene (**14**)[12] and bis(9,9′-9*H*-fluorenylidene)azine (**15**)[13] were identified as side products in all of the cyclopropanation reactions, even though 9-diazo-9*H*-fluorene (**2**) was added slowly over the course of the reaction.

The cyclopropanation of 1-alkoxy-1,3-butadienes proceeded regioselectively, to yield the vinylcyclopropanes **9**−**13** as single regioisomers. The products were identified by the chemical shifts and the coupling constants of 2-H and 3-H in the ^{1}H NMR spectra (Table 2), and the chemical shift of the signal of the quaternary C-1 atom. Neither GC-MS analysis nor NMR spectroscopic analysis of the crude reaction mixture indicated the formation of additional regioisomers. The incorporation of chiral auxiliaries, such as (−)-menthol or (1*R*)-phenylethanol,[14] into the diene did not result in any detectable diastereoselectivity in the formation of **12** or **13**. The chiral centres in these alkoxy substituents were probably too far away from the less substituted diene terminus, i.e. that involved in the carbene transfer in the transition state, to influence the course of the reaction.

The structure of (2*R*)-**12** was independently established by X-ray analysis, thus confirming that the regioselective cyclopropanation occurs across the 3-positions of the diene.

X-ray Crystal Structure of Spiro-Vinylcyclopropane (2*R*)-12

Crystals of (2*R*)-**12** suitable for X-ray analysis were grown from a dilute solution of **12** in acetone at room temp. by slow evaporation of the solvent (Figure 3, Table 4). The assignment of the (*R*) configuration to the newly formed stereogenic centre was based on the stereochemical information from the (−)-menthyl group. The C3−C5 bond [1.552(2) Å] is significantly longer than the C3−C4 [1.492(2) Å] and C4−C5 [1.518(3) Å] bonds. This remarkable fact is consistent with the features previously reported for the vinylspiro[2.4]heptane skeleton,[15] and may result from the influence of the spiro centre C-5 atom and the vinyl substituent.

Cyclopropanations with Ethyl α-Diazophenylacetate (3)

The cyclopropanation reactions of 1-alkoxy-1,3-butadienes with 9-diazo-9*H*-fluorene (**2**) afford the products as single regioisomers. These results have been extended to the pentacarbonylchromium-catalysed [2+1]-cycloaddition with ethyl α-diazophenylacetate (**3**).[16] We wondered whether this type of carbene-transfer reagent would give a significant *trans* selectivity in the cyclopropanation reaction. Earlier reports on cyclopropanations of electron-rich alkenes with ethyl diazoacetate (EDA) describe only moderate *trans* selectivities.[17] Even the cyclopropanation of 1-alkoxy-1,3-dienes with ethyl α-diazoacetate only gave poor selectivity.[18] In order to increase the diastereoselectivity, a bulky substituent, such as phenyl, was introduced at the α-position of ethyl α-diazoacetate. This resulted in a remark-

Table 2. Selected NMR spectroscopic data of spiro-vinylcyclopropanes **9**−**13**

Vinylcyclopropane	C-1[a] (δ in ppm)	2-H (δ in ppm)	2-H ($^3J_{H,H}$ in Hz)	3-H (δ in ppm)		3-H ($^3J_{H,H}$ in Hz)	
				cis	*trans*	*cis*	*trans*
9[b]	35.1	2.56	8.9/7.6	1.85	2.11	7.6	8.9
10[b]	33.6	2.70	9.2/7.1	2.10	2.10	7.1	9.2
11[c]	33.9	2.30	9.2/7.5	1.66	1.73	7.5	9.2
12[c] (2*R*)	34.7	2.56	9.5/8.0	1.90	1.83	8.0	9.5
12[c] (2*S*)	34.5	2.56	9.5/8.0	1.87	1.84	8.0	9.5
13[b] (diastereomer I)	33.6	2.64	9.6/8.5	1.98	2.02	8.5	9.6
13[b] (diastereomer II)	33.6	2.62	10.6/8.2	1.84	2.00	8.2	10.6

[a] Quaternary carbon atom. [b] Recorded in $CDCl_3$. [c] Recorded in C_6D_6.

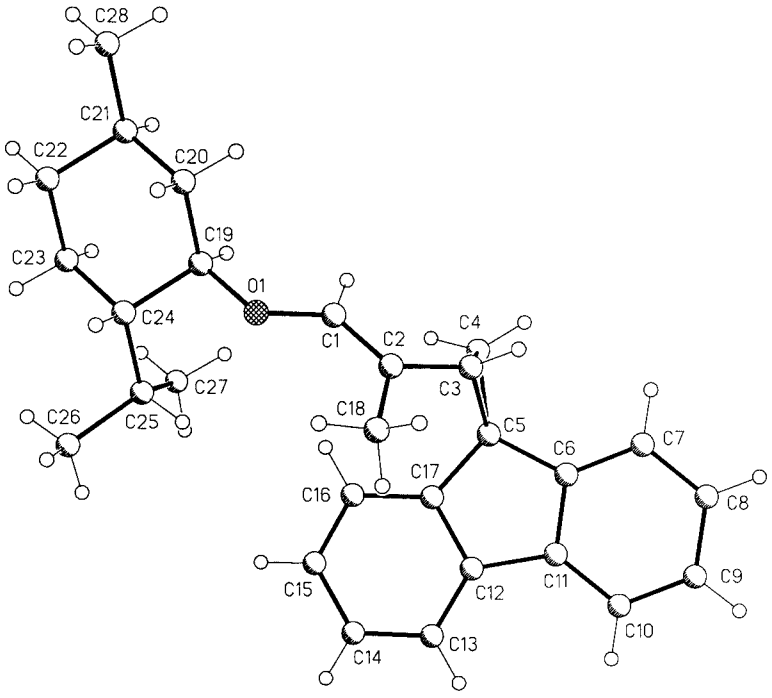
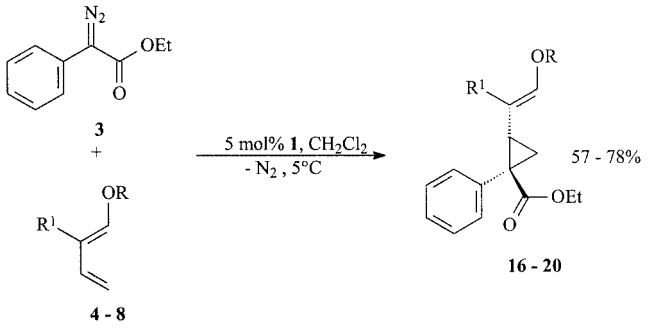


