Reactions of Complex Ligands, 81[◇]

Chromium Complex Catalyzed Synthesis of Spirocyclopropanes from Diaryl Diazo Compounds – Direct NMR-Spectroscopic Observation of a Carbene Complex Intermediate

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Received December 30, 1997

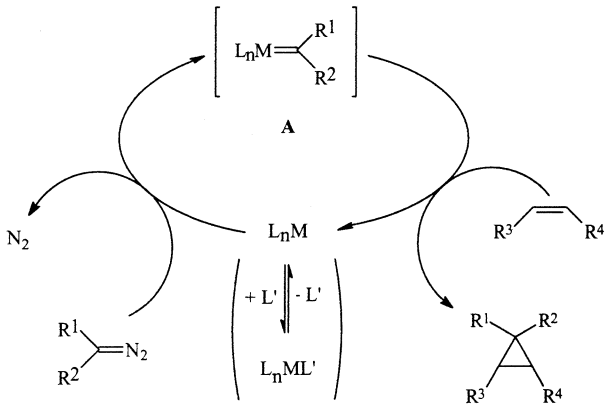
Keywords: Cyclopropanation / Chromium / Catalysis / Carbene complex / Diazo compounds

The [2 + 1] cycloaddition reaction of electron-rich alkenes such as enol ethers with 9-diazo-9*H*-fluorene (**1**) is efficiently catalyzed by pentacarbonyl(η²-*cis*-cyclooctene)chromium(0) (**2**). This cyclopropanation reaction shows a pronounced preference for electron-rich C=C bonds, as demonstrated by the regioselective reactions of allyl vinyl ether and 2-vinyloxyethyl acrylate; the [2 + 1] cycloaddition proceeds via the carbene complex intermediate **13**, which has been detected by ^{13}C-NMR spectroscopy in the course of the reaction. (*Z*)-Propenyl benzyl ether yields spirocyclopropane **21** with retention of the configuration of the former olefinic double bond. Whereas diazo compounds **22** and **23** react with ethyl vinyl ether to give low yields of cyclopropanes, the dibenzocycloheptenylidene and diarylcarbene precursors **24** and **25** afford moderate yields of olefin metathesis products **29**–**31**. The competition between cyclopropanation and olefin metathesis reflects the propensity of the carbene complex intermediates to undergo decarbonylation.

Introduction

Cyclopropanes are versatile synthetic building blocks in organic synthesis[1] as well as structural elements in various interesting naturally occurring compounds, such as the very potent insecticide chrysanthemum acid.[2] One of the most important methods for the synthesis of cyclopropanes is the metal complex catalyzed [2 + 1]-cycloaddition reaction of aliphatic diazo compounds[3] with alkenes, which has been studied in detail especially for copper, rhodium and platinum complexes.[4] The mechanisms of these reactions are assumed to proceed via metal carbene complex intermediates of type **A** (Figure 1). Support for the involvement of such species is provided by a high asymmetric induction when chiral metal complexes are employed,[2b][5] and by the synthesis of stable carbene complexes from diazo alkanes.[6][7] Recently, we reported the first efficient chromium complex catalyzed approach to cyclopropanes.[8] We now present a full account of the mechanism and discuss the regio- and stereochemical implications of this type of reaction.

Figure 1. Proposed catalytic cycle for metal complex catalyzed reactions of diazo compounds with alkenes



Results and Discussion

Cyclopropanations with 9-Diazo-9H-fluorene (**1**): Addition of a solution of 9-diazo-9*H*-fluorene (**1**)[9] in dichloromethane to a solution of the respective electron-rich olefin (molar ratio **1**/alkene = 1:1) and 2 mol% pentacarbonyl(η²-*cis*-cyclooctene)chromium(0) (**2**)[10] in dichloromethane over a period of 8 h, followed by stirring for a further 8 h, gave spirocyclopropanes **3**−**7** in 15−93% yield after chromatographic work-up (Scheme 1, Table 1).

[◇] Part 80: A. Longen, M. Nieger, K. Airola, K. H. Dötz, *Organometallics*, in press.
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Scheme 1. Synthesis of cyclopropanes **3**−**7**; a) 2 mol% **2**, CH_2Cl_2, addition of the diazo compound over 8 h, room temp., then stirring for a further 8 h

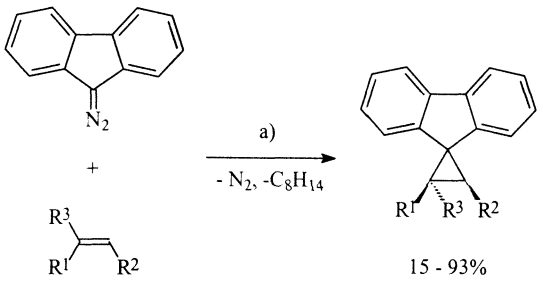


Table 1. Cyclopropanation of electron-rich alkenes with 9-diazo-9*H*-fluorene (**1**) catalyzed by chromium complex **2**

Product	R^1	R^2	R^3	Yield [%]
3	OC_2H_5	H	H	93
4	OCH_3	H	CH_3	87
5	$-O-CH_2-CH_2-$		H	73
6	$-O-CH_2-CH_2-CH_2-$		H	15
7	C_6H_5	H	H	25

Alkyl-substituted alkenes (e.g. 1-hexene, cyclohexene) and furan did not give [2 + 1] cycloaddition products, whereas the electron-deficient olefin ethyl acrylate yielded spirocyclopropane **8** even in the absence of the catalyst **2**.[11] In all reactions involving **2**, varying amounts of 9,9′-bifluorenylidene (**9**)[12] and bis(9,9′-9*H*-fluorenylidene)azine (**10**)[13] were obtained as by-products. The cyclopropanes **3**−**8** were identified by the characteristic coupling constants, $^1J_{CH}$ = 160−200 Hz, of their cyclopropyl carbon atoms in the ^{13}C-NMR spectra (Table 2).

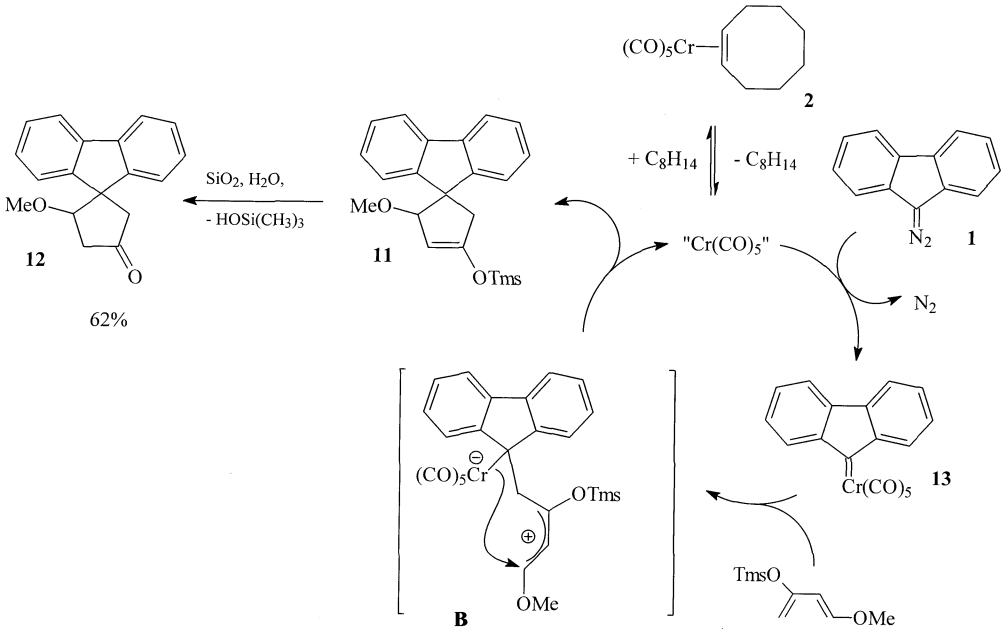
Surprisingly, the reaction of diazo compound **1** with (*E*)-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (Danishefsky's diene) did not afford a [2 + 1] cycloaddition product. NMR spectra of the reaction mixture recorded prior to work-up indicated the formation of spirocyclopentene **11**, arising from a formal [4 + 1] cycloaddition reaction. Hydrolysis during chromatographic work-up on silica gel led to 62% of the spirocyclopentanone **12**. Previously reported reactions of group 6 metal carbene complexes with dienes required much higher temperatures and led to cyclopropanes without ring-opening of the [2 + 1] cycloaddition product.[14] As a consequence, we assume that no cyclopropanes are involved as intermediates in the reaction presented here.[15] Instead, the zwitterionic transition state **B** may be formed by reaction of the diene with the postulated carbene complex intermediate **13** (Scheme 2), which can be

Table 2. ^{13}C-NMR data of the cyclopropyl carbon atoms of compounds **3**−**8**, **14**−**16**, **19**, **21** and **26**−**27** (coupling constants J_{CH} in Hz given in parentheses)

Cyclopropane	C1	C2	C3
3	35.47	67.27 (185.1)	23.59 (163.6)
4	41.50	70.30[a]	30.36 (160.8)
5[b]	43.84	71.57 (199.4)	33.59 (173.3)
6[c]	37.04	63.24 (192.1)	26.96 (165.6)
7	35.55	34.94 (160.6)	22.28 (162.3)
8	33.09	36.93 (167.8)	20.53 (167.1, 163.3)
14	35.46	67.04 (185.5)	23.65 (162.6)
15	37.20	32.50 (167.3)	20.74 (170.9)
16	35.50	67.50 (186.1)	23.54 (162.9)
19[d]	39.74	77.04[a]	21.01 (162.9)
21	37.79	69.09 (185.4)	28.73 (158.9)
26[e]	39.91	67.07 (186.1)	21.76 (163.6)
26[f]	39.71	64.97 (172.7)	21.28 (161.1)
27	38.83	69.94 (185.4)	19.07 (158.9)

[a] Quarternary carbon atom. − [b] C1 ≡ C6, C2 ≡ C1, C3 ≡ C5, according to the nomenclature. − [c] C1 ≡ C7, C2 ≡ C1, C3 ≡ C6, according to the nomenclature. − [d] C1 ≡ C9, C2 ≡ C1′′, C3 ≡ C3′ according to the nomenclature. − [e] Major isomer. − [f] Minor isomer.

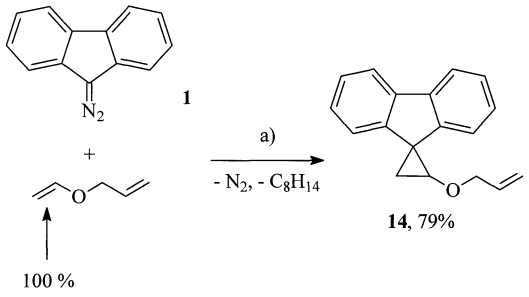
Scheme 2. Chromium-catalyzed synthesis of cyclopentanone **12**



isolated from the reaction of stoichiometric amounts of the diazo compound **1** and the chromium complex **2** in the absence of alkenes.[16]

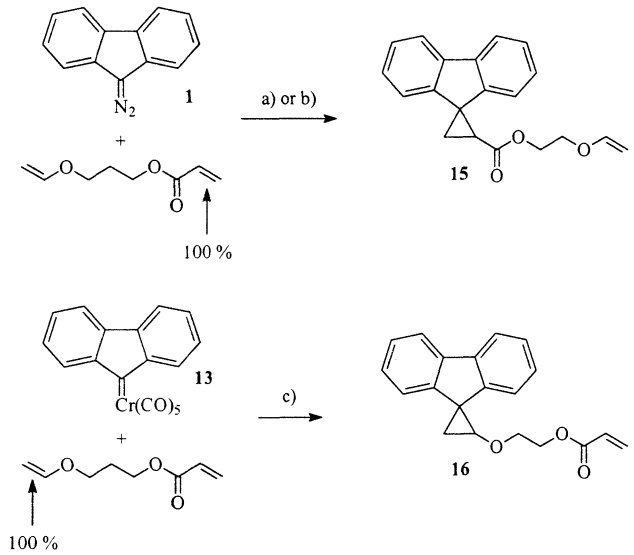
Regioselectivity: The pronounced preference for the cyclopropanation reaction to occur at electron-rich C=C double bonds was verified by the chromium complex catalyzed reactions of **1** with allyl vinyl ether and with 2-vinyloxyethyl acrylate.[17] These substrates bear electronically different alkene functionalities of similar steric demand. In the case of the reaction of allyl vinyl ether, cyclopropane **14** was obtained in 79% yield as a single regioisomer (Scheme 3).

Scheme 3. Regioselective synthesis of cyclopropane **14**; a) 2 mol% **2**, CH_2Cl_2, addition of the diazo compound over 8 h, room temp., then stirring for a further 8 h



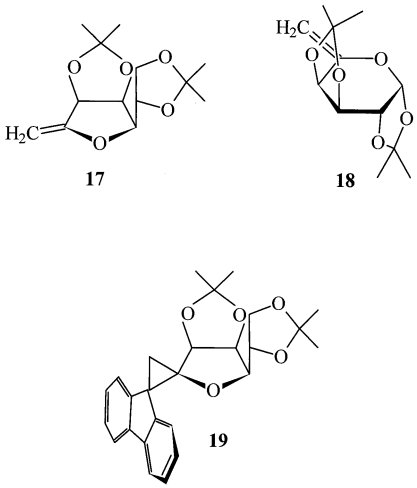
Reaction of **1** with 2-vinyloxyethyl acrylate, in the absence as well as in the presence of 2 mol% of the catalyst **2**, gave only cyclopropane **15** as a result of a [2 + 1] cycloaddition reaction at the electron-poor C=C double bond. This indicates that the uncatalyzed reaction is much faster than the metal-catalyzed reaction pathway (Scheme 4). Evidence for the preference of the postulated metal carbene intermediate **13** to react with electron-rich C=C double bonds was provided by the reaction of stoichiometric amounts of 2-vinyloxyethyl acrylate with pentacarbonyl(9*H*-9-fluorenylidene)chromium (**13**),[16] which resulted in the isolation of a 56% yield of cyclopropane **16** as a single regioisomer. The structures of cyclopropanes **15** and **16** have been assigned on the basis of their ^{1}H-NMR spectra, in particular based on the chemical shifts of the vinylic protons.