Figure 3. Molecular structure of (−)-menthyl-derived vinylcyclopropane (2*R*)-**12**; the numbering of atoms does not correspond to the numbering used in the NMR spectra

able increase in the *trans* selectivity. Furthermore, a preferential attack at the unsubstituted position of electron-rich 1,3-butadienes has been observed for diazoacetates in the [2+1]-cycloaddition catalysed by rhodium, copper or palladium.[19] Davies et. al. conducted several studies to synthesise vinylcyclopropanes, and described another very interesting procedure, in which the vinyl functionality within the diazo component was introduced diastereoselectively and even enantioselectively. However, the synthesis of the starting materials for this procedure requires more steps.[20] Our experiments have led us to a further improvement in the synthesis of vinylcyclopropanes. We are now able to present a highly regio- and diastereoselective route to these compounds from easily available electron-rich dienes: only the 3-position of the conjugated dienes was attacked, and this occurred with an extremely high *trans* selectivity (> 95%). A solution of ethyl α-diazophenylacetate (**3**) in dichloromethane was added at 5 °C over a period of 4 h to a solution of 1-alkoxy-1,3-butadiene (molar ratio **3**/diene = 1:2) and 5 mol % pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) in dichloromethane. The resulting mixture was stirred for a further 8 h. Only the *trans*-vinylcyclopropanes **16**−**20** were isolated, in 57−78% yield after chromatographic work-up (Scheme 3, Table 3).

In these reactions, the previously observed dimer or azine side products could not be detected by GC-MS, TLC, or NMR spectroscopy of the crude reaction mixture. Thus, unchanged starting material was conveniently recovered.

Obviously, the catalyst precursor **1** suffers from partial deactivation during the cyclopropanation reaction; however, the reaction can be driven to completion upon addition of further amounts of the chromium catalyst precursor **1**. Attempts to induce chirality using alkoxy auxiliaries in the diene were unsuccessful.



Scheme 3. Synthesis of *trans*-vinylcyclopropanes **16**−**20**

Table 3. [2+1]-Cycloaddition of 1-alkoxy-1,3-dienes with ethyl α-diazophenylacetate (**3**) catalysed by chromium complex **1**

Vinylcyclopropane	R	R^1	Yield [%]	*trans* [%]	*de* [%]
16	Me	H	78	> 95	
17	Et	Me	57	> 95	
18	$-CH_2-CH_2-CH_2-$		64	> 95	
19	(−)-menthyl	Me	67	> 95	0
20	(1*R*)-Ph(Me)CH	Me	59	> 95	0

The vinylcyclopropanes were identified by ^1H and ^{13}C NMR spectroscopy. The *trans* selectivity was confirmed by NOESY NMR spectroscopy.

Conclusions

The catalytic system involving 9-diazo-9*H*-fluorene (**2**) and the (*cis*-cyclooctene)chromium(0) complex **1** has been successfully applied to electron-rich dienes. The [2+1]-cycloaddition proceeds in a highly regioselective way at the unsubstituted 3-position of the conjugated dienes to furnish the corresponding cyclopropanes in good to excellent yields. These results could be extended to α-diazophenylacetate **3**. It turned out that this new system also exhibits great diastereoselectivities: all the reactions were strictly *trans*-selective, reflecting the mild reaction conditions.

Experimental Section

General Remarks: All reactions were performed in flame-dried glassware and under dry argon. Dichloromethane was dried by distillation from calcium hydride and saturated with argon. Silica gel (E. Merck, grade 60, 0.062−0.200 mm) was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded with Bruker AVANCE 300, AVANCE 400 and DRX 500 instruments. All chemical shifts are given relative to TMS as external standard; δ values are given in ppm, *J* values are given in Hz. MS (EI) and HR-MS (EI) were recorded with Kratos MS-50 and Thermoquest MAT 95 XL instruments. GC-MS was performed using a Hewlett−Packard 5890 Series-II Gas Chromatograph with 5972 Series-Mass Selective Detector, using an HP-5 column (crosslinked 5% PH ME Siloxane, 12m × 0.2 mm × 0.33μm); program: injection temperature 70 °C, heating rate 20 °C/min to 250 °C, hold for 1 min, then 50 °C/min to 280 °C, this was held for 10 min. TLC was carried out on Merck pre-coated silica gel sheets, $60F_{254}$.

Starting Materials: Liquid starting compounds were degassed under vacuum and saturated with argon. Pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**),[11] 9-diazo-9*H*-fluorene (**2**),[10] ethyl α-diazophenylacetate (**3**),[16] (*E*)-1-ethoxy-2-methyl-1,3-butadiene (**5**),[21] 5-ethenyl-3,4-dihydro-2*H*-pyran (**6**)[22] (*E*)-2-methyl-1-(−)-menthoxy-1,3-butadiene (**7**),[14] (1*E*,1′*R*/*S*)-2-methyl-1-(1′-phenylethoxy)-1,3-butadiene (**8**),[14] were prepared according to literature procedures. All other chemicals were used as received from commercial sources.

General Procedure for the Chromium Complex Catalysed Reactions of 9-Diazo-9*H*−fluorene (2) with 1-Alkoxy-1,3-butadienes: A solution of 9-diazo-9*H*-fluorene (**2**) in CH_2Cl_2 (30 mL) was added over a period of 8 h at room temp. to a stirred solution containing an equimolar amount of the corresponding 1-alkoxy-1,3-butadiene and 2 mol % of chromium(0) complex **1** in CH_2Cl_2 (10 mL). Evolution of N_2 was accompanied by a colour change of the reaction mixture, from yellow to violet. After stirring for a further 8 h followed by removal of the solvent under reduced pressure, work-up was performed by column chromatography.

2-[(*E*)-2′′-Methoxyvinyl]spiro[cyclopropane-1,9′[9′*H*]-fluorene] (9): Reaction of **2** (0.57 g, 3 mmol) with **4** (0.25 g, 3 mmol) in the presence of **1** (0.02 g, 0.06 mmol, 2 mol %) gave **9** (0.72 g, 97%) after work-up (eluent: petroleum ether/CH_2Cl_2, 2:1, R_f = 0.43) as a colourless oil. GC-MS: t_R = 9.48 min. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.85 (dd, $^2J_{H,H}$ = 5.2, $^3J_{H,H}$ = 7.6 Hz, 1 H, H-3$_{cis}$), 2.11 (dd, $^2J_{H,H}$ = 5.2, $^3J_{H,H}$ = 8.9 Hz, 1 H, H-3$_{trans}$), 2.36 (dddd, $^3J_{H,H}$ = 7.6, $^3J_{H,H}$ = 7.6, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 1.0 Hz, 1 H, H-2), 3.35 (s, 3 H, OCH_3), 4.77 (dd, $^3J_{H,H}$ = 12.6, $^3J_{H,H}$ = 7.6 Hz, 1 H, H-1′′), 6.38 (dd, $^3J_{H,H}$ = 12.6, $^4J_{H,H}$ = 0.9 Hz, 1 H, H-2′′), 6.89 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, Ar-H), 7.03 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ar-H), 7.12−7.24 (m, 4 H, Ar-H), 7.67 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, Ar-H), 7.71 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.0 (C-3), 29.9 (C-2), 35.1 (C-1), 56.9 (OCH_3), 100.0 (C-1′′), 118.2, 119.7, 120.0, 121.8, 125.8, 126.0, 126.8 (8 × Ar-C), 129.3, 140.7, 144.4, 148.2 (4 × Ar-C_q), 150.2 (C-2′′) ppm. MS (70 eV): *m*/*z* (%) = 248 (69) [M^+], 233 (5) [$M^+ - CH_3$], 215 (100), [$M^+ - CH_3 - H_2O$], 189 (15), [$M^+ - CH_3 - H_2O - C_2H_2$], 165 (25) [$C_{13}H_9^+$]. HR-MS: calcd. 248.1201, found 248.1202 for [M^+].

2-[(*E*)-2′′-Ethoxy-1′′-methylvinyl)spiro[cyclopropane-1,9′[9′*H*]-fluorene] (10): Reaction of **2** (0.57 g, 3 mmol) with **5** (0.34 g, 3 mmol) in the presence of **1** (0.02 g, 0.06 mmol, 2 mol %) gave **10** (0.51 g, 62%) after work-up (eluent: CH_2Cl_2/cyclohexane, 3:2, R_f = 0.63) as a yellowish oil. GC-MS: t_R = 10.74 min. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.46 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 1.50 (s, 3 H, CH_3), 2.10 (d, $^3J_{H,H}$ = 7.1 Hz, 1 H, H-3$_{cis}$), 2.10 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H, H-3$_{trans}$), 2.70 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,H}$ = 9.2 Hz, 1 H, H-2), 4.01 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, OCH_2CH_3), 6.38 (s, 1 H, H-2′′), 7.21 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar-H), 7.39−7.41 (m, 2 H, Ar-H), 7.45 (dt, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.1 Hz, 1 H, Ar-H), 7.48−7.53 (m, 2 H, Ar-H), 7.99 (t, $^3J_{H,H}$ = 7.1 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (OCH_2CH_3), 15.4 (CH_3), 22.1 (C-3), 33.6 (C-1), 35.0 (C-2), 67.5 (OCH_2CH_3), 110.6 (C-1′′), 118.3, 119.6, 119.7, 120.8, 125.6, 125.7 126.2, 126.6 (8 × Ar-C), 139.4, 140.1, 144.6, 148.5 (4 × Ar-C_q), 144.8 (C-2′′) ppm. MS (70 eV): *m*/*z* (%) = 276 (100) [M^+], 261 (5) [$M^+ - CH_3$], 247 (20) [$M^+ - C_2H_5$], 230 (30) [$M^+ - H_2O - C_2H_4$], 215 (55) [$M^+ - CH_3 - H_2O - C_2H_4$], 165 (100) [$C_{13}H_9^+$]. HR-MS: calcd. 276.1514, found 276.1522 for [M^+].

2-(3′′,4′′-Dihydro-2*H*-pyran-5′′-yl)spiro[cyclopropane-1,9′[9′*H*]-fluorene] (11): Reaction of **2** (0.57 g, 3 mmol) with **6** (0.33 g, 3 mmol) in the presence of **1** (0.02 g, 0.06 mmol, 2 mol %) gave **11** (0.42 g, 51%) after work-up (eluent: CH_2Cl_2/cyclohexane, 1:1, R_f = 0.46) as a yellowish oil. GC-MS: t_R = 13.15 min. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.01−1.11 (m, 1 H, CH_2), 1.18−1.42 (m, 3 H, CH_2), 1.66 (dd, $^2J_{H,H}$ = 4.9, $^3J_{H,H}$ = 7.5 Hz, 1 H, H-3$_{cis}$), 1.73 (dd, $^2J_{H,H}$ = 4.9, $^3J_{H,H}$ = 9.2 Hz, 1 H, H-3$_{trans}$), 2.30 (dd, $^3J_{H,H}$ = 7.5, $^3J_{H,H}$ = 9.2 Hz, 1 H, H-2), 3.65 (t, $^3J_{H,H}$ = 4.8 Hz, 2 H, H-2′′), 6.66 (s, 1 H, H-6′′), 6.83 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar-H), 7.18−7.34 (m, 5 H, Ar-H), 7.74 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar-H), 7.77 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 21.1 (C-3′′), 22.3 (C-4′′), 24.4 (C-3), 33.9 (C-1), 34.6 (C-2), 65.5 (C-2′′), 109.6 (C-5′′), 118.6, 120.1, 120.2, 121.2, 126.0, 126.2 126.3, 127.1 (8 × Ar-C), 139.9, 140.8, 145.0, 148.9 (4 × Ar-C_q), 143.6 (C-6′′) ppm. MS (70 eV): *m*/*z* (%) = 274 (89) [M^+], 215 (100) [$M^+ - H_2O - C_3H_5$], 165 (40) [$C_{13}H_9^+$]. HR-MS: calcd. 274.1358, found 274.1358 for [M^+].