Scheme 4. Regioselective synthesis of cyclopropanes **15** and **16**; a) CH_2Cl_2, room temp., 12 h, 70%, $-N_2$; b) 2 mol% **2**, CH_2Cl_2, addition of **1** over 8 h, room temp., $-N_2$, $-C_8H_{14}$, then stirring for a further 8 h, 65%; c) CH_2Cl_2, 8 h, $-20 \rightarrow 20$°C, 56%



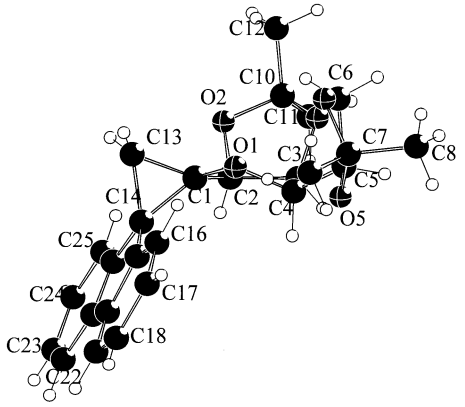
In order to explore the scope and the compatibility of the chromium-catalyzed cyclopropanation reactions with more complex and more sterically crowded vinyl ethers, *exo*-methylene sugars **17**[18] and **18**[19] were reacted with diazo compound **1** in the presence of 2 mol% chromium complex **2** (Figure 2). Whereas no [2 + 1] cycloaddition product could be obtained from the reaction with **18**, which was recovered in 95% yield, the methylene furanose **17** gave 68% of cyclopropane **19** after chromatographic work-up as a single diastereomer. The different reactivity observed for these two sugar enol ethers may be rationalized in terms of a high degree of conformational flexibility of the pyranoid ring of **18**, as a result of which the isopropylidene groups effectively shield both faces of the C=C double bond. As a consequence, the approach of the postulated carbene complex intermediate **13** may be hampered in the case of **18**. In contrast, due to the more rigid conformation of the furanoid ring of **17**, only the *si*-face is severely shielded, whereas the *re*-face can be approached by **13**.

Figure 2. *exo*-Methylene sugars **17**, **18** and cyclopropane **19**



X-ray Crystal Structure of Cyclopropane **19**: The stereochemical outcome of the reaction of *exo*-methylene sugar **17** with 9-diazo-9*H*-fluorene (**1**) was unequivocally established by X-ray crystal structure analysis of spirocyclopropane **19** after suitable crystals had been obtained from a dilute solution in hexane at 4°C (Figure 3, Table 3). As expected, attack from the sterically less shielded *re*-face of the C=C bond leads to *R*-configuration at the newly formed stereogenic center. In the solid state, the furanose ring adopts a ^4T_O-*twist* conformation,[20] with C4 [torsion angle C1−C2−C3−C4 = 11.1° (0.2)] being almost as far above as O1 [torsion angle C3−C2−C1−O1 = 10.9° (0.2)] is below the C1−C2−C3 plane. Surprisingly, the C1−C13 bond [1.466(2) Å] of the cyclopropane system is significantly shorter than the C1−C14 [1.547(2) Å] and C13−C14 bonds [1.526(2) Å].

Figure 3. X-ray crystal structure of cyclopropane **19**[21]



Mechanistic Studies: Besides the evidence mentioned in the introduction, two further important studies support the intermediacy of a carbene complex in transition metal catalyzed [2 + 1] cycloaddition reactions. Reactivity/selectivity correlations between reactions catalyzed by $Rh_2(OAc)_4$ and stoichiometric reactions of $(CO)_5W{=}C(H)Ph$ with alkenes indicate a similar mechanism for these two types of reactions.[22] Only recently, a chiral ruthenium complex that catalyzes the cyclopropanation of ethyl diazoacetate and styrene in high yield was obtained; the corresponding carbene complex, which also catalyzes this reaction, is isolable in the absence of styrene.[23] Following the latter strategy to support the intermediacy of a carbene complex in the cyclo-

Table 3. Crystal data and summary of data collection and refinement of cyclopropanes **19** and **21**

Compound	**19**	**21**
Formula	$C_{26}H_{28}O_5$	$C_{23}H_{20}O$
M_r	420.5	312.4
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$ (no. 19)	$Pca2_1$ (no. 29)
a [Å]	7.927(1)	13.055(2)
b [Å]	12.796(1)	17.609(2)
c [Å]	21.444(3)	7.644(1)
V [Å^3]	2175.1(4)	1757.2 (4)
Z	4	4
$\rho_{calcd.}$ [g cm^3]	1.28	1.18
μ [mm^{-1}]	0.71	0.54
F(000)	896	664
Crystal size [mm]	0.48 × 0.40 × 0.13	0.90 × 0.15 × 0.10
Diffractometer	Enraf-Nonius MACH3	
Radiation	Cu-K_α	Cu-K_α
λ [Å]	1.54178	1.54178
T [K]	200(2)	293(2)
Scan type	2θ/ω	2θ/ω
max 2θ [°]	136	136
index range	$-1 \le h \le 9$	$-15 \le h \le 15$
	$-1 \le k \le 15$	$-21 \le k \le 21$
	$-25 \le l \le 25$	$-1 \le l \le 9$
No. of data	5523	7568
No. of unique data	3941	1965
R_{int}	0.049	0.060
No. of data with $I > 2\sigma(I)$	3810	1399
Parameters/restraints	281/0	218/1
R(F) for $I > 2\sigma(I)$	0.035	0.054
wR_2 (F^2) for all data	0.088	0.139
Goodn. of fit on F^2	1.07	1.12
Largest diff. peak and hole [eÅ^{-3}]	0.244/−0.185	0.139/−0.174

Figure 4. ^{13}C-NMR spectrum recorded during the reaction of **1** with ethyl vinyl ether catalyzed by **2** (125.6 MHz, $CDCl_3$, 243 K)

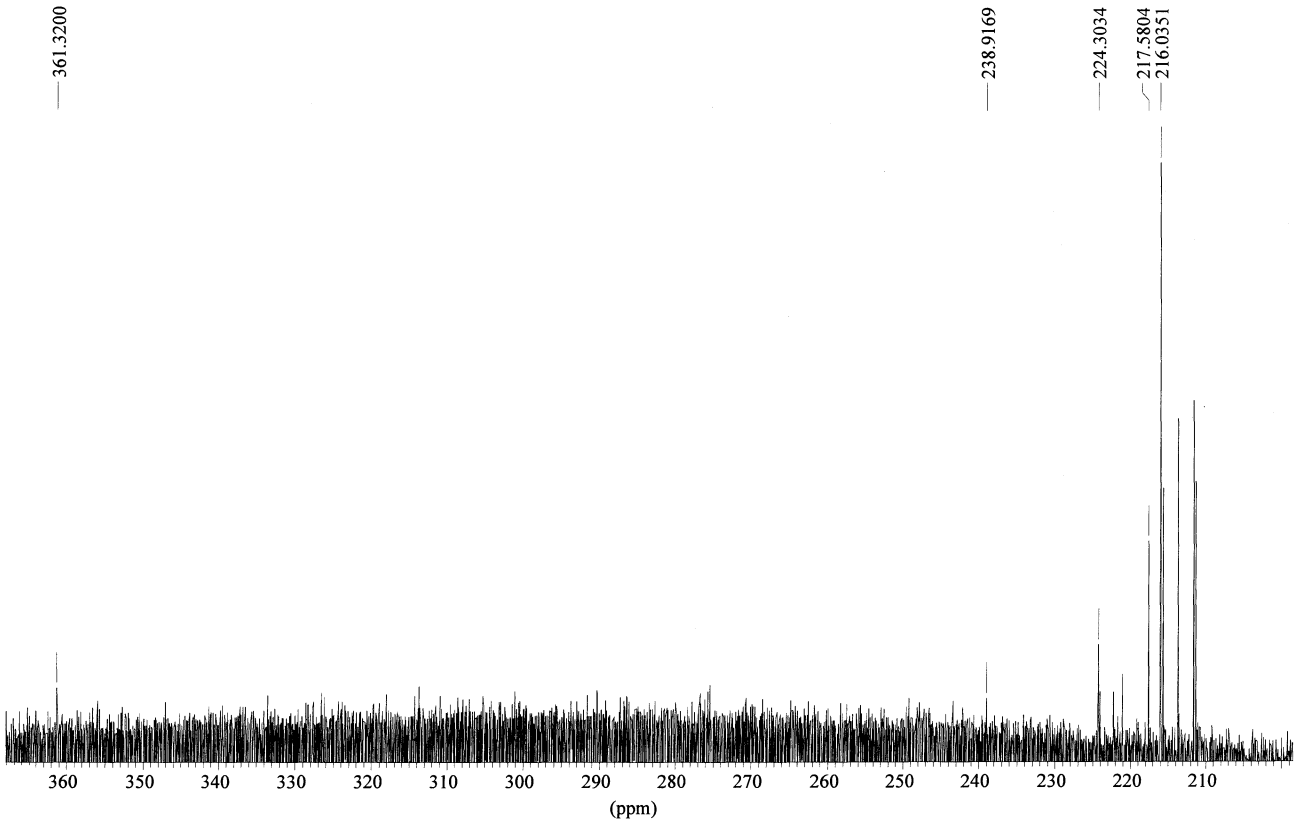
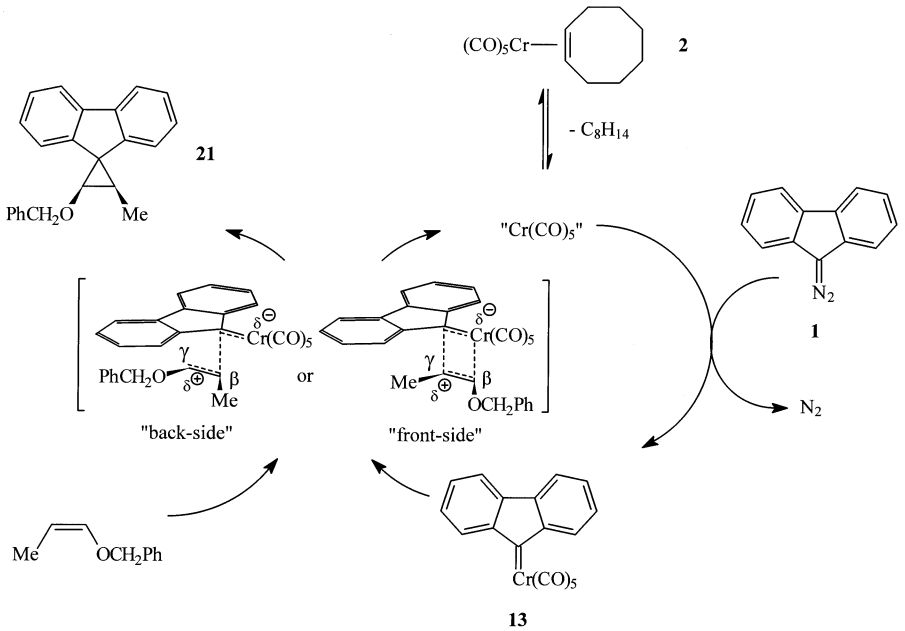


Figure 5. Mechanism of the chromium-catalyzed [2 + 1] cycloaddition reaction of (*Z*)-propenyl benzyl ether with diazo compound **1**



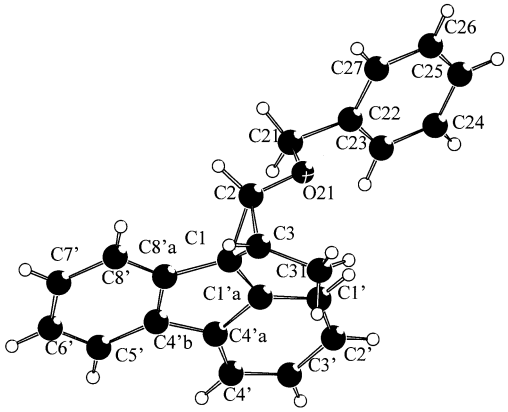
propanations presented here, the reaction of 9-diazo-9*H*-fluorene (**1**) with ethyl vinyl ether was performed in the presence of catalytic amounts (2 mol%) of fluorenylidene complex **13** and pentacarbonyl(9*H*-9-xanthenylidene)chromium(0) (**20**),[16] giving cyclopropane **3** in 87% and 79% yield, respectively.[23]

Direct evidence for the intermediacy of **13** in the reaction of diazo compound **1** with ethyl vinyl ether in the presence of the catalyst **2** was obtained by recording a ^{13}C-NMR spectrum of the "frozen" reaction at −30°C. In the region of 200−380 ppm, the ^{13}C-NMR spectrum exhibits the signals of **13** (δ = 217.58, 238.92 and 361.32), **2** (δ = 216.04 and 224.31) and hexacarbonylchromium(0) (δ = 212.00) (Figure 4). In addition, further signals were observed, which could not be assigned.