(2*R*/*S*,1′′′*R*,2′′′*S*,5′′′*R*)-2-[(*E*)-2′′-(2′′′-Isopropyl-5′′′-methylcyclohexanoxy)-1′′-methylvinyl]spiro[cyclopropane-1,9′[9′*H*]-fluorene][(2*R*/*S*)-12]: Reaction of **2** (0.57 g, 3 mmol) with **7** (0.67 g, 3 mmol) in the presence of **1** (0.02 g, 0.06 mmol, 2 mol %) gave **12** (0.96 g, 83%) after work-up (eluent: CH_2Cl_2/petroleum ether, 1:1, R_f = 0.51) as yellowish crystals or yellowish oil. The (2*R*/*S*) diastereomers could not be separated by column chromatography. Their NMR spectrum was recorded as a mixture of diastereomers. Their signals could be assigned to the (2*R*) and the (2*S*) diastereomer on the basis of an independent X-ray analysis for the (2*R*) isomer.

(2*R*)-12: GC-MS: t_R = 12.68 min. ^{1}H NMR (500 MHz, C_6D_6): δ = 0.91 (m, 1 H, H-4$_a$′′′), 0.93 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 0.94 (m, 1 H, H-6$_a$′′′), 0.98 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.01 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 1.2−1.65 (m, 5 H, H-3$_a$′′′, H-2$_a$′′′, H-5$_a$′′′, H-3$_e$′′′, H-4$_e$′′′), 1.83 (dd, $^3J_{H,H}$ = 9.5, $^2J_{H,H}$ = 5.0 Hz, 1 H, H-3$_{trans}$), 1.90 (dd, $^3J_{H,H}$ = 8.0, $^2J_{H,H}$ = 5.0 Hz, 1 H, H-3$_{cis}$), 2.00 (m, 1 H, H-6$_e$′′′), 2.40 (dquint, $^3J_{H,H}$ = 2.7, $^3J_{H,H}$ = 7.1 Hz, 1 H, H-7′′′), 2.56 (dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 8.0 Hz, 1 H, H-2), 3.30 (ddd, $^3J_{H,H}$ = 10.8, $^3J_{H,H}$ = 10.8, $^3J_{H,H}$ = 4.5 Hz, 1 H, H-1′′′), 6.26 (s, 1 H, H-2′′), 6.93 (d, $^3J_{H,H}$ = 5.9 Hz, 1 H, Ar-H), 7.25−7.46 (m, 5 H, Ar-H), 7.83 (dd, $^3J_{H,H}$ = 6.5, $^3J_{H,H}$ = 5.9 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 15.0 (CH_3), 17.1 (CH_3), 21.0 (CH_3), 22.5 (C-3), 22.6 (CH_3), 24.2 (C-3′′′), 26.5 (C-7′′′), 31.8 (C-5′′′), 34.5 (C_q-1), 34.7 (C-4′′′), 35.7 (C-2), 42.5 (C-6′′′), 48.2 (C-2′′′), 81.9 (C-1′′′), 110.0 (C_q-1′′), 118.9, 120.3, 120.4, 121.7, 126.2, 126.4, 126.5, 127.2 (8 × Ar-C), 144.9 (C-2′′), 140.2, 141.1, 145.5, 149.2 (4 × Ar-C_q) ppm. MS (70 eV): *m*/*z* (%) = 386 (7) [M^+], 248 (75) [$M^+ - C_{10}H_{18}$], 178 (90) [$M^+ - C_{10}H_{18} - C_4H_6O$], 165 (100) [$C_{13}H_9^+$], 83 (95) [$M^+ - C_{10}H_{18} - C_{13}H_9$]. HR-MS: calcd. 386.2609, found 386.2608 for [M^+].

(2*S*)-12: GC-MS: t_R = 12.74 min. ^{1}H NMR (500 MHz, C_6D_6): δ = 0.90 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 0.91 (m, 1 H, H-4$_a$′′′), 0.94 (m, 1 H, H-6$_a$′′′), 0.95 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3), 0.98 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.51 (s, 3 H, CH_3), 1.2−1.65 (m, 5 H, H-3$_a$′′′, H-2$_a$′′′, H-5$_a$′′′, H-3$_e$′′′, H-4$_e$′′′), 1.84 (dd, $^3J_{H,H}$ = 9.5, $^2J_{H,H}$ = 4.9 Hz, 1 H, H-3$_{trans}$), 1.87 (dd, $^3J_{H,H}$ = 8.0, $^2J_{H,H}$ = 4.9 Hz, 1 H, H-3$_{cis}$), 2.08 (m, 1 H, H-6$_e$′′′), 2.39 (dquint, $^3J_{H,H}$ = 2.7, $^3J_{H,H}$ = 7.1 Hz, 1 H, H-7′′′),2.56 (dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 8.0 Hz, 1 H, H-2), 3.34 (ddd, $^3J_{H,H}$ = 10.6, $^3J_{H,H}$ = 10.6, $^3J_{H,H}$ = 4.6 Hz, 1 H, H-1′′′), 6.28 (s, 1 H, H-2′′), 6.94 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, Ar-H), 7.25−7.46 (m, 5 H, Ar-H), 7.79 (dd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 6.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 15.0 (CH_3), 17.0 (CH_3), 21.1 (CH_3), 22.4 (C-3), 22.5 (CH_3), 24.0 (C-3′′′), 26.7 (C-7′′′), 31.8 (C-5′′′), 34.5 (C_q-1), 34.7 (C-4′′′), 35.6 (C-2), 42.2 (C-6′′′), 48.3 (C-2′′′), 81.6 (C-1′′′), 109.4 (C_q-1′′), 118.9, 120.3, 120.4, 121.6, 126.2, 126.4, 126.5, 127.2 (8 × Ar-C), 144.7 (C-2′′), 140.2, 141.1, 145.5, 149.2 (4 × Ar-C_q) ppm. MS (70 eV): *m*/*z* (%) = 386 (7) [M^+], 248 (75) [$M^+ - C_{10}H_{18}$], 178 (90) [$M^+ - C_{10}H_{18} - C_4H_6O$], 165 (100) [$C_{13}H_9^+$], 83 (95) [$M^+ - C_{10}H_{18} - C_{13}H_9$]. HR-MS: calcd. 386.2609, found 386.2608 for [M^+].

Crystal Structure Determination of Vinylspirocyclopropane (2*R*)-12: Pale yellow crystals of (2*R*)-**12** were grown from acetone at room temp. Crystallographic data were collected with a Nonius−Kappa CCD diffractometer at 123 K. The molecular structure was solved by direct methods (SHELXS-97).[23] The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-97);[24] hydrogen atoms were refined isotropically using a riding model. Selected bond lengths [Å] and bond angles [°] (for the atom numbering, see Figure 3; standard deviations are given in parentheses): C(2)−C(3) 1.485(2), C(4)−C(3) 1.492(2), C(4)−C(5) 1.518(3), C(5)−C(6) 1.485(2), C(5)−C(17) 1.487(3), C(5)−C(3) 1.552(2), C(2)−C(3)−C(4) 123.02(14), C(2)−C(3)−C(5) 119.59(14), C(4)−C(3)−C(5) 59.75(11), C(3)−C(4)−C(5) 62.09(11), C(6)−C(5)−C(17) 104.60(14), C(6)−C(5)−C(4) 123.24(15), C(17)−C(5)−C(4) 124.08(15), C(6)−C(5)−C(3) 119.66(14), C(17)−C(5)−C(3) 121.93(13), C(4)−C(5)−C(3) 58.16(11). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-221923. Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk./conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336−033; E-mail: deposit@ccdc.cam.ac.uk).

(2*R*/*S*,1′′′*R*)-2-[(*E*)-2′′-(1′′′-Phenylethoxy)-1′′-methylvinyl]spiro[cyclopropane-1,9′[9′*H*]-fluorene] [(2*R*/S)-13]: Reaction of **2** (0.57 g, 3 mmol) with **8** (0.56 g, 3 mmol) in the presence of **1** (0.02 g, 0.06 mmol, 2 mol %) gave **13** (0.80 g, 76%) after work-up (eluent: CH_2Cl_2/petroleum ether, 3:2, R_f = 0.41) as a colourless oil. The (2*R*/*S*) diastereomers could not be separated by column chromatography. Their NMR spectrum was recorded as a mixture of diastereomers.

Diastereomer I: GC-MS: t_R = 12.35 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.54 (s, 3 H, CH_3), 1.74 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.98 (dd, $^3J_{H,H}$ = 8.5, $^2J_{H,H}$ = 4.9 Hz, 1 H, H-3a), 2.02 (dd, $^3J_{H,H}$ = 9.6, $^2J_{H,H}$ = 4.9 Hz, 1 H, H-3b), 2.64 (dd, $^3J_{H,H}$ = 8.6, $^3J_{H,H}$ = 9.6 Hz, 1 H, H-2), 5.00 (q, $^3J_{H,H}$ = 6.6 Hz, 1 H, H-1′′), 6.38 (q, $^4J_{H,H}$ = 1.6 Hz, 1 H, H-2′′), 6.75−8.0 (m, 13 H, Ar-H) ppm. ^{13}C NMR: δ = (125 MHz, $CDCl_3$): δ = 14.6 (CH_3), 22.2 (C-3), 23.8 (CH_3), 33.6 (C_q-1), 35.0 (C-2), 79.8 (C-1′′′), 111.2 (C_q-1′′), 118.2, 119.6, 119.7, 120.8, 125.5, 125.7, 2 × 126.0, 126.2, 126.6, 127.5, 2 × 128.6 (13 × Ar-C), 143.7 (C-2′′), 139.4, 140.1, 143.3, 144.5, 148.5 (5 × Ar-C_q) ppm. MS (70 eV): *m*/*z* (%) = 352 (5) [M^+], 247 (80) [$M^+ - C_8H_9O$], 229 (30) [$M^+ - C_8H_{11}O$], 165 (100) [$C_{13}H_9^+$], 105 (65) [$C_8H_9^+$]. HR-MS: calcd. 352.1827, found 352.1833 for [M^+].

Diastereomer II: GC-MS: t_R = 12.44 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.50 (s, 3 H, CH_3), 1.73 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.84 (dd, $^3J_{H,H}$ = 8.2, $^2J_{H,H}$ = 4.9 Hz, 1 H, H-3a), 2.00 (dd, $^3J_{H,H}$ = 10.6, $^2J_{H,H}$ = 4.9 Hz, 1 H, H-3b), 2.62 (dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 10.6 Hz, 1 H, H-2), 4.97 (q, $^3J_{H,H}$ = 6.6 Hz, 1 H, H-1′′′), 6.37 (q, $^4J_{H,H}$ = 1.7 Hz, 1 H, H-2′′), 6.75−8.0 (m, 13 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.6 (CH_3), 21.8 (C-3),

Table 4. Crystal data and structure refinement parameters of (2*R*)-**12**

	(2*R*)-**12**
Empirical formula	$C_{28}H_{34}O$
M_r	386.55
T [K]	123(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1$(no.4)
a [Å]	7.6262(1)
b [Å]	6.1798(1)
c [Å]	24.4208(5)
β [°]	98.705(1)
V [Å^3]	1137.66(3)
Z	2
$\rho_{calcd.}$[g cm^{-3}]	1.128
μ[mm^{-1}]	0.066
F(000)	420
Crystal size [mm]	0.60 × 0.40 × 0.20
Diffractometer	Nonius-Kappa CCD
Radiation	Mo-K_α
θ range for data collection [°]	2.95−25.00°
Index range	$-9 \le h \le 9$ $-7 \le k \le 7$ $-29 \le l \le 29$
Collected reflections	18580
Unique reflections	3977
Parameters/restraints	263/1
Goodness-of-fit on F^2	1.058
R (F) for $I > 2\sigma(I)$	0.0362
$wR2$ (F^2) for all data	0.0920

23.9 (CH_3), 33.6 (C_q-1), 35.0 (C-2), 79.4 (C-1′′′), 111.3 (C_q-1′′), 118.3, 119.5, 119.6, 120.7, 125.6, 125.6, 2 × 125.8, 126.2, 126.6, 127.8, 2 × 128.4 (13 × Ar-C), 143.5 (C-2′′), 139.4, 140.0, 143.5, 144.8, 148.5 (5 × Ar-C_q) ppm. MS (70 eV): *m*/*z* (%) = 352 (5) [M^+], 247 (80) [$M^+ - C_8H_9O$], 229 (30) [$M^+ - C_8H_{11}O$], 165 (100) [$C_{13}H_9^+$], 105 (65) [$C_8H_9^+$]. HR-MS: calcd. 352.1827, found 352.1833 for [M^+].