To assess the stereoselectivity of the chromium-catalyzed cyclopropanation reactions, we extended our studies to acyclic vicinal disubstituted enol ethers. Reaction of (*Z*)-propenyl benzyl ether[24] with **1** in the presence of catalyst **2** afforded a 22% yield of cyclopropane **21** as a single diastereomer, in which the *cis*-stereochemistry of the alkene precursor is retained [70% unreacted (*Z*)-propenyl benzyl ether recovered]. This result is in accordance with a mechanism involving an open-chain transition state, which collapses to form the cyclopropane before rotation about the $C_\beta-C_\gamma$ bond can take place (Figure 5). Whether the alkene approaches in a "back-side" or "front-side" manner remains an open question.[4c][25]

X-ray Crystal Structure of Cyclopropane **21**: The retention of the configuration of the former olefinic double bond in cyclopropane **21** was established by X-ray crystal structure analysis after suitable crystals had been obtained by slow evaporation of the solvent from a dilute solution in hexane (Figure 6, Table 3). As already observed for cyclopropane **19**, one of the C−C bonds of the cyclopropyl ring [C2−C3, 1.477(5) Å] is significantly shorter than the other two [C1−C2, 1.533(5) Å; C1−C3, 1.550(5) Å].

Figure 6. X-ray crystal structure of cyclopropane **21**[21]



Reactions with Other Diazo Compounds: 1-Diazo-1*H*-indene (**22**),[26] 9-diazo-9,10-dihydro-10,10-dimethylanthracene (**23**),[27] 5-diazo-5*H*-dibenzo[*a,d*]cycloheptene (**24**)[28] and (4-methoxyphenyl)phenyldiazomethane (**25**)[29] were also reacted with ethyl vinyl ether in the presence of catalytic amounts of chromium complex **2** as described above. Whereas diazo compounds **22** and **23** yielded the corresponding cyclopropanes *endo*/*exo*-**26** (ratio of isomers: 1.94:1) and **27**, respectively, no cycloaddition products could be obtained from **24** and **25** (Scheme 5, Table 4). Instead, reaction of **24** gave the olefin metathesis products **29**[30] (39% yield) and **30** (42% yield). The reaction of diazo compound **25** afforded a 15% yield of the metathesis product **31**[31] along with (*E*/*Z*)-bis[4-methoxyphenyl(phenyl)methanone]azine (**32**)[32] as the major product (71%).

The different product distributions in the chromium complex catalyzed reactions of diazo compounds **1** and **22**−**25**

Scheme 5. Chromium-catalyzed reactions of diazo compounds **22**−**25** with ethyl vinyl ether; a) 2 mol% **2**, CH_2Cl_2, addition of the diazo compound over 8 h, room temp., $-N_2$, $-C_8H_{14}$, then stirring for a further 8 h

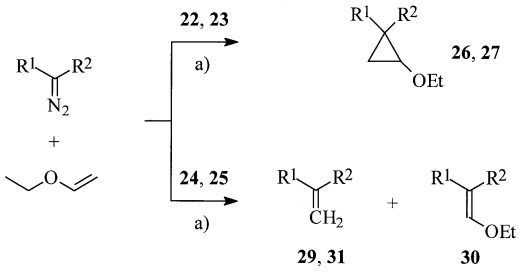
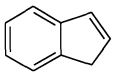
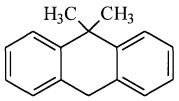
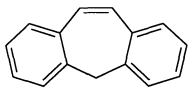


Table 4. Chromium-catalyzed reactions of diazo compounds **22**−**25** with ethyl vinyl ether

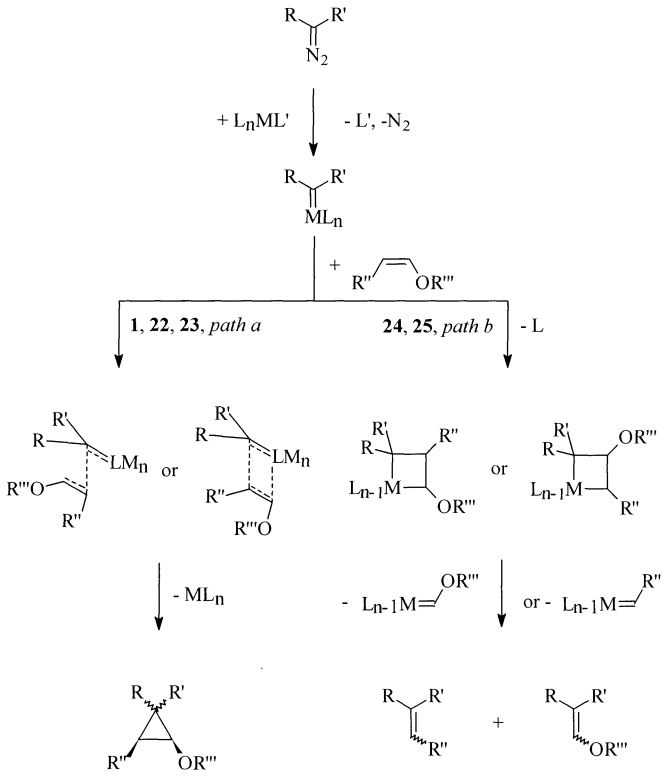
Diazo compound	Product	Yield [%]
22, R^1, R^2 =	**26**	18
		
23, R^1, R^2 =	**27**	13
		
	28	77
24, R^1, R^2 =	**29**	39
		
	30	42
25, R^1 = *p*-OCH_3-C_6H_4, R^2 = C_6H_5	**31**	15
	32	71

probably reflect the differing tendencies of the carbene complex intermediates to undergo decarbonylation (Figure 7).[33] Assuming a slow carbon monoxide dissociation from the carbene complexes derived from diazo compounds **1**, **22** and **23** − which benefit from a more efficient stabilization of the metal carbene moiety as a result of the almost planar carbene ligand (**1** and **22**) and the conformational flexibility of the tricyclic system of **23**, respectively − the metathesis pathway via metallacyclobutane intermediates cannot successfully compete with the formation of cyclopropanes (path a). In contrast, the non-planarity of the dibenzo[*a*,*d*]cycloheptenylidene and the non-bridged diarylcarbene ligands derived from the reactions of diazo compounds **24** and **25** with chromium complex **2** results in an enhanced propensity for decarbonylation, which favors the formation of metallacyclic intermediates leading to olefin metathesis products via a retro [2 + 2] cycloaddition reaction (path b).[25][34]

Conclusions

The reaction of (di)aryl diazo compounds with electron-rich alkenes can be efficiently catalyzed by the easily accessible chromium *cis*-cyclooctene complex **2** to give either the corresponding cyclopropanes with high regio- and stereoselectivity or olefin metathesis products in moderate to excellent yields. The fluorenylidene complex **13** was detected by ^{13}C-NMR spectroscopy in the course of the reaction of 9-diazo-9*H*-fluorene (**1**) with ethyl vinyl ether. This constitutes the first direct evidence for the intermediacy of a metal carbene complex in a metal complex catalyzed [2 + 1] cycloaddition reaction.

Figure 7. Suggested mechanism for the competing formation of cyclopropanes and olefin metathesis products



Support by the *Fonds der Chemischen Industrie* and the "*Graduiertenkolleg Spektroskopie isolierter und kondensierter Moleküle*" is gratefully acknowledged.

Experimental Section

General: All reactions were performed in flame-dried glassware under an atmosphere of argon. ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker AM 250, AM 400 and DRX 500 instruments. All chemical shifts are quoted relative to TMS as external standard; δ in ppm, *J* in Hz. − FT-IR: Nicolet Magna 550, measured as KBr pellets or as films between NaCl plates. − MS (EI) and MS (HR-EI): Kratos MS-50 (70 eV). − Elemental analyses: Heraeus CHN-O-Rapid. − Melting points: Büchi SMP 20, uncorrected. − TLC: Merck precoated sheets, $60F_{254}$. − Column chromatography: Merck silica gel, grade 60 (0.062−0.200 mm).

Starting Materials: Dichloromethane and hexane were dried by distillation from calcium hydride, diethyl ether from sodium hydride under argon. Liquid starting compounds were degassed under vacuum and stored over molecular sieves (4 Å). Compounds **1**,[9] **2**,[10] **13**,[16] **17**,[18] **18**,[19] **20**,[16] **22**−**25**,[26][27][28][29] 2-vinyloxyethyl acrylate[17] and (*Z*)-propenyl benzyl ether[24] were prepared according to published procedures. All other chemicals were used as received from commercial sources.

Crystal Structure Determination of Cyclopropanes **19** *and* **21**: The structures were solved by direct methods (SHELXTL-Plus).[35] The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-93).[36] H atoms were refined isotropically using a riding model. An extinction correction (**19**) and an absorption correction on the basis of ψ-scans were applied (**21**: $T_{max./min.} = 0.854/0.594$). In **19**, the absolute configuration was determined by refinement of Flack's parameter[37] [$x = -0.1(2)$], in **21** the absolute configuration could not be determined reliably [$x = -0.3(6)$]. Further details are given in Table 3. 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-100968. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44 (0)1223 336033; e-mail: deposit@ccdc.cam.ac.uk].

Molecular Structure of Cyclopropane **19**: Selected bond lengths [Å] and angles [°] (for the atom numbering, see Figure 3; standard deviations are given in parentheses): O(1)−C(1) 1.405(2), O(1)−C(4) 1.436(2), O(2)−C(2) 1.423(2), O(2)−C(10) 1.430(2), O(3)−C(10) 1.421(2), O(3)−C(3) 1.421(2), O(4)−C(7) 1.417(2), O(4)−C(6) 1.428(2), O(5)−C(7) 1.419(2), O(5)−C(5) 1.430(2), C(1)−C(13) 1.466(2), C(1)−C(2) 1.508(2), C(1)−C(14) 1.547(2), C(2)−C(3) 1.543(2), C(3)−C(4) 1.524(2), C(4)−C(5) 1.511(2), C(5)−C(6) 1.535(2), C(7)−C(9) 1.513(2), C(7)−C(8) 1.519(2), C(10)−C(12) 1.502(3), C(10)−C(11) 1.514(3), C(13)−C(14) 1.526(2); C(1)−O(1)−C(4) 106.8(1), C(2)−O(2)−C(10) 108.3(1), C(10)−O(3)−C(3) 106.9(1), C(7)−O(4)−C(6) 106.2(1), C(7)−O(5)−C(5) 108.2(1), O(1)−C(1)−C(13) 114.9(1), O(1)−C(1)−C(2) 108.4(1), C(13)−C(1)−C(2) 126.7(1), O(1)−C(1)−C(14) 116.9(1), C(13)−C(1)−C(14) 60.8(1), C(2)−C(1)−C(14) 122.5(1), O(2)−C(2)−C(1) 111.3(1), O(2)−C(2)−C(3) 104.8(1), C(1)−C(2)−C(3) 103.8(1), O(3)−C(3)−C(4) 111.5(1), O(3)−C(3)−C(2) 103.4(1), C(4)−C(3)−C(2) 103.7(1), O(1)−C(4)−C(5) 109.9(1), O(1)−C(4)−C(3) 104.5(1), C(5)−C(4)−C(3) 117.0(1), O(5)−C(5)−C(4) 107.3(1), O(5)−C(5)−C(6) 104.0(1), C(4)−C(5)−C(6) 116.3(1), O(4)−C(6)−C(5) 104.5(1), O(4)−C(7)−O(5) 104.9(1), O(4)−C(7)−C(9) 108.2(1), O(5)−C(7)−C(9) 108.4(1), O(4)−C(7)−C(8) 110.9(1), O(5)−C(7)−C(8) 110.6(1), C(9)−C(7)−C(8) 113.5(1), O(3)−C(10)−O(2) 104.4(1), O(3)−C(10)−C(12) 109.2(2), O(2)−C(10)−C(12) 108.1(2), O(3)−C(10)−C(11) 111.2(2), O(2)−C(10)−C(11) 109.6(2), C(12)−C(10)−C(11) 113.9(2), C(1)−C(13)−C(14) 62.2(1), C(15)−C(14)−C(1) 121.9(1), C(26)−C(14)−C(1) 124.6(1), C(13)−C(14)−C(1) 57.0(1).

Molecular Structure of Cyclopropane **21**: Selected bond lengths [Å] and angles [°] (for the atom numbering, see Figure 6; standard deviations are given in parentheses): C(1)−C(8′a) 1.474(5), C(1)−C(2) 1.533(5), C(2)−O(21) 1.383(4), C(3)−C(31) 1.500(6), O(21)−C(21) 1.447(5), C(1)−C(1′a) 1.487(5), C(1)−C(3) 1.550(5), C(2)−C(3) 1.477(5), C(21)−C(22) 1.510(5); C(8′a)−C(1)−C(1′a) 106.1(3), C(1′a)−C(1)−C(2) 123.4(3), C(1′a)−C(1)−C(3) 123.3(3), O(21)−C(2)−C(3) 116.6(3), C(3)−C(2)−C(1) 62.0(2), C(2)−C(3)−C(1) 60.8(3), C(8′a)−C(8′)−C(7′) 118.9(4), C(8′)−C(8′a)−C(1) 130.7(3), C(2)−O(21)−C(21) 111.6(3), C(23)−C(22)−C(21) 122.5(4), C(8′a)−C(1)−C(2) 122.0(3), C(8′a)−C(1)−C(3) 118.5(3), C(2)−C(1)−C(3) 57.3(3), O(21)−C(2)−C(1) 119.0(3), C(2)−C(3)−C(31) 122.9(4), C(31)−C(3)−C(1) 122.4(4), C(1′)−C(1′a)−C(1) 133.2(4), C(4′b)−C(8′a)−C(1) 108.9(3), O(21)−C(21)−C(22) 107.4(3), C(27)−C(22)−C(21) 120.0(4).

General Procedure for the Chromium Complex Catalyzed Reactions of (Di)aryl Diazo Compounds with Alkenes: A solution of the diazo compound in 30 ml CH_2Cl_2 was added over a period of 8 h to a stirred solution containing an equimolar amount of the corresponding alkene and 2 mol% of chromium complex **2** in 10 ml of CH_2Cl_2. Evolution of N_2 was accompanied by a color change of the reaction mixture from yellow to brown-violet (**1**) or brown-red (**22**−**25**), respectively. After stirring for a further 8 h followed by removal of the solvent under reduced pressure, work-up was performed according to one of the following procedures.