General Procedure for the Chromium Complex Catalysed Reactions of Ethyl α-diazophenylacetate (3) with 1-Alkoxy-1,3-butadienes: A solution of ethyl α-diazophenylacetate (**3**) in CH_2Cl_2 (20 mL) was added over a period of 4 h at 5 °C to a stirred solution containing the corresponding 1-alkoxy-1,3-butadiene (2 equiv.) and chromium(0) complex **1** (5 mol %) in CH_2Cl_2 (5 mL). Evolution of N_2 was accompanied by a colour change of the reaction mixture from yellow to dark red. After stirring for a further 8 h followed by removal of the solvent under reduced pressure, work-up was performed by column chromatography.

Ethyl *trans*-2-[(*E*)-2′-Methoxyvinyl]-1-phenylcyclopropanecarboxylate (16): Reaction of **3** (0.57 g, 3 mmol) with **4** (0.50 g, 6 mmol) in the presence of **1** (0.05 g, 0.15 mmol, 5 mol %) gave **16** (0.58 g, 78%) after work-up (eluent: CH_2Cl_2/petroleum ether, 2:1, R_f = 0.38) as a colourless oil. GC-MS: t_R = 8.21 min. ^{1}H NMR (500 MHz, C_6D_6): δ = 0.81 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.10 (dd, $^3J_{H,H}$ = 6.7, $^2J_{H,H}$ = 4.3 Hz, 1 H, H-3a), 1.99 (dd, $^3J_{H,H}$ = 9.1, $^2J_{H,H}$ = 4.3 Hz, 1 H, H-3b), 2.57 (ddd, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 9.1, $^3J_{H,H}$ = 9.2 Hz, 1 H, H-2), 2.85 (s, 3 H, OCH_3), 3.80 (dd, $^3J_{H,H}$ = 9.2, $^3J_{H,H}$ = 12.7 Hz, 1 H, H-1′), 3.93 (m, 1 H, OCH_2), 6.27 (d, $^3J_{H,H}$ = 12.7 Hz, 1 H, H-2′), 7.11 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar-H_p), 7.20 (dd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 7.2 Hz, 2 H, Ar-H_m), 7.31 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, Ar-H_o) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 14.1 (CH_3), 21.9 (C-3), 28.2 (C-2), 34.7 (C-1), 55.3 (OCH_3), 60.9 (OCH_2), 101.7 (C-1′), 127.2, 2 × 128.1, 2 × 132.2 (5 × Ar-C), 136.9 (Ar-C_q), 148.9 (C-2′), 173.5 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 246 (67) [M^+], 173 (95) [$M^+ - C_3H_5O_2$], 157 (100) [$M^+ - C_3H_5O_2 - CH_3$], 141 (85) [$M^+ - C_3H_5O_2 - OCH_3$], 129 (95) [$M^+ - C_3H_5O_2 - C_2H_4O$], 105 (25) [$C_7H_5O^+$], 91 (45) [$C_7H_7^+$], 77 (20) [$C_6H_5^+$]. HR-MS: calcd. 246.1256, found 246.1260 for [M^+].

Ethyl *trans*-2-[(*E*)-2′-Ethoxy-1′-methylvinyl]-1-phenylcyclopropanecarboxylate (17): Reaction of **3** (0.57 g, 3 mmol) with **5** (0.68 g, 6 mmol) in the presence of **1** (0.05 g, 0.15 mmol, 5 mol %) gave **17** (0.47 g, 57%) after work-up (eluent: CH_2Cl_2/petroleum ether, 2:1, R_f = 0.30) as a colourless oil. GC-MS: t_R = 8.80 min. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.94 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.05 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.07 (d, $^4J_{H,H}$ = 1.1 Hz, 3 H, CH_3), 1.52 (dd, $^3J_{H,H}$ = 7.4, $^2J_{H,H}$ = 4.8 Hz, 1 H, H-3a), 1.62 (dd, $^3J_{H,H}$ = 9.2, $^2J_{H,H}$ = 4.8 Hz, 1 H, H-3b), 2.32 (dd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 9.2 Hz, 1 H, H-2), 3.48 (q, $^3J_{H,H}$ = 6.9 Hz, 1 H, OCH_2), 3.52 (q, $^3J_{H,H}$ = 6.9 Hz, 1 H, OCH_2), 3.95 (q, $^3J_{H,H}$ = 7.1 Hz, 1 H, OCH_2), 3.99 (q, $^3J_{H,H}$ = 7.1 Hz, 1 H, O−CH_2), 5.69 (q, $^4J_{H,H}$ = 1.1 Hz, 1 H, H-2′), 7.1−7.3 (m, 5 H, Ar-H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 12.9 (CH_3), 14.1 (CH_3), 15.0 (CH_3), 17.4 (C-3), 32.9 (C-2), 34.9 (C_q-1), 61.0 (OCH_2), 67.5 (OCH_2), 109.3 (C_q-1′), 126.9, 2 × 127.7, 2 × 131.5 (5 × Ar-C), 136.3 (Ar-C_q), 144.3 (C-2′), 173.9 (C=O−) ppm. MS (70 eV): *m*/*z* (%) = 274 (35) [M^+], 228 (30) [$M^+ - C_2H_6O$], 201 (55) [$M^+ - C_3H_5O_2$], 171 (100) [$M^+ - C_3H_5O_2 - C_2H_6$], 155 (50) [$M^+ - C_3H_5O_2 - C_2H_6O$], 143 (55) [$M^+ - C_3H_5O_2 - C_2H_6 - C_2H_3$], 128 (40) [$M^+ - C_3H_5O_2 - C_4H_9O$], 91 (45) [$C_7H_7^+$]. HR-MS: calcd. 274.1569, found 274.1578 for [M^+].

Ethyl *trans*-2-(3′,4′-Dihydro-2*H*-pyran-5′-yl)-1-phenylcyclopropanecarboxylate (18): Reaction of **3** (0.57 g, 3 mmol) with **6** (0.66 g, 6 mmol) in the presence of **1** (0.05 g, 0.15 mmol, 5 mol %) gave **18** (0.52 g, 64%) after work-up (eluent: CH_2Cl_2/petroleum ether, 3:2, R_f = 0.26) as a colourless oil. GC-MS: t_R = 11.63 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.14 (m, 2 H, H-3′), 1.44 (m, 2 H, H-4′), 1.47 (dd, $^3J_{H,H}$ = 7.4, $^2J_{H,H}$ = 4.9 Hz, 1 H, H-3$_{cis}$), 1.65 (dd, $^3J_{H,H}$ = 9.2, $^2J_{H,H}$ = 4.9 Hz, 1 H, H-3$_{trans}$), 2.30 (dd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 9.2 Hz, 1 H, H-2), 3.51 (dt, $^3J_{H,H}$ = 5.6, $^2J_{H,H}$ = 10.7 Hz, 1 H, H-2′a), 3.62 (dt, $^3J_{H,H}$ = 5.0, $^2J_{H,H}$ = 10.7 Hz, 1 H, H-2′b), 3.98 (q, $^3J_{H,H}$ = 7.1 Hz, 1 H, O−CH_2), 4.04 (q, $^3J_{H,H}$ = 7.1 Hz, 1 H, OCH_2), 6.14 (s, 1 H, H-6′), 7.15−7.40 (m, 4 H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (CH_3), 17.1 (C-3′′), 22.1 (C-3), 22.9 (C-4′′), 32.0 (C-2), 34.0 (C-1), 61.0 (OCH_2), 65.4 (C-2′′), 108.2 (C-5′′), 125.7, 2 × 128.4, 2 × 131.0 (5 × Ar-C), 136.4 (Ar-C_q), 142.7 (C-6′′), 174.4 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 272 (30) [M^+], 199 (75) [$M^+ - C_3H_5O_2$], 155 (25) [$M^+ - C_3H_5O_2 - C_3H_8$], 105 (100) [$C_7H_5O^+$], 91 (45) [$C_7H_7^+$]. HR-MS: calcd. 272.1412, found 272.1413 for [M^+].

Ethyl (1′′*R*,2′′*S*,5′′*R*)-*trans*-2-[(*E*)-2′-(2′′-Isopropyl-5′′-methylcyclohexanoxy)-1′-methylvinyl]-1-phenylcyclopropanecarboxylate (19): Reaction of **3** (0.57 g, 3 mmol) with **7** (1.34 g, 6 mmol) in the presence of **1** (0.05 g, 0.15 mmol, 5 mol %) gave **19** (0.77 g, 67%) as a 1:1 mixture of diastereomers after work-up (eluent: CH_2Cl_2/petroleum ether, 1:1, R_f = 0.43) as a colourless oil. The diastereomers could not be separated by column chromatography. Their NMR spectrum was recorded as a mixture of diastereomers.

Diastereomer I: GC-MS: t_R = 12.13 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.74 (d, $^3J_{H,H}$ = 5.7 Hz, 3 H, CH_3), 0.84 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH_3), 0.90 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, CH_3), 1.14 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 0.6−1.55 (m, 8 H, H-4$_a$′′′, H-6$_a$′′′, H-3$_a$′′′, H-2$_a$′′′, H-5$_a$′′′, H-3$_e$′′′, H-4$_e$′′′, H-6$_e$′′′), 1.58 (s, 3 H, CH_3),

1.74 (dd, $^3J_{H,H}$ = 9.6, $^2J_{H,H}$ = 4.7 Hz, 1 H, H-3$_{trans}$), 1.90 (m, 1 H, H-7‴), 2.01 (dd, $^3J_{H,H}$ = 8.1, $^2J_{H,H}$ = 4.7 Hz, 1 H, H-3$_{cis}$), 2.40 (dd, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 8.1 Hz, 1 H, H-2), 3.30 (ddd, 1 H, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 9.4, $^3J_{H,H}$ = 4.2 Hz, H-1‴), 4.08 (q, $^3J_{H,H}$ = 6.3 Hz, 2 H, OCH_2), 5.81 (s, 1 H, H-2″), 7.10−7.41 (m, 5 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.4 (CH_3), 14.1 (CH_3), 16.5 (CH_3), 17.5 (C-3), 20.6 (CH_3), 22.1 (CH_3), 23.6 (C-3‴), 25.8 (C-7‴), 31.5 (C-2), 33.0 (C-5‴), 34.3 (C_q-1), 35.1 (C-4‴), 41.4 (C-6‴), 47.6 (C-2‴), 60.8 (OCH_2), 81.4 (C-1‴), 108.4 (C_q-1″), 126.8, 2 × 127.4, 2 × 131.2 (5 × Ar-C), 135.9 (Ar-C_q), 143.4 (C-2″), 174.1 (C=O) ppm. MS (70 eV): *m/z* (%) = 384 (40) [M^+], 246 (50) [$M^+ - C_{10}H_{18}$], 200 (40) [$M^+ - C_{10}H_{18} - C_2H_6O$], 173 (80) [$M^+ - C_{10}H_{18} - C_3H_5O_2$], 139 (50) [$C_{10}H_{19}^+$], 105 (30) [$C_8H_9^+$], 83 (100) [$M^+ - C_{10}H_{18} - C_4H_6O_2$]. HR-MS: calcd. 384.2664, found 384.2668 for M^+.