Procedure A: Work-up by column chromatography.

Procedure B: The residue was repeatedly washed with 10 ml portions of petroleum ether (40/60) until only azine **10** remained detectable in the filtered washings [TLC control, petroleum ether (40:60)/CH_2Cl_2, 1:1, $R_f = 0.35$]. The collected extracts were concentrated, and the products were isolated by chromatographic work-up.

2-Ethoxyspiro[cyclopropane-1,9′-[9H]fluorene] (**3**): Reaction of 3 mmol **1** (0.57 g) with 3 mmol ethyl vinyl ether (0.22 g) in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%) gave 0.65 g of **3** (2.79 mmol, 93%) after work-up according to procedure A (eluent: CH_2Cl_2/petroleum ether, 3:2, $R_f = 0.55$) as a colorless oil. − IR (film): $\tilde{\nu} = 3062\ cm^{-1}$ (m), 2974 (m), 2896 (m), 1481 (s), 1454 (s), 1205 (vs), 1073 (vs, COC), 738 (vs). − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.11 (t, $J = 7.02$, 3 H, CH_3), 2.02 (pt, $^{2/3}J_{HH} = 6.72$, 1 H, 3-H_{cis}), 2.14 (dd, $^2J_{HH} = 6.31$, $^3J_{HH} = 4.95$, 1 H, 3-H_{trans}), 3.06 [dq, $^2J_{HH} = 9.22$, $^3J_{HH} = 7.02$, 1 H, C***H***(H)], 3.39 [dq, $^2J_{HH} = 9.22$, $^3J_{HH} = 7.02$, 1 H, CH(***H***)], 4.16 (dd, $^3J_{HH} = 4.95$, 6.72, 1 H, 2-H), 7.01 (d, $^3J_{HH} = 7.55$, 1 H, Ar-H), 7.33 (t, $^3J_{HH} = 7.45$, 1 H, Ar-H), 7.35 (t, $^3J_{HH} = 7.50$, 1 H, Ar-H), 7.41 (t, $^3J_{HH} = 7.89$, 1 H, Ar-H), 7.42 (t, $^3J_{HH} = 7.49$, 1 H, Ar-H), 7.50 (d, $^3J_{HH} = 7.55$, 1 H, Ar-H), 7.88 (d, $^3J_{HH} = 8.24$, 1 H, Ar-H), 7.90 (d, $^3J_{HH} = 8.24$, 1 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 14.67 (q, CH_3), 23.59 (t, $^1J_{CH} = 163.6$, C-3), 35.47 (s, C-1), 66.79 (t, CH_2), 67.27 (d, $^1J_{CH} = 185.1$, C-2), 118.37 (d, Ar-C_t), 119.80 (d, 2 C, Ar-C_t), 121.77 (d, Ar-C_t), 125.85 (d, Ar-C_t), 125.91 (d, Ar-C_t), 126.5 (d, Ar-C_t), 126.66 (d, Ar-C_t), 139.50, 140.13, 143.80, 146.74 (s, 4 C, C-4a′, C-4b′, C-8a′, C-9a′). − MS (70 eV); *m/z* (%): 236 (25) [M^+], 207 (21) [$M^+ - C_2H_5$], 179 (100) [$M^+ - C_2H_5 - CO$]. − MS (HR-EI): 236.1202 ($C_{17}H_{16}O$, calcd. 236.1201). − $C_{17}H_{16}O$ (236.31): calcd. C 86.41, H 6.82; found C 86.16, H 6.74.

2-Methoxy-2-methylspiro[cyclopropane-1,9′-[9H]fluorene] (**4**): Reaction of 3 mmol **1** (0.57 g) with 3 mmol 2-methoxypropene (0.22 g) in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%) gave 0.61 g of **4** (2.61 mmol, 87%) after work-up according to procedure A (eluent: CH_2Cl_2/petroleum ether, 1:1, $R_f = 0.55$) as colorless crystals, m.p. 67−68°C. − IR (KBr): $\tilde{\nu} = 3059\ cm^{-1}$ (m), 2962 (m), 1473, 1442 (s), 1240 (vs), 1065 (vs, COC), 813 (s), 736 (vs). − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.82 (d, $^4J_{HH} = 0.53$, 3 H, CH_3), 1.91 (d, $^2J_{HH} = 6.15$, 1 H, 3-H), 2.27 (dd, $^2J_{HH} = 6.15$, $^4J_{HH} = 0.53$, 1 H, 3-H), 3.04 (s, 3 H, OCH_3), 7.18 (d, $^3J_{HH} = 7.67$, 1 H, Ar-H), 7.32 (t, $^3J_{HH} = 7.53$, 1 H, Ar-H), 7.34 (t, $^3J_{HH} = 7.55$, 1 H, Ar-H), 7.39 (t, $^3J_{HH} = 7.45$, 1 H, Ar-H), 7.41 (t, $^3J_{HH} = 7.43$, 1 H, Ar-H), 7.52 (d, $^3J_{HH} = 7.65$, 1 H, Ar-H), 7.88 (d, $^3J_{HH} = 7.18$, 1 H, Ar-H), 7.89 (d, $^3J_{HH} = 7.16$, 1 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 16.80 (q, CH_3), 30.36 (t, $^1J_{CH} = 160.8$, C-3), 41.50 (s, C-1), 54.78 (q, OCH_3), 70.30 (s, C-2), 119.47 (d, Ar-C_t), 119.93 (d, Ar-C_t), 121.46 (d, Ar-C_t), 122.67 (d, Ar-C_t), 125.78 (d, Ar-C_t), 125.82 (d, Ar-C_t), 126.03 (d, Ar-C_t), 126.53 (d, Ar-C_t), 139.89, 141.07, 144.69, 144.94 (s, 4 C, C-4a′, C-4b′, C-8a′, C-9a′). − MS (70 eV); *m/z* (%): 236 (95) [M^+], 221 (100) [$M^+ - CH_3$], 205 (35) [$M^+ - OCH_3$], 178 (50) [$C_{14}H_{10}^+$], 165 (44) [$C_{13}H_9^+$], 152 (25) [$C_{12}H_8^+$]. − MS (HR-EI): 236.1204 ($C_{17}H_{16}O$, calcd. 236.1201). −

$C_{17}H_{16}O$ (236.31): calcd. C 86.41, H 6.82; found C 86.11, H 6.82.

Reaction of **1** *with 2,3-Dihydrofuran:* Reaction of 3 mmol **1** (0.57 g) with 3 mmol 2,3-dihydrofuran (0.21 g) in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%) gave 0.51 g of **5** (2.19 mmol, 73%) and 0.08 g of azine **10** (0.22 mmol, 15% based on **1**) after work-up according to procedure A (eluent: CH_2Cl_2/petroleum ether, 2:1).

Spiro[2-oxabicyclo[3.1.0]hexane-6,9′-[9H]fluorene] (**5**): Colorless crystals, m.p. 149−150°C, R_f = 0.5. − IR (KBr): $\tilde{\nu}$ = 3032 cm^{-1} (m), 2968 (m), 1438 (vs), 1340 (vs), 1039 (s, COC), 927 (s), 744 (vs). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.31−2.48 (m, 2 H, 4-H), 2.62 (ddd, $^3J_{HH}$ = 1.76, 5.72, 7.37, 1 H, 5-H), 4.39−4.48 (m, 2 H, 3-H), 4.65 (d, $^3J_{HH}$ = 5.72, 1 H, 1-H), 6.80 (d, $^3J_{HH}$ = 7.55, 1 H, Ar-H), 7.24 (t, $^3J_{HH}$ = 7.14, 1 H, Ar-H), 7.25 (d, $^3J_{HH}$ = 7.40, 1 H, Ar-H), 7.32 (t, $^3J_{HH}$ = 7.51, 2 H, Ar-H), 7.40 (t, $^3J_{HH}$ = 7.45, 1 H, Ar-H), 7.75 (d, $^3J_{HH}$ = 7.55, 1 H, Ar-H), 7.87 (d, $^3J_{HH}$ = 7.55, 1 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 25.61 (t, C-4), 33.59 (d, $^1J_{CH}$ = 173.3, C-5), 43.84 (s, C-6), 71.57 (d, $^1J_{CH}$ = 199.43, C-1), 77.02 (t, C-3), 118.45 (d, Ar-C_t), 119.47 (d, Ar-C_t), 120.22 (d, Ar-C_t), 123.00 (d, Ar-C_t), 125.94 (d, Ar-C_t), 125.95 (d, Ar-C_t), 126.21 (d, Ar-C_t), 126.82 (d, Ar-C_t), 138.30, 141.44, 141.62, 145.88 (s, 4 C, C-4a′, C-4b′, C-8a′, C-9a′). − MS (70 eV), *m/z* (%): 234 (78) [M^+], 205 (85) [$M^+ - C_2H_5$], 178 (100) [$C_{14}H_{10}^+$], 165 (25) [$C_{13}H_9^+$]. − MS (HR-EI): 234.1043 ($C_{17}H_{14}O$, found 234.1045). − $C_{17}H_{14}O$ (234.30): calcd. C 87.15, H 6.02; found C 86.73, H 6.05.

Bis(9,9′-9H-fluorenylidene)azine (**10**): Orange crystals, m.p. 265−267°C (ref.[13] 265°C), R_f = 0.4. − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (m), 1623 (m), 1598 (m, C=N), 1446 (s), 1429 (s), 790 (s), 720 (vs), 647 (s). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24 (t, $^3J_{HH}$ = 7.55, 2 H, Ar-H), 7.40 (t, $^3J_{HH}$ = 7.55, 2 H, Ar-H), 7.41 (t, $^3J_{HH}$ = 7.43, 2 H, Ar-H), 7.48 (t, $^3J_{HH}$ = 7.45, 2 H, Ar-H), 7.65 (d, $^3J_{HH}$ = 7.45, 2 H, Ar-H), 7.66 (d, $^3J_{HH}$ = 7.35, 2 H, Ar-H), 8.06 (d, $^3J_{HH}$ = 7.15, 2 H, Ar-H), 8.14 (d, $^3J_{HH}$ = 7.55, 2 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 120.03 (2 C, Ar-C_t), 120.11 (2 C, Ar-C_t), 122.87 (2 C, Ar-C_t), 128.19 (2 C, Ar-C_t), 128.23 (2 C, Ar-C_t), 129.79 (2 C, Ar-C_t), 130.96 (2 C, Ar-C_t), 131.39 (2 C, Ar-C_t), 136.45 (2 C, Ar-C_q), 141.23 (2 C, Ar-C_q), 142.23 (2 C, Ar-C_q), 154.77 (2 C, Ar-C_q), 156.76 (2 C, C=N). − MS (70 eV), *m/z* (%): 356 (100) [M^+], 327 (45), 178 (34) [$C_{13}H_8N^+$], 164 (15) [$C_{13}H_8^+$], 152 (18) [$C_{12}H_8^+$]. − MS (HR-EI): 356.1311 ($C_{26}H_{16}N_2$, calcd. 356.1313). − $C_{26}H_{16}N_2$ (356.43): calcd. C 87.62, H 4.52, N 7.86; found C 87.31, H 4.52, N 7.71.

Reaction of **1** *with 2,3-Dihydropyran:* Reaction of 3 mmol **1** (0.57 g) with 3 mmol 2,3-dihydropyran (0.25 g) in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%) gave 0.11 g of **6** (0.45 mmol, 15%), 0.07 g of **9** (0.21 mmol, 14% based on **1**) and 0.37 g of azine **10** (1.04 mmol, 69% based on **1**) after work-up according to procedure B (eluent: CH_2Cl_2/petroleum ether, 1:1).

Spiro[2-oxabicyclo[4.1.0]heptane-7,9′-[9H]fluorene] (**6**): Colorless crystals, m.p. 137−138°C, R_f = 0.7. − IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1} (m), 2922 (m), 1481 (s), 1439 (s), 1056 (vs, COC), 798 (s), 746 (vs). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.81−1.88 (m, 1 H, 4-H), 1.96−2.03 (dddd, $^2J_{HH}$ = 14.42, $^3J_{HH}$ = 7.82, 6.46, 3.33, 1 H, 5-H), 2.13 (m, 1 H, 4-H), 2.17 (dt, $^3J_{HH}$ = 6.23, 3.33, 1 H, 6-H), 2.24 (ddt, $^2J_{HH}$ = 14.60, $^3J_{HH}$ = 8.95, 5.61, 1 H, 5-H), 3.80 (ddd, $^2J_{HH}$ = 10.02, $^3J_{HH}$ = 9.38, 5.56, 1 H, 3-H), 4.09 (ddd, $^2J_{HH}$ = 10.02, $^3J_{HH}$ = 7.07, 4.15, 1 H, 3-H), 4.41 (d, $^3J_{HH}$ = 6.23, 1 H, 1-H), 6.85 (d, $^3J_{HH}$ = 7.55, 1 H, Ar-H), 7.29 (t, $^3J_{HH}$ = 7.55, 1 H, Ar-H), 7.32 (t, $^3J_{HH}$ = 7.48, 1 H, Ar-H), 7.35 (t, $^3J_{HH}$ = 7.43, 1 H, Ar-H), 7.41 (t, $^3J_{HH}$ = 7.45, 1 H, Ar-H), 7.49 (d, $^3J_{HH}$ = 7.55, 1 H, Ar-H), 7.81 (d, $^3J_{HH}$ = 7.47, 1 H, Ar-H), 7.89 (d, $^3J_{HH}$ = 7.55, 1 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 13.24 (t, C-4), 20.81 (t, C-5), 26.96 (d, $^1J_{CH}$ = 165.6, C-6), 37.04 (s, C-7), 63.24 (d, $^1J_{CH}$ = 192.08, C-1), 64.53 (t, C-3), 118.12 (d, Ar-C_t), 119.58 (d, Ar-C_t), 120.06 (d, Ar-C_t), 124.59 (d, Ar-C_t), 125.89 (d, Ar-C_t), 125.93 (d, Ar-C_t), 126.19 (d, Ar-C_t), 126.79 (d, Ar-C_t), 139.06, 141.54, 141.75, 147.52 (s, 4 C, C-4a′, C-4b′, C-8a′, C-9a′). − MS (70 eV), *m/z* (%): 248 (68) [M^+], 205 (29) [$M^+ - OC_2H_3$], 191 (45) [$M^+ - OC_3H_5$], 178 (100) [$C_{14}H_{10}^+$], 165 (52) [$C_{13}H_9^+$]. − HR-MS: 248.1203 ($C_{18}H_{16}O$, calcd. 248.1201). − $C_{18}H_{16}O$ (248.32): calcd. C 87.06, H 6.49; found C 86.77, H 6.39.