Diastereomer II: GC-MS: t_R = 12.13 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.57 (d, $^3J_{H,H}$ = 5.8 Hz, 3 H, CH_3), 0.76 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 0.84 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH_3), 1.19 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 0.6−1.55 (m, 8 H, H-4$_a$‴, H-6$_a$‴, H-3$_a$‴, H-2$_a$‴, H-5$_a$‴, H-3$_e$‴, H-4$_e$‴, H-6$_e$‴), 1.58 (s, 3 H, CH_3), 1.74 (dd, $^3J_{H,H}$ = 9.6, $^2J_{H,H}$ = 4.7 Hz, 1 H, H-3$_{trans}$), 1.86 (m, 1 H, H-7‴), 2.01 (dd, $^3J_{H,H}$ = 8.1, $^2J_{H,H}$ = 4.7 Hz, 1 H, H-3$_{cis}$), 2.40 (dd, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 8.1 Hz, 1 H, H-2), 3.30 (ddd, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 9.4, $^3J_{H,H}$ = 4.2 Hz, 1 H, H-1‴), 4.08 (q, $^3J_{H,H}$ = 6.3 Hz, 2 H, O−CH_2), 5.72 (s, 1 H, H-2″), 7.10−7.41 (m, 5 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.1 (CH_3), 14.1 (CH_3), 16.4 (CH_3), 17.5 (C-3), 20.5 (CH_3), 22.0 (CH_3), 23.6 (C-3‴), 25.9 (C-7‴), 31.4 (C-2), 32.9 (C-5‴), 34.3 (C_q-1), 34.8 (C-4‴), 41.0 (C-6‴), 47.5 (C-2‴), 60.8 (OCH_2), 81.3 (C-1‴), 108.0 (C_q-1″), 126.7, 2 × 127.4, 2 × 131.2 (5 × Ar-C), 135.8 (Ar-C_q), 143.2 (C-2″), 174.1 (C=O) ppm. MS (70 eV): *m/z* = 384 (40) [M^+], 246 (50) [$M^+ - C_{10}H_{18}$], 200 (40) [$M^+ - C_{10}H_{18} - C_2H_6O$], 173 (80) [$M^+ - C_{10}H_{18} - C_3H_5O_2$], 139 (50) [$C_{10}H_{19}^+$], 105 (30) [$C_8H_9^+$], 83 (100) [$M^+ - C_{10}H_{18} - C_4H_6O_2$]. HR-MS: calcd. 384.2664, found 384.2668 for M^+.

Ethyl (1″*R*)-*trans*-2-[(*E*)-2′-(1″-Phenylethoxy]-1′-methylvinyl)-1-phenylcyclopropanecarboxylate (20): Reaction of **3** (0.57 g, 3 mmol) with **8** (1.12 g, 6 mmol) in the presence of **1** (0.05 g, 0.15 mmol, 5 mol %) gave **20** (0.62 g, 59%) as an 1:1 mixture of diastereomers after work-up (eluent: CH_2Cl_2/petroleum ether, 2:1, R_f = 0.43) as a colourless oil. The diastereomers could not be separated by column chromatography. Their NMR spectrum was recorded as a mixture of diastereomers.

Diastereomer I: GC-MS: t_R = 11.58 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.07 (d, $^4J_{H,H}$ = 1.2 Hz, 3 H, CH_3), 1.31 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.45 (dd, $^3J_{H,H}$ = 7.4, $^2J_{H,H}$ = 4.8 Hz, 1 H, H-3$_{cis}$), 1.64 (dd, $^3J_{H,H}$ = 9.2, $^2J_{H,H}$ = 4.8 Hz, 1 H, H-3$_{trans}$), 2.30 (dd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 9.2 Hz, 1 H, H-2), 3.95 (m, 2 H, OCH_2), 4.54 (q, $^3J_{H,H}$ = 6.4 Hz, 1 H, OCH), 5.74 (q, $^4J_{H,H}$ = 1.2 Hz, 1 H, H-2′), 6.95−7.1 (m, 10 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.9 (CH_3), 14.0 (CH_3), 17.4 (C-3), 23.5 (CH_3), 32.5 (C-2), 34.4 (C-1), 60.8 (O−CH_2), 79.2 (OCH), 109.6 (C_q-1′), 2 × 125.6, 126.7, 127.4, 2 × 127.5, 2 × 128.3, 2 × 131.2 (10 × Ar-C), 135.7, 143.0 (2 × Ar-C_q), 143.0 (C-2′), 174.1 (C=O) ppm. MS (70 eV): *m/z* (%) = 350 (10) [M^+], 246 (5) [$M^+ - C_8H_8$], 177 (5) [$M^+ - C_8H_8 - C_4H_5O$], 149 (15) [$M^+ - C_8H_8 - C_4H_5O - C_2H_4$], 105 (100) [$C_8H_9^+$], 91 (5) [$C_7H_7^+$], 77 (10) [$C_6H_5^+$]. HR-MS: calcd. 350.1882, found 350.1888 for [M^+].

Diastereomer II: GC-MS: t_R = 11.58 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.14 (d, $^4J_{H,H}$ = 1.1 Hz, 3 H, CH_3), 1.21 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3), 1.40 (dd, $^3J_{H,H}$ = 7.3, $^2J_{H,H}$ = 4.8 Hz, 1 H, H-3$_{cis}$), 1.58 (dd, $^3J_{H,H}$ = 9.2, $^2J_{H,H}$ = 4.8 Hz, 1 H, H-3$_{trans}$), 2.30 (dd, $^3J_{H,H}$ = 7.3, $^3J_{H,H}$ = 9.2 Hz, 1 H, H-2), 3.98 (m, 2 H, OCH_2), 4.48 (q, $^3J_{H,H}$ = 6.5 Hz, 1 H, OCH), 5.72 (q, $^4J_{H,H}$ = 1.1 Hz, 1 H, H-2′), 6.95−7.1 (m, 10 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.6 (CH_3), 14.1 (CH_3), 17.8 (C-3), 23.4 (CH_3), 32.8 (C-2), 34.6 (C-1), 60.8 (OCH_2), 79.0 (OCH), 110.2 (C_q-1′), 2 × 125.8, 126.7, 127.2, 2 × 127.5, 2 × 128.3, 2 × 131.1 (10 × Ar-C), 135.9, 143.2 (2 × Ar-C_q), 143.2 (C-2′), 174.0 (C=O) ppm. MS (70 eV): *m/z* (%) = 350 (10) [M^+], 246 (5) [$M^+ - C_8H_8$], 177 (5) [$M^+ - C_8H_8 - C_4H_5O$], 149 (15) [$M^+ - C_8H_8 - C_4H_5O - C_2H_4$], 105 (100) [$C_8H_9^+$], 91 (5) [$C_7H_7^+$], 77 (10) [$C_6H_5^+$]. HR-MS: calcd. 350.1882, found 350.1888 for [M^+].

Acknowledgments

Financial support from the Fonds der Chemischen Industrie and the Ministry of Science and Research NRW is gratefully acknowledged.

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Received October 30, 2003