9,9′-Bifluorenylidene (**9**): Red crystals, m.p. 186°C (ref.[12] 185−187°C), R_f = 0.8. − IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} (m), 1477 (m), 1444 (s, C=C), 1348 (m), 763 (s), 721 (vs). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, $^3J_{HH}$ = 7.82, 4 H, Ar-H), 7.40 (t, $^3J_{HH}$ = 7.43, 4 H, Ar-H), 7.70 (d, $^3J_{HH}$ = 7.43, 4 H, 4-H, 4′-H, 5-H, 5′-H), 8.32 (d, $^3J_{HH}$ = 7.82, 4 H, 1-H, 1′-H, 8-H, 8′-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 119.63 (4 C, Ar-C_t), 119.82 (2 C, C-9, C-9′), 125.79 (4 C, Ar-C_t), 127.55 (4 C, Ar-C_t), 129.16 (4 C, Ar-C_t), 136.51 (4 C, Ar-C_q), 140.18 (4 C, Ar-C_q). − MS (70 eV), *m/z* (%): 328 (100) [M^+], 300 (10), 163 (15). − MS (HR-EI): 328.1247 ($C_{26}H_{16}$, calcd. 328.1252).

Reaction of **1** *with Styrene:* Reaction of 3 mmol **1** (0.57 g) with 3 mmol styrene (0.31 g) in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%) gave 0.20 g of **7** (0.75 mmol, 25%) and 0.37 g of azine **10** (1.04 mmol, 69% based on **1**) after work-up according to procedure B (eluent: petroleum ether/diethyl ether, 5:1).

2-Phenylspiro[cyclopropane-1,9′-[9H]fluorene] (**7**): Colorless crystals, m.p. 133−135°C, R_f = 0.7. − IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} (m), 3034 (m), 1496 (m), 1444 (s), 777 (vs), 748 (vs), 696 (vs). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (d, $^3J_{HH}$ = 8.41, 2 H, 3-H), 3.38 (t, $^3J_{HH}$ = 8.41, 1 H, 2-H), 6.15 (d, $^3J_{HH}$ = 7.83, 1 H, Ar-H), 6.92 (t, $^3J_{HH}$ = 7.58, 1 H, Ar-H), 7.17−7.30 (m, 7 H, Ar-H), 7.36 (t, $^3J_{HH}$ = 7.34, 1 H, Ar-H), 7.41 (t, $^3J_{HH}$ = 7.24, 1 H, Ar-H), 7.80 (d, $^3J_{HH}$ = 7.63, 1 H, Ar-H), 7.85 (d, $^3J_{HH}$ = 6.45, 1 H, Ar-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.28 (t, $^1J_{CH}$ = 162.3, C-3), 34.94 (d, $^1J_{CH}$ = 160.6, C-2), 35.55 (s, C-1), 118.52 (d, Ar-C_t), 119.62 (d, Ar-C_t), 119.74 (d, Ar-C_t), 121.56 (d, Ar-C_t), 125.73 (d, Ar-C_t), 125.86 (d, Ar-C_t), 126.00 (d, Ar-C_t), 126.76 (d, Ar-C_t), 126.84 (d, Ar-C_t), 128.13 (d, 2 C, Ar-C_t), 130.09 (d, 2 C, Ar-C_t), 137.05, 139.60, 140.35, 144.23, 148.25 (s, 5 C, C-4a′, C-4b′, C-8a′, C-9a′, C-1′′). − MS (70 eV), *m/z* (%): 268 (100) [M^+], 252 (40) [$M^+ - CH_2$], 165 (25) [$C_{13}H_9^+$], 91 (17) [$C_7H_7^+$]. − MS (HR-EI): 268.1249 ($C_{21}H_{16}$, calcd. 268.1252).

Reaction of **1** *with (E)-1-Methoxy-3-trimethylsilyloxy-1,3-butadiene:* Reaction of 1 mmol **1** (0.57 g) dissolved in 10 ml CH_2Cl_2 with a solution of 1 mmol (*E*)-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (0.17 g) and 0.006 g **2** (0.02 mmol, 2 mol%) in 4 ml CH_2Cl_2 gave spirocyclopentene **11**. After work-up according to procedure A, 0.17 g of spirocyclopentanone **12** (0.62 mmol, 62%) and 0.04 g of azine **10** (0.11 mmol, 10% based on **1**) were obtained (eluent: diethyl ether/petroleum ether, 3:1).

2-Methoxy-4-(trimethylsilyloxy)spiro[cyclopent-3-ene-1,9′-[9H]fluorene] (**11**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.39 [s, 9 H, $Si(CH_3)_3$], 2.63 (d, $^2J_{HH}$ = 16.49, 1 H, 5-H), 2.72 (s, 3 H, OCH_3), 3.11 (d, $^3J_{HH}$ = 16.49, 1 H, 5-H), 4.31 (br s, 1 H, 2-H), 5.12 (br s, 1 H, 3-H), 7.31−7.50 (m, 4 H, Ar-H), 7.54 (d, $^3J_{HH}$ = 7.35, 1 H, Ar-H), 7.72−7.79 (m, 3 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 0.06 [q, 3 C, $Si(CH_3)_3$], 45.07 (t, $^1J_{CH}$ = 133.4, C-5), 57.48 (q, OCH_3), 57.8 (s, C-1), 90.54 (d, $^1J_{CH}$ = 150.3, C-2), 103.19 (d, $^1J_{CH}$ = 167.7, C-3), 119.32 (d, Ar-C_t), 119.61 (d, Ar-C_t), 121.84 (d, Ar-C_t), 126.10 (d, Ar-C_t), 127.04 (d, Ar-C_t), 127.19 (d, 2 C, Ar-C_t), 127.52 (d, Ar-C_t), 139.36, 140.29, 147.08, 152.57, 158.95 (s, 5 C, C-4, C-4a′, C-4b′, C-8a′, C-9a′). − MS (70 eV), *m/z*

(%): 336 (100) [M^+], 321 (4) [$M^+ - CH_3$], 205 (40) [$M^+ - OCH_3$], 304 (30) [$M^+ - 2CH_3$], 291 (10) [$M^+ - 3CH_3$], 264 (10) [$M^+ - Si(CH_3)_2CH_2$], 246 (11) [$M^+ - Si(CH_3)_3OH$], 232 (50) [$M^+ - OCH_3 - Si(CH_3)_3$], 215 (30) [$M^+ - OCH_3 - Si(CH_3)_3OH$], 203 (60) [$C_{16}H_{11}^+$], 189 (15) [$C_{15}H_9^+$], 178 (60) [$C_{14}H_{10}^+$], 165 (20) [$C_{13}H_9^+$], 89 (30) [$OSi(CH_3)_3^+$], 73 (100) [$Si(CH_3)_3^+$]. − MS (HR-EI): 336.1544 ($C_{21}H_{24}O_2Si$, calcd. 336.1546).

2-Methoxyspiro[cyclopentan-4-one-1,9′-[9H]fluorene] (**12**): Colorless crystals, m.p. 128−129°C, R_f = 0.55. − IR (KBr): $\tilde{\nu}$ = 3039 cm^{-1} (m), 2928 (m), 2831 (m), 1744 (vs, C=O), 1460 (m), 1404 (m), 1197 (s), 1118 (s, COC), 995 (m), 778 (m), 736 (m). − ^1H NMR (400 MHz, $CDCl_3$): δ = 2.68 (d, $^2J_{HH}$ = 18.39, 1 H, 5-H), 2.82 (dd, $^2J_{HH}$ = 19.32, $^3J_{HH}$ = 6.22, 1 H, 3-H), 2.96 (d, $^2J_{HH}$ = 18.39, 1 H, 5-H), 2.97 (s, 3 H, OCH_3), 3.09 (dd, $^2J_{HH}$ = 19.32, $^3J_{HH}$ = 6.22, 1 H, 3-H), 4.06 (t, $^3J_{HH}$ = 6.22, 1 H, 2-H), 7.30−7.49 (m, 5 H, Ar-H), 7.55 (d, $^3J_{HH}$ = 7.59, 1 H, Ar-H), 7.78 (d, $^3J_{HH}$ = 7.43, 2 H, Ar-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 44.37 (t, $^1J_{CH}$ = 128.5, CH_2), 48.32 (t, $^1J_{CH}$ = 130.5, CH_2), 58.19 (q, OCH_3), 58.55 (s, C-1), 84.91 (d, $^1J_{CH}$ = 148.1, C-2), 119.95 (d, Ar-C_t), 120.25 (d, Ar-C_t), 122.38 (d, Ar-C_t), 125.68 (d, Ar-C_t), 127.32 (d, Ar-C_t), 127.56 (d, Ar-C_t), 127.96 (d, Ar-C_t), 128.01 (d, Ar-C_t), 140.43, 140.51, 146.03, 148.59 (s, 4 C, C-4a′, C-4b′, C-8a′, C-9a′), 215.46 (s, C=O). − MS (70 eV), *m/z* (%): 264 (14) [M^+], 232 (10) [$M^+ - CH_3OH$], 204 (8) [$M^+ - CH_3OH - CO$], 178 (100) [$C_{14}H_{10}^+$], 152 (8) [$C_{12}H_8^+$]. − MS (HR-EI): 264.1156 ($C_{18}H_{16}O_2$, calcd. 264.1150). − $C_{18}H_{16}O_2$ (264.32): calcd. C 81.79, H 6.10; found C 81.04, H 6.13.

Reaction of **1** *with Allyl Vinyl Ether:* Reaction of 3 mmol **1** (0.57 g) with 3 mmol allyl vinyl ether (0.25 g) in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%) gave 0.59 g of cyclopropane **14** (2.37 mmol, 79%) and 0.06 g of azine **10** (0.16 mmol, 11% based on **1**) after work-up according to procedure A (eluent: CH_2Cl_2/petroleum ether, 1:1).

2-Allyloxyspiro[cyclopropane-1,9′-[9H]fluorene] (**14**): Colorless oil, R_f = 0.4. − IR (film): $\tilde{\nu}$ = 3062 cm^{-1} (m), 3016 (m), 2858 (m), 1481 (vs), 1448 (vs), 1340 (s), 1192 (s, COC), 1070 (m), 1047 (m), 987 (m), 742 (vs), 727 (vs). − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.99 (pt, $^{2/3}J_{HH}$ = 6.51, 1 H, 3-H_{cis}), 2.13 (dd, $^2J_{HH}$ = 6.51, $^3J_{HH}$ = 4.89, 1 H, 3-H_{trans}), 3.61 [ddt, $^2J_{HH}$ = 12.33, $^3J_{HH}$ = 5.48, $^4J_{HH}$ = 1.37, 1 H, OC(H)***H***CH=CH_2], 3.72 [ddt, $^2J_{HH}$ = 12.33, $^3J_{HH}$ = 6.06, $^4J_{HH}$ = 1.27, 1 H, OC(***H***)HCH=CH_2], 4.18 (dd, $^3J_{HH}$ = 4.89, 6.51, 1 H, 2-H), 5.09 [ddt, $^2J_{HH}$ = 1.47, $^3J_{HH}$ = 10.37, $^4J_{HH}$ = 1.27, 1 H, OCH_2CH=CH(***H***$_{trans}$)], 5.13 [ddt, $^2J_{HH}$ = 1.56, $^3J_{HH}$ = 17.21, $^4J_{HH}$ = 1.47, 1 H, OCH_2CH=C***H***$_{cis}$(H)], 5.78 (dddd, $^3J_{HH}$ = 5.48, 6.06, 10.37, 17.21, 1 H, OCH_2C***H***=CH_2), 6.97 (d, $^3J_{HH}$ = 7.62, 1 H, Ar-H), 7.29 (t, $^3J_{HH}$ = 7.43, 1 H, Ar-H), 7.31 (d, $^3J_{HH}$ = 7.53, 1 H, Ar-H), 7.37 (t, $^3J_{HH}$ = 7.44, 1 H, Ar-H), 7.39 (t, $^3J_{HH}$ = 7.53, 1 H, Ar-H), 7.46 (d, $^3J_{HH}$ = 7.63, 1 H, Ar-H), 7.84 (d, $^3J_{HH}$ = 7.63, 1 H, Ar-H), 7.86 (d, $^3J_{HH}$ = 7.82, 1 H, Ar-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.65 (t, $^1J_{CH}$ = 162.6, C-3), 35.46 (s, C-1), 67.04 (d, $^1J_{CH}$ = 185.5, C-2), 72.15 (t, OCH_2), 117.46 (t, CH_2CH=***C***H_2), 118.41 (d, Ar-C_t), 119.83 (d, 2 C, Ar-C_t), 121.95 (d, Ar-C_t), 125.96 (d, Ar-C_t), 125.98 (d, Ar-C_t), 126.59 (d, Ar-C_t), 126.70 (d, Ar-C_t), 133.43 (d, OCH2***C***H=CH_2), 139.55, 140.20, 143.72, 146.63 (s, 4 C, C-4a′, C-4b′, C-8a′, C-9a′). − MS (70 eV), *m/z* (%): 248 (5) [M^+], 207 (30) [$M^+ - C_3H_5$], 179 (100) [$M^+ - C_3H_5 - CO$], 152 (8) [$C_{12}H_8^+$]. − HR-MS: 248.1200 ($C_{18}H_{16}O$, calcd. 248.1201). − $C_{18}H_{16}O$ (248.32): calcd. C 87.06, H 6.49; found C 87.38, H 6.57.

Reaction of **1** *with exo-Methylene Sugar* **17***:* Reaction of 1 mmol **1** (0.19 g) dissolved in 10 ml CH_2Cl_2 with a solution of 1 mmol *exo*-methylene sugar **17** (0.26 g) and 0.006 g **2** (0.02 mmol, 2 mol%) in 4 ml CH_2Cl_2 gave 0.28 g of cyclopropane **19** (0.68 mmol, 68%) and 0.04 g of azine **10** (0.11 mmol, 22% based on **1**) after work-up according to procedure A (eluent: diethyl ether/petroleum ether, 1:2).

(2′R)-Dispiro[9H-fluorene-9,1′-cyclopropane[2′.1′′]-1′′-deoxy-2′′,3′′:5′′,6′′-di-O-isopropylidene-D-mannofuranose] (**19**): Colorless crystals, m.p. 85−86°C, R_f = 0.3. − IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1} (w), 2985 (w), 2935 (w), 2875 (w), 1481 (s), 1450 (s), 1371 (s), 1213 (vs), 1070 (vs, COC), 844 (m), 738 (vs). − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.25 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 2.24 (d, $^2J_{HH}$ = 7.45, 1 H, 3′-H), 2.32 (d, $^2J_{HH}$ = 7.45, 1 H, 3′-H), 2.91 (dd, $^3J_{HH}$ = 3.18, 8.36, 1 H, 4′′-H), 3.89 (dd, $^2J_{HH}$ = 8.62, $^3J_{HH}$ = 4.47, 1 H, 6′′-H), 4.14 (dd, $^2J_{HH}$ = 8.62, $^3J_{HH}$ = 6.27, 1 H, 6′′-H), 4.41 (ddd, $^3J_{HH}$ = 4.47, 6.27, 8.36, 1 H, 5′′-H), 4.59 (dd, $^3J_{HH}$ = 3.18, 5.56, 1 H, 3′′-H), 5.03 (d, $^3J_{HH}$ = 5.56, 1 H, 2′′-H), 7.15 (d, $^3J_{HH}$ = 7.15, 1 H, Ar-H), 7.31 (t, $^3J_{HH}$ = 7.48, 1 H, Ar-H), 7.34 (t, $^3J_{HH}$ = 7.43, 1 H, Ar-H), 7.36−7.41 (m, 3 H, Ar-H), 7.82 (d, $^3J_{HH}$ = 7.65, 1 H, Ar-H), 7.84 (d, $^3J_{HH}$ = 7.85, 1 H, Ar-H). − ^{13}C NMR (125.6 Hz, $CDCl_3$): δ = 21.01 (t, $^1J_{CH}$ = 162.9, C-3′), 24.94 (q, CH_3), 25.56 (q, CH_3), 26.27 (q, CH_3), 26.55 (q, CH_3), 39.74 (s, C-9), 67.16 (t, C-6′′), 72.48 (d, C_{sugar}), 77.04 (s, C-1′′), 80.19 (d, C_{sugar}), 80.91 (d, C_{sugar}), 81.51 (d, C_{sugar}), 109.19 (s, C_{acetal}), 113.20 (s, C_{acetal}), 119.75 (d, Ar-C_t), 120.15 (d, Ar-C_t), 120.86 (d, Ar-C_t), 122.23 (d, Ar-C_t), 126.18 (d, Ar-C_t), 126.34 (d, Ar-C_t), 126.41 (d, Ar-C_t), 126.49 (d, Ar-C_t), 139.67, 140.36, 142.62, 143.94 (s, 4 C, C-4a, C-4b, C-8a, C-9a). − MS (70 eV), *m/z* (%): 420 (15) [M^+], 405 (3) [$M^+ - CH_3$], 362 (20) [$M^+ - OC(CH_3)_2$], 347 (3) [$M^+ - OC(CH_3)_2 - CH_3$], 287 (10) [$M^+ - OC(CH_3)_2 - C_3H_7O_2$], 206 (15), 178 (100) [$C_{14}H_{10}^+$], 101 (18) [$C_8H_5^+$]. − MS (HR-EI): 420.1945 ($C_{26}H_{28}O_5$, calcd. 420.1938). − $C_{26}H_{28}O_5$ (420.51): calcd. C 74.26, H 6.71; found C 74.26, H 6.78.

Reaction of **1** *with Ethyl Vinyl Ether Catalyzed by Carbene Complex* **13**: Reaction of 3 mmol 9-diazo-9*H*-fluorene (**1**) (0.57 g) with 3 mmol ethyl vinyl ether (0.22 g) in the presence of pentacarbonyl[9*H*-9-fluorenylidene]chromium(0) (**13**) (0.021 g, 0.06 mmol, 2 mol%) gave 0.62 g of spirocyclopropane **3** (2.61 mmol, 87%) after work-up according to procedure A (eluent: CH_2Cl_2/petroleum ether, 3:2, R_f = 0.55).

Reaction of **1** *with Ethyl Vinyl Ether Catalyzed by Carbene Complex* **20**: Reaction of 3 mmol 9-diazo-9*H*-fluorene (**1**) (0.57 g) with 3 mmol ethyl vinyl ether (0.22 g) in the presence of pentacarbonyl[9*H*-9-xanthenylidene]chromium(0) (**20**) (0.022 g, 0.06 mmol, 2 mol%) gave 0.56 g of spirocyclopropane **3** (2.37 mmol, 79%) after work-up according to procedure A (eluent: CH_2Cl_2/petroleum ether, 3:2, R_f = 0.55).

Reaction of **1** *with (Z)-Propenyl Benzyl Ether:* Reaction of 3 mmol **1** (0.57 g) with 3 mmol (*Z*)-propenyl benzyl ether (0.44 g) in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%) gave 0.21 g of cyclopropane **21** (0.66 mmol, 22%), 0.10 g of **9** (0.30 mmol, 20% based on **1**) and 0.27 g of azine **10** (0.75 mmol, 50% based on **1**) after Kugelrohr distillation (0.31 g, 2.1 mmol, 70% (*Z*)-propenyl benzyl ether recovered) and work-up of the residue according to procedure B (eluent: CH_2Cl_2/petroleum ether, 1:1).

cis-2-Benzyloxy-3-methylspiro[cyclopropane-1,9′-[9H]fluorene] (**21**): Colorless crystals, m.p. 103−104°C, R_f = 0.6. − IR (KBr): $\tilde{\nu}$ = 3036 cm^{-1} (w), 2957 (w), 1457 (m), 1445 (m), 1330 (m), 1045 (vs, COC), 750 (vs), 701 (m). − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.56 (d, $^3J_{HH}$ = 6.69, 3 H, CH_3), 2.21 (p quint., $^3J_{HH}$ = 6.69, 1 H, 3-H), 4.30 (s, 2 H, OCH_2Ph), 4.31 (d, $^3J_{HH}$ = 6.69, 1 H, 2-H), 6.96 (d, $^3J_{HH}$ = 7.55, 1 H, Ar-H), 7.27−7.29 (m, 2 H, Ar-H), 7.32−7.37 (m, 5 H, Ar-H), 7.41 (t, $^3J_{HH}$ = 7.36, 1 H, Ar-H), 7.45 (t, $^3J_{HH}$ =

7.55, 1 H, Ar-H), 7.61 (d, $^3J_{HH}$ = 7.68, 1 H, Ar-H), 7.89 (d, $^3J_{HH}$ = 7.48, 1 H, Ar-H), 7.96 (d, $^3J_{HH}$ = 7.52, 1 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 6.72 (q, CH_3), 28.73 (d, $^1J_{CH}$ = 158.9, C-3), 37.79 (s, C-1), 69.09 (d, $^1J_{CH}$ = 185.4, C-2), 73.16 (t, OCH_2), 118.12 (d, Ar-C_t), 119.61 (d, Ar-C_t), 120.00 (d, Ar-C_t), 124.67 (d, Ar-C_t), 125.65 (d, Ar-C_t), 125.69 (d, Ar-C_t), 126.23 (d, Ar-C_t), 126.76 (d, Ar-C_t), 127.74 (d, Ar-C_t), 128.04 (d, 2 C, Ar-C_t), 128.28 (d, 2 C, Ar-C_t), 137.16, 139.09, 141.15, 141.38, 147.78 (s, 5 C, C-4a′, C-4b′, C-8a′, C-9a′, C-1′′). − MS (70 eV), *m/z* (%): 312 (18) [M^+], 255 (3), 221 (25) [$M^+ - C_7H_7$], 193 (100) [$M^+ - C_7H_7 - CO$], 178 (70) [$M^+ - C_7H_7 - CO - CH_3$], 165 (25) [$C_{13}H_9^+$], 152 (30) [$C_{12}H_8^+$], 91 (35) [$C_7H_7^+$]. − MS (HR-EI): 312.1514 ($C_{23}H_{20}O$, calcd. 312.1514). − $C_{23}H_{20}O$ (312.41): calcd. C 88.43, H 6.45; found C 88.09, H 6.47.

Reaction of 1-Diazo-1H-indene (**22**) *with Ethyl Vinyl Ether:* 3 mmol **22** (0.43 g) and 3 mmol ethyl vinyl ether (0.21 g) were reacted in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%). After filtration, which removed 0.20 g of an unidentified insoluble black solid, 0.24 g of diazo compound **22** (1.7 mmol, 57%) and 0.10 g of cyclopropane *endo*/*exo*-**26** (0.53 mmol, 18%; ratio of isomers: 1.94:1; an unequivocal stereochemical assignment could not be made) were obtained by column chromatographic work-up under argon at −10°C (eluent: CH_2Cl_2/petroleum ether, 1:1).

(endo/exo)-2-Ethoxyspiro[cyclopropane-1,1′-[1H]indene] (**26**): Colorless oil, R_f = 0.5. − IR (film): $\tilde{\nu}$ = 3053 cm^{-1} (m), 2974 (m), 2928 (m), 2889 (m), 2872 (m), 1456 (s), 1375 (m), 1350 (m), 1060 (vs, COC), 765 (vs), 752 (m). − ^{1}H NMR (500 MHz, $CDCl_3$): Major isomer: δ = 1.22 (t, $^3J_{HH}$ = 7.05, 3 H, CH_3), 1.86 (dd, $^2J_{HH}$ = 5.33, $^3J_{HH}$ = 6.65, 1 H, 3-H), 2.20 (dd, $^2J_{HH}$ = 5.33, $^3J_{HH}$ = 4.77, 1 H, 3-H), 3.44 (dq, $^2J_{HH}$ = 9.44, $^3J_{HH}$ = 7.05, 1 H, CH_2), 3.51 (dq, $^2J_{HH}$ = 9.43, $^3J_{HH}$ = 7.05 Hz, 1 H, CH_2), 4.24 (dd, $^3J_{HH}$ = 4.77, 6.65, 1 H, 2-H), 6.52 (d, $^3J_{HH}$ = 5.46, 1 H, alkene-H), 6.95 (d, $^3J_{HH}$ = 6.95, 1 H, Ar-H), 7.00 (d, $^3J_{HH}$ = 5.46, 1 H, alkene-H), 7.21 (t, $^3J_{HH}$ = 7.45, 1 H, Ar-H), 7.30 (t, $^3J_{HH}$ = 7.50, 1 H, Ar-H), 7.47 (d, $^3J_{HH}$ = 7.45, 1 H, Ar-H). Minor isomer: δ = 1.12 (t, $^3J_{HH}$ = 7.06, 3 H, CH_3), 1.99 (dd, $^2J_{HH}$ = 6.05, $^3J_{HH}$ = 6.81, 1 H, 3-H), 2.04 (dd, $^2J_{HH}$ = 6.05, $^3J_{HH}$ = 5.24, 1 H, 3-H), 3.05 (dq, $^2J_{HH}$ = 9.17, $^3J_{HH}$ = 7.06, 1 H, CH_2), 3.40 (dq, $^2J_{HH}$ = 9.17, $^3J_{HH}$ = 7.06, 1 H, CH_2), 4.26 (dd, $^3J_{HH}$ = 5.24, 6.81, 1 H, 2-H), 6.15 (d, $^3J_{HH}$ = 5.36, 1 H, alkene-H), 6.93 (d, $^3J_{HH}$ = 5.36, 1 H, alkene-H), 7.22 (t, $^3J_{HH}$ = 7.45, 1 H, Ar-H), 7.31 (t, $^3J_{HH}$ = 7.46, 1 H, Ar-H), 7.41 (d, $^3J_{HH}$ = 7.65, 1 H, Ar-H), 7.48 (d, $^3J_{HH}$ = 7.55, 1 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): Major isomer: δ = 14.92 (q, CH_3), 21.76 (t, $^1J_{CH}$ = 163.6, C-3), 49.91 (s, C-1), 67.01 (d, $^1J_{CH}$ = 186.1, C-2), 67.07 (t, OCH_2), 117.44 (d, Ar-C_t), 121.36 (d, Ar-C_t), 124.18 (d, Ar-C_t), 125.52 (d, Ar-C_t), 129.23 (d, Ar-C_t), 136.36 (d, Ar-C_t), 143.39 (s, Ar-C_q), 146.38 (s, Ar-C_q). Minor isomer: δ = 14.63 (q, CH_3), 21.28 (t, $^1J_{CH}$ = 161.1, C-3), 39.71 (s, C-1), 64.97 (d, $^1J_{CH}$ = 172.7, C-2), 66.71 (t, OCH_2), 120.63 (d, Ar-C_t), 121.27 (d, Ar-C_t), 124.03 (d, Ar-C_t), 125.35 (d, Ar-C_t), 128.49 (d, Ar-C_t), 138.36 (d, Ar-C_t), 143.77 (s, Ar-C_q), 143.85 (s, Ar-C_q). − MS (70 eV), *m/z* (%): 186 (28) [M^+], 157 (15) [$M^+ - C_2H_5$], 142 (30) [$M^+ - C_2H_4O$], 129 (100) [$M^+ - C_3H_5O$]. − MS (HR-EI): 186.1041 ($C_{13}H_{14}O$, calcd. 186.1045).

Reaction of 9-Diazo-9,10-dihydro-10,10-dimethylanthracene (**23**) *with Ethyl Vinyl Ether:* Reaction of 3 mmol **23** (0.70 g) with 3 mmol ethyl vinyl ether (0.21 g) in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%) gave 0.09 g of cyclopropane **27** (0.38 mmol, 13%) and 0.51 g of azine **28** (1.16 mmol, 77% based on **23**) after work-up according to procedure B (eluent: CH_2Cl_2/petroleum ether, 1:1).

2-Ethoxy-9′,10′-dihydro-10′,10′-dimethylspiro[cyclopropane-1,9′-anthracene] (**27**): Colorless oil, R_f = 0.3. − IR (film): $\tilde{\nu}$ = 3063 cm^{-1} (w), 3034 (w), 2974 (w), 2927 (w), 2868 (w), 1662 (m), 1660 (m), 1473, 1448 (m), 1325 (m), 1292 (m), 1113 (s), 1068 (s, COC). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.01 (pt, $^3J_{HH}$ = 7.03, 3 H, $CH_2C\boldsymbol{H}_3$), 1.54 (s, 3 H, CH_3), 1.93 (s, 3 H, CH_3), 2.02−2.07 (m, 2 H, 3-H), 3.14 [dq, $^2J_{HH}$ = 9.41, $^3J_{HH}$ = 7.03, 1 H, C(***H***)HCH_3], 3.33 (dd, $^3J_{HH}$ = 4.67, 6.65, 1 H, 2-H), 3.40 [dq, $^2J_{HH}$ = 9.41, $^3J_{HH}$ = 7.03, 1 H, C(H)***H***CH_3], 6.88 (d, $^3J_{HH}$ = 7.75, 1 H, Ar-H), 7.21−7.32 (m, 5 H, Ar-H), 7.60 (d, $^3J_{HH}$ = 7.69, 1 H, Ar-H), 7.61 (d, $^3J_{HH}$ = 8.09, 1 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 14.79 (q, $CH_2C\boldsymbol{H}_3$), 19.07 (t, $^1J_{CH}$ = 158.9, C-3), 28.91 (q, CH_3), 32.93 (s, C-10), 34.28 (q, CH_3), 38.83 (s, C-1), 65.93 (t, CH_2), 69.94 (d, $^1J_{CH}$ = 185.4, C-2), 121.66 (d, Ar-C_t), 124.71 (d, Ar-C_t), 124.84 (d, Ar-C_t), 124.91 (d, Ar-C_t), 125.14 (d, Ar-C_t), 125.87 (d, Ar-C_t), 125.96 (d, Ar-C_t), 126.15 (d, Ar-C_t), 132.61, 137.50, 144.75, 145.36 (s, 4 C, Ar-C_q). − MS (70 eV), *m/z* (%): 278 (50) [M^+], 263 (8) [$M^+ - CH_3$], 249 (40) [$M^+ - C_2H_5$], 234 (20) [$M^+ - CH_3 - C_2H_5$], 232 (20), 217 (78) [$M^+ - CH_3 - C_2H_6O$], 207 (100) [$M^+ - C_2H_5 - C_2H_2O$], 191 (20), 178 (30) [$C_{14}H_{10}^+$], 143 (30), 91 (20) [$C_7H_7^+$]. − MS (HR-EI): 278.1666 ($C_{20}H_{22}O$, calcd. 278.1671).

Bis(9,10-dihydro-10,10-dimethyl-9-anthracenylidene)azine (**28**): Orange crystals, m.p. 212−213°C, R_f = 0.45 (CH_2Cl_2). − IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1} (m), 2969 (m), 1591 (s), 1560 (s, C=N), 1476 (s), 1448 (s), 1261 (s), 792 (s), 756 (vs), 669 (s). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.71 (s, 12 H, CH_3), 7.27 (t, $^3J_{HH}$ = 7.55, 2 H, Ar-H), 7.32 (t, $^3J_{HH}$ = 7.43, 2 H, Ar-H), 7.38 (t, $^3J_{HH}$ = 7.75, 2 H, Ar-H), 7.39 (t, $^3J_{HH}$ = 7.80, 2 H, Ar-H), 7.58 (d, $^3J_{HH}$ = 7.35, 2 H, Ar-H), 7.64 (d, $^3J_{HH}$ = 7.84, 2 H, Ar-H), 8.06 (d, $^3J_{HH}$ = 7.85, 2 H, Ar-H), 8.19 (d, $^3J_{HH}$ = 7.60, 2 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 31.59 (4 C, CH_3), 39.54 (2 C, C-10, C-10′), 123.89 (2 C, Ar-C_t), 124.28 (2 C, Ar-C_t), 125.55 (2 C, Ar-C_t), 126.14 (2 C, Ar-C_t), 126.60 (2 C, Ar-C_t), 129.08 (2 C, Ar-C_t), 129.57 (2 C, Ar-C_q), 129.85 (2 C, Ar-C_t), 130.44 (2 C, Ar-C_t), 134.41 (2 C, Ar-C_q), 145.99 (2 C, Ar-C_q), 148.05 (2 C, Ar-C_q), 149.24 (2 C, C=N). − MS (70 eV), *m/z* (%): 440 (66) [M^+], 425 (100) [$M^+ - CH_3$], 410 (40) [$M^+ - 2CH_3$], 395 (18) [$M^+ - 3CH_3$], 246 (22), 207 (37), 191 (28), 149 (25). − MS (HR-EI): 440.2254 ($C_{32}H_{28}N_2$, calcd. 440.2252). − $C_{32}H_{28}N_2$ (440.59): calcd. C 87.24, H 6.41, N 6.36; found C 87.06, H 6.35, N 6.24.

Reaction of 5-Diazo-5H-dibenzo[a,d]cycloheptenylidene (**24**) *with Ethyl Vinyl Ether:* Reaction of 3 mmol **24** (0.65 g) with 3 mmol ethyl vinyl ether (0.21 g) in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%) gave the olefin metathesis products **29** (0.23 g, 1.17 mmol, 39%) and **30** (0.31 g, 1.26 mmol, 42%) after work-up according to procedure A (eluent: CH_2Cl_2/petroleum ether, 1:2).

5-Methylene-5H-dibenzo[a,d]cycloheptenylidene (**29**): Colorless crystals, m.p. 118°C (ref.[30] 118.4−119.4°C), R_f = 0.6. − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (m), 1621 (m, C=CH_2), 1481 (m), 1431 (m), 1384 (m), 906 (s), 800 (s), 775 (vs). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.28 (s, 2 H, CH_2), 6.83 (s, 2 H, 10-H, 11-H), 7.28 (d, $^3J_{HH}$ = 7.55, 2 H, Ar-H), 7.31 (t, $^3J_{HH}$ = 7.35, 2 H, Ar-H), 7.37 (t, $^3J_{HH}$ = 7.28, 2 H, Ar-H), 7.42 (d, $^3J_{HH}$ = 7.65, 2 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 120.50 (CH_2), 127.39 (2 C, Ar-C_t), 128.01 (2 C, Ar-C_t), 128.59 (2 C, Ar-C_t), 128.77 (2 C, Ar-C_t), 131.22 (2 C, Ar-C_t), 133.88 (2 C, Ar-C_q), 140.77 (2 C, Ar-C_q), 150.75 (1 C, C-5). − MS (70 eV), *m/z* (%): 204 (100) [M^+], 177 (5), 101 (8). − MS (HR-EI): 204.0940 ($C_{16}H_{12}$, calcd. 204.0939). − $C_{16}H_{12}$ (204.27): calcd. C 94.08, H 5.92; found C 93.71, H 5.90.

5-Ethoxymethylene-5H-dibenzo[a,d]cycloheptenylidene (**30**): Colorless crystals, m.p. 45−46°C, R_f = 0.5. − IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1} (m), 3018 (m), 2978 (m), 2929 (m), 2879 (m), 1639 (s, C=C_{alkene}), 1489 (m), 1433 (m, C=C_{aryl}), 1201 (vs, COC), 1084 (s), 798 (s), 771 (vs), 719 (m). − ^{1}H NMR (500 MHz, $CDCl_3$): δ =

1.30 (pt, $^3J_{HH}$ = 7.09, 3 H, CH_3), 3.92 (dq, $^2J_{HH}$ = 14.26, $^3J_{HH}$ = 7.09, 1 H, CH_2), 3.94 (dq, $^2J_{HH}$ = 14.26, $^3J_{HH}$ = 7.09, 1 H, CH_2), 6.13 [s, 1 H, CH(OEt)], 6.72 (d, $^3J_{HH}$ = 11.99, 1 H, HC=C***H***), 6.75 (d, $^3J_{HH}$ = 11.99, 1 H, ***H***C=CH), 7.10−7.30 (m, 7 H, Ar-H), 7.35 (d, $^3J_{HH}$ = 7.73, 1 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 15.23 (CH_3), 68.49 (OCH_2), 120.11 (C-5), 126.57 (Ar-C_t), 126.73 (Ar-C_t), 127.88 (Ar-C_t), 128.24 (Ar-C_t), 128.49 (Ar-C_t), 128.72 (Ar-C_t), 129.08 (Ar-C_t), 130.22 (Ar-C_t), 131.02 (Ar-C_t), 131.91 (Ar-C_t), 134.74 (Ar-C_q), 136.07 (Ar-C_q), 136.29 (Ar-C_q), 139.08 (Ar-C_q), 145.77 [C=***C***(OEt)H]. − MS (70 eV), *m/z* (%): 248 (100) [M^+], 219 (55) [$M^+ - C_2H_5$], 203 (12) [$M^+ - OC_2H_5$], 191 (53) [$C_{15}H_{11}^+$], 165 (15) [$C_{13}H_9^+$]. − MS (HR-EI): 248.1206 ($C_{18}H_{16}O$, calcd. 248.1211). − $C_{18}H_{16}O$ (248.32): calcd. C 87.06, H 6.49; found C 86.64, H 6.36.

Reaction of (4-Methoxyphenyl)phenyldiazomethane (**25**) *with Ethyl Vinyl Ether:* Reaction of 3 mmol **25** (0.64 g) with 3 mmol ethyl vinyl ether (0.21 g) in the presence of **2** (0.02 g, 0.06 mmol, 2 mol%) gave 0.09 g of olefin metathesis reaction product **31** (0.43 mmol, 15%) and 0.45 g of azine **32** (1.07 mmol, 71% based on **25**, *E*/*Z* = 1:1) after work-up according to procedure A (eluent: CH_2Cl_2).

4-(1-Phenyl)vinylanisole (**31**): Colorless crystals, m.p. 73−74°C (ref.[31] 74−75°C), R_f = 0.8. − IR (KBr): $\tilde{\nu}$ = 3009 cm^{-1} (w), 2956 (w), 1610 (s), 1515 (s, C=C), 1442 (m), 1252 (vs), 1032 (vs, COC), 905 (vs), 845 (vs), 787 (vs), 712 (vs). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.07 (s, 3 H, CH_3), 5.61 [br s, 1 H, C=C(***H***)H], 5.63 [br s, 1 H, C=C(H)***H***], 7.12 (d, $^3J_{HH}$ = 8.54, 2 H, 3-H, 5-H), 7.52 (d, $^3J_{HH}$ = 8.54, 2 H, 2-H, 6-H), 7.53−7.64 (m, 5 H, C_6H_5). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 55.28 (CH_3), 112.94 (C=***C***H_2), 113.49 (2 C, C-3, C-5), 127.62 (C-4′), 128.10 (2 C, Ar-C_t), 128.29 (2 C, Ar-C_t), 129.37 (2 C, C-2, C-6), 133.95 (Ar-C_q), 141.78 (Ar-C_q), 149.47 (Ar-C_q), 159.29 (C-4). − MS (70 eV), *m/z* (%): 210 (100) [M^+], 195 (66) [$M^+ - CH_3$], 179 (15) [$M^+ - OCH_3$], 165 (50) [$M^+ - OCH_3 - CH_2$], 152 (40). − MS (HR-EI): 210.1044 ($C_{15}H_{14}O$, calcd. 210.1045). − $C_{15}H_{14}O$ (210.28): calcd. C 85.68, H 6.71; found C 84.97, H 6.74.

(E/Z)-Bis[4-methoxyphenyl(phenyl)methanone]azine (**32**): Yellow crystals, m.p. 132°C (ref.[32] 131−132°C), R_f = 0.2. − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (w), 2932 (w), 2835 (w), 1609 (s), 1514 (s, C=N), 1450 (m), 1440 (m, C=C), 1258 (vs), 1177 (vs, COC), 1033 (s), 839 (s), 783 (m), 701 (s). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.79 (d, $^3J_{HH}$ = 8.94, 2 H, Ar-H), 6.83 (d, $^3J_{HH}$ = 8.94, 2 H, Ar-H), 6.91 (t, $^3J_{HH}$ = 8.74, 4 H, Ar-H), 7.25−7.46 (m, 24 H, Ar-H), 7.51 (d, $^3J_{HH}$ = 9.04, 2 H, Ar-H), 7.54 (d, $^3J_{HH}$ = 6.95, 2 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 55.15 (2 C, OCH_3), 55.18 (OCH_3), 55.21 (OCH_3), 113.00 (2 C, C-3, C-5), 113.06 (2 C, C-3, C-5), 113.31 (2 C, C-3, C-5), 113.38 (2 C, C-3, C-5), 127.66 (2 C, Ar-C_t), 127.71 (2 C, Ar-C_t), 127.84 (2 C, Ar-C_t), 127.91 (2 C, Ar-C_t), 128.35 (C-4′), 128.43 (C-4′), 128.83 (4 C, Ar-C_t), 129.16 (2 C, Ar-C_t), 129.29 (C-4′), 129.31 (C-4′), 129.32 (2 C, Ar-C_t), 130.11 (4 C, Ar-C_t), 130.76 (Ar-C_q), 130.82 (Ar-C_q), 131.41 (2 C, Ar-C_t), 131.53 (2 C, Ar-C_t), 131.82 (Ar-C_q), 132.49 (Ar-C_q), 135.76 (Ar-C_q), 135.87 (Ar-C_q), 138.74 (Ar-C_q), 138.78 (Ar-C_q), 158.51, 159.11, 159.16, 159.71, 159.79, 159.96, 160.81, 160.82 (8 C, 4 × C-4 and 4 × N=C). − MS (70 eV), *m/z* (%): 420 (40) [M^+], 389 (8) [$M^+ - OCH_3$], 343 (45) [$M^+ - C_6H_5$], 313 (28), 212 (40), 195 (25), 153 (20), 135 (100), 77 (70) [$C_6H_5^+$]. − MS (HR-EI): 420.1839 ($C_{28}H_{24}N_2O_2$, calcd. 420.1838). − $C_{28}H_{24}N_2O_2$ (420.51): calcd. C 79.98, H 5.75, N 6.66; found C 79.73, H 5.79, N 6.43.

Reaction of 2-Vinyloxyethyl Acrylate with 9-Diazo-9H-fluorene (**1**): A solution of 1 mmol **1** in 10 ml CH_2Cl_2 was added to a stirred solution of 1 mmol of 2-vinyloxyethyl acrylate (0.14 g) in 4 ml CH_2Cl_2 over a period of 8 h. After stirring for a further 8 h, removal of the solvent under reduced pressure and chromatographic work-up, 0.21 g of cyclopropane **15** (0.70 mmol, 70%) was obtained (eluent: CH_2Cl_2/petroleum ether, 2:1).

2′′-Vinyloxyethyl Spiro[cyclopropane-1,9′-[9H]fluorene]-2-carboxylate (**15**): Pale-green oil, R_f = 0.3. − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.19 (dd, $^2J_{HH}$ = 5.29, $^3J_{HH}$ = 8.41, 1 H, 3-H), 2.52 (dd, $^2J_{HH}$ = 5.29, $^3J_{HH}$ = 7.53 Hz, 1 H, 3-H), 2.85 (dd, $^3J_{HH}$ = 7.53, 8.41, 1 H, 2-H), 3.78 (ddd, $^2J_{HH}$ = 11.29, $^3J_{HH}$ = 6.83, 3.24, 1 H, OCH_2), 3.84 (ddd, $^2J_{HH}$ = 11.29, $^3J_{HH}$ = 5.71, 3.19, 1 H, OCH_2), 4.04 (dd, $^2J_{HH}$ = 2.31, $^3J_{HH}$ = 6.81, 1 H, OCH=C***H***$_{trans}$H), 4.18 (dd, $^2J_{HH}$ = 2.31, $^3J_{HH}$ = 14.34, 1 H, OCH=C***H***$_{cis}$H), 4.25 (ddd, $^2J_{HH}$ = 12.14, $^3J_{HH}$ = 5.71, 3.19, 1 H, OCH_2), 4.43 (ddd, $^2J_{HH}$ = 12.14, $^3J_{HH}$ = 6.83, 3.24, 1 H, OCH_2), 6.42 (dd, $^3J_{HH}$ = 6.81, 14.34, 1 H, OC***H***=CH_2), 7.05 (d, $^3J_{HH}$ = 7.58, 1 H, Ar-H), 7.35 (d, $^3J_{HH}$ = 7.49, 1 H, Ar-H), 7.42 (t, $^3J_{HH}$ = 7.46, 1 H, Ar-H), 7.39 (t, $^3J_{HH}$ = 7.69, 1 H, Ar-H), 7.45 (t, $^3J_{HH}$ = 7.43, 1 H, Ar-H), 7.72 (d, $^3J_{HH}$ = 7.72, 1 H, Ar-H), 7.85 (d, $^3J_{HH}$ = 7.60, 1 H, Ar-H), 7.89 (d, $^3J_{HH}$ = 7.56, 1 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 20.74 (t, $^1J_{CH}$ = 170.9, C-3), 32.46 (d, $^1J_{CH}$ = 167.3, C-2), 37.16 (s, C-1), 62.90 (t, OCH_2), 65.39 (t, OCH_2), 86.89 (dd, OCH=***C***H_2), 118.6 (d, Ar-C_t), 119.74 (d, Ar-C_t), 119.76 (d, Ar-C_t), 120.14 (d, Ar-C_t), 126.76 (d, Ar-C_t), 126.93 (d, Ar-C_t), 126.96 (d, Ar-C_t), 127.02 (d, Ar-C_t), 139.64, 140.88, 142.20, 146.12 (s, 4 C, C-4a′, C-4b′, C-8a′, C-9a′), 151.09 (d, O***C***H=CH_2), 169.22 (s, C=O). − MS (70 eV), *m/z* (%): 306 (8) [M^+], 218 (10) [$M^+ - HOCH_2CH_2OC_2H_3$], 191 (14) [$M^+ - CO_2CH_2CH_2OC_2H_3$], 180 (100) [$C_{14}H_{12}^+$], 152 (45) [$C_{12}H_8^+$]. − MS (HR-EI): 306.1257 ($C_{20}H_{18}O_3$, calcd. 306.1256). − $C_{20}H_{18}O_3$ (306.36): calcd. C 78.41, H 5.92; found C 77.95, H 5.85.

Reaction of 2-Vinyloxyethyl Acrylate with Pentacarbonyl(9H-9-fluorenylidene)chromium(0) (**13**): 1 mmol **13** (0.36 g) and 1 mmol of 2-vinyloxyethyl acrylate (0.14 g) were dissolved in 40 ml CH_2Cl_2 at −20°C. The solution was stirred and allowed to warm to room temperature over a period of 8 h. After removal of the solvent under reduced pressure, 0.04 g of dimer **9** (0.12 mmol, 24% based on **13**) followed by 0.17 g of cyclopropane **16** (0.56 mmol, 56%) were obtained upon chromatographic work-up (eluent: CH_2Cl_2/petroleum ether, 2:1).

2-(2′′-Acryloxy)ethoxyspiro[cyclopropane-1,9′-[9H]fluorene] (**16**): Colorless crystals, R_f = 0.3. − IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1} (w), 2958 (w), 2923 (w), 1728 (vs, C=O), 1448 (s), 1406 (s), 1184 (s, COC), 808 (s), 742 (s). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.04 (t, $^{2/3}J_{HH}$ = 6.54, 1 H, 3-H), 2.16 (dd, $^2J_{HH}$ = 6.54, $^3J_{HH}$ = 4.92, 1 H, 3-H), 3.33 [ddd, $^2J_{HH}$ = 3.54, $^3J_{HH}$ = 5.47, 8.94, 1 H, OC(H)***H***CH_2OC(O)CH=CH_2], 3.55 [ddd, $^2J_{HH}$ = 3.54, $^3J_{HH}$ = 5.96, 9.64, 1 H, OC(***H***)HCH_2OC(O)CH=CH_2], 4.22 [m, 3 H, C(O)OC***H2***CH2O, 2-H], 5.87 [dd, $^2J_{HH}$ = 1.09, $^3J_{HH}$ = 10.39, 1 H, C(O)CH=C(H)***H***$_{trans}$], 6.15 [dd, $^3J_{HH}$ = 10.39, 17.31, 1 H, C(O)C***H***=CH_2], 6.44 [dd, $^2J_{HH}$ = 1.09, $^3J_{HH}$ = 17.31 Hz, 1 H, C(O)CH=C(H)***H***$_{cis}$], 7.00 (d, $^3J_{HH}$ = 7.55, 1 H, Ar-H), 7.32 (t, $^3J_{HH}$ = 7.06, 1 H, Ar-H), 7.33 (t, $^3J_{HH}$ = 7.11, 1 H, Ar-H), 7.38−7.43 (m, 2 H, Ar-H), 7.47 (d, $^3J_{HH}$ = 7.65, 1 H, Ar-H), 7.86 (d, $^3J_{HH}$ = 8.74, 1 H, Ar-H), 7.89 (d, $^3J_{HH}$ = 8.45, 1 H, Ar-H). − ^{13}C NMR (125.6 MHz, $CDCl_3$): δ = 23.54 (t, $^1J_{CH}$ = 162.9, C-3), 35.46 (s, C-1), 63.29 (t, CH_2O), 67.53 (d, $^1J_{CH}$ = 186.1, C-2), 69.04 (t, OCH_2), 118.44 (d, Ar-C_t), 119.92 (d, Ar-C_t), 119.96 (d, Ar-C_t), 121.89 (d, Ar-C_t), 126.12 (d, Ar-C_t), 126.14 (d, Ar-C_t), 126.65 (d, Ar-C_t), 126.78 (d, Ar-C_t), 128.09 (d, Ar-C_t), 131.08 (t, CH=***C***H_2), 139.59, 140.29, 143.36, 146.43 (s, 4 C, C-4a′, C-4b′, C-8a′, C-9a′), 165.97 (s, C=O). − MS (70 eV), *m/z* (%): 306 (1) [M^+], 279 (0.1)

$[M^+ - C_2H_3]$, 251 (1) $[M^+ - C(O)C_2H_3]$, 178 (33) $[C_{14}H_{10}^+]$, 99 (100) $[CH_2{=}CH{-}C(O)OCH_2CH_2^+]$, 55 (44) $[C(O)C_2H_3^+]$. – MS (HR-EI): 306.1261 ($C_{20}H_{18}O_3$, calcd. 306.1266).

Control Reactions: For each of the aforementioned reactions catalyzed by chromium complex **2**, two control experiments in the absence of **2** and in the presence of 10 mol% hexacarbonylchromium(0), respectively, were performed. Only from the reactions of 9-diazo-9*H*-fluorene with ethyl acrylate was the corresponding cyclopropane **8** obtained (84% yield after chromatographic work-up).

Ethyl Spiro[cyclopropane-1,9′-[9H]fluorene]-2-carboxylate (**8**): Colorless crystals, m.p. 121°C, R_f = 0.4 (eluent: petroleum ether/dichloromethane, 1:1). – IR (KBr): $\tilde{\nu}$ = 2981 cm^{-1} (w), 1714 (s, C=O), 1454 (s, C=C), 1199 (vs), 746 (s), 754 (s). – ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 1.31 (t, $^3J_{HH}$ = 7.12, 3 H, CH_3), 2.26 (dd, $^2J_{HH}$ = 5.07, $^3J_{HH}$ = 8.54, 1 H, 3-H), 2.38 (dd, $^2J_{HH}$ = 5.07, $^3J_{HH}$ = 7.45, 1 H, 3-H), 2.85 (dd, $^3J_{HH}$ = 7.54, 8.54, 1 H, 2-H), 4.05 (dq, $^2J_{HH}$ = 10.86, $^3J_{HH}$ = 7.12, 1 H, OCH_2), 4.12 (dq, $^2J_{HH}$ = 10.86, $^3J_{HH}$ = 7.12, 1 H, OCH_2), 7.29 (d, $^3J_{HH}$ = 7.62, 1 H, Ar-H), 7.30 (t, $^3J_{HH}$ = 7.60, 1 H, Ar-H), 7.36 (t, $^3J_{HH}$ = 7.45, 1 H, Ar-H), 7.41 (t, $^3J_{HH}$ = 7.5, 1 H, Ar-H), 7.42 (t, $^3J_{HH}$ = 7.35, 1 H, Ar-H), 7.56 (d, $^3J_{HH}$ = 7.75, 1 H, Ar-H), 7.92 (d, $^3J_{HH}$ = 7.55, 1 H, Ar-H), 7.94 (d, $^3J_{HH}$ = 7.65, 1 H, Ar-H). – ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 14.01 (q, CH_3), 20.53 (dd, $^1J_{CH}$ = 167.1, 163.3, C-3), 33.09 (s, C-1), 36.93 (d, $^1J_{CH}$ = 167.8, C-2), 60.93 (t, OCH_2), 119.63 (d, Ar-C_t), 120.19 (d, Ar-C_t), 120.32 (d, Ar-C_t), 123.16 (d, Ar-C_t), 127.10 (d, Ar-C_t), 127.41 (d, Ar-C_t), 127.45 (d, Ar-C_t), 127.71 (d, Ar-C_t), 139.99, 143.02, 146.92, 147.44 (s, 4 C, C-4a′, C-4b′, C-8a′, C-9a′), 169.21 (s, C=O). – MS (70 eV), *m/z* (%): 264 (38) $[M^+]$, 235 (15) $[M^+ - C_2H_5]$, 219 (15) $[M^+ - OC_2H_5]$, 218 (35) $[M^+ - OC_2H_6]$, 191 (100) $[M^+ - C_2H_5 - CO]$, 165 (30) $[C_{13}H_9^+]$. – MS (HR-EI): 264.1152 ($C_{18}H_{16}O_2$, calcd. 264.1153). – $C_{18}H_{16}O_2$ (264.32): calcd. C 81.79, H 6.10; found C 81.77, H 6.04.

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