2- and 3-Haloalkoxy Fischer Carbene Complexes of Chromium as Synthons for either Hydroxycyclopropanation or Oxaspirocyclopropanation of Alkenes

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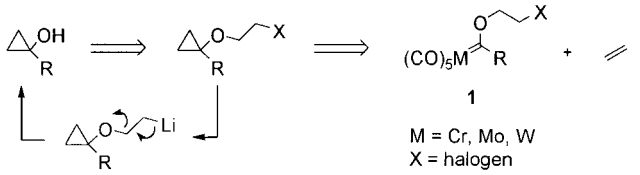
Abstract: The thermal reaction of 2-haloethoxy- and 3-chloropropoxy(alkenyl)carbene complexes of chromium with electronically neutral alkenes furnished diastereoselectively the corresponding 1-haloalkoxy-1-vinylcyclopropanes that, subjected to subsequent halogen–lithium exchange reactions, provided vinylcyclopropanols or compounds containing the spiro[cyclopropane–tetrahydrofuran/tetrahydropyran] structure, depending on the nature of both the halogen atom and the lithiating reagent. The hydroxycyclopropanation reaction can be efficiently achieved in a one-pot fashion.

Keywords: alkenes · carbene complexes · cyclopropanation · hydroxycyclopropanation · lithiation · oxaspirocyclopropanation

Introduction

The direct preparation of cyclopropanols by formal [2+1] cycloaddition of Group 6 metal hydroxycarbene complexes with alkenes is an unknown process. This is presumably due to the thermal instability of this type of carbene complexes, which can be prepared in solution and isolated at low temperatures (−30, −20 °C)[1] but, on warming to room temperature, rapidly decompose to usually give the corresponding aldehyde.[2, 3] Although a few isolated examples of more stable hydroxycarbene complexes containing an adequately positioned additional heteroatom have been characterized,[4] their chemical behavior remains unexplored. However, alkoxycarbene complexes readily react with electron-deficient[5] and electron-rich[6] alkenes to give functionalized alkoxycyclopropanes, and we have also recently shown that electronically neutral alkenes can be smoothly cyclopropanated in an intermolecular fashion with alkenyl- and heteroarylcarbene complexes of chromium.[7] Accordingly, we envisaged that 2-haloethoxycarbene complexes **1** could behave as hydroxycarbene complex equivalents, which in this case would allow the synthesis of cyclopropanols by initial transfer of their carbene ligand to an olefin followed by a halogen–lithium exchange reaction. The unstable β-alkoxy-substituted organolithium compound thus generated would undergo spontaneous β-elimination of the corresponding lithium cyclopropyl oxide (Scheme 1). A potential alternative



Scheme 1. Designed hydroxycyclopropanation reaction.

to this envisaged two-step hydroxycyclopropanation reaction could be found in the cyclopropanation of enol ethers[8a] and dienol silyl ethers[8b,c] with in situ generated acyloxycarbene complexes that afforded functionalized cyclopropyl carboxylates. But, so far, the subsequent ester cleavage required to liberate the corresponding cyclopropanol has not been carried out.

Herein, we report the first realization of the proposed hydroxycyclopropanation reaction of alkenes in a highly stereoselective manner with 2-iodoethoxycarbene complexes of chromium. In addition, we describe a two-step oxaspirocyclopropanation reaction of alkenes that was unexpectedly observed using a similar methodology with the same type of alkenylcarbene complexes but bearing a chlorine atom instead of an iodine.

Results and Discussion

Preparation of 2-haloethoxy and 3-chloropropoxy carbene complexes of chromium 1: The new carbene complexes **1** were

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Supporting information for this article (chart showing observed difference NOEs enhancements for compounds **2** and **9** and NOEs enhancements from 2D NOESY spectra for compounds **3a**,**b**, **4a**,**b**, **6**, **7b**, **8a**,**b**, **10** and **14**) is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author.

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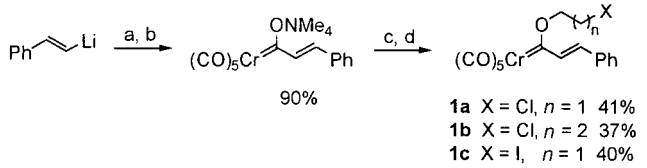
synthesized by the successive reaction of (*E*)-2-phenylethenyllithium with hexacarbonylchromium and tetramethylammonium bromide, followed by O-acylation of the resulting tetramethylammonium acylate complex with pivaloyl chloride and subsequent exchange with the corresponding 2- or 3-halogen-substituted alcohol (Scheme 2).[9, 10] After silica gel column chromatography, carbene complexes **1a–c** were isolated as stable dark garnet crystalline solids.

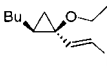
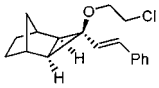
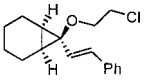
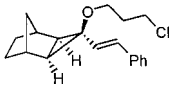
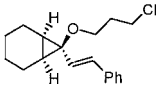


Scheme 2. Preparation of haloalkoxycarbene complexes **1**. Reaction conditions: a) $[Cr(CO)_6]$, Et_2O, 0 °C; b) Me_4NBr, CH_2Cl_2, 20 °C; c) $(CH_3)_3CCOCl$, CH_2Cl_2, −40 °C; d) $HOCH_2(CH_2)_nX$, −40 to 20 °C.

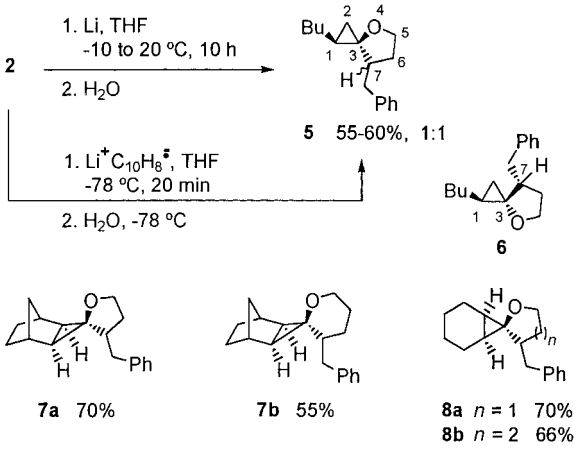
Oxaspyrocyclopropanation of alkenes: The 2-chloroethoxy(alkenyl)carbene complex **1a** was initially chosen as a more convenient reagent to accomplish the designed alkene cyclopropanation/halogen–lithium exchange reaction sequence. The thermal treatment of this carbene complex **1a** with 1-hexene, under the standard reaction conditions previously described,[7b] occurred smoothly to give vinylcyclopropane **2** with good diastereoselectivity (Table 1, entry 1). These two diastereoisomers were separated by silica gel column chromatography. Subsequently, this (2-chloroethoxy)cyclopropane **2** was treated with an excess of lithium powder, added at −10 °C, and the reaction allowed to reach room temperature and stirred for 10 h. After hydrolysis, oxaspirocyclopropane **5** was unexpectedly isolated instead of the anticipated corresponding cyclopropanol (Scheme 3). The same result was obtained by using a tetrahydrofuran solution of lithium–naphthalene. The reaction of compound **2** with two equivalents of this very active lithiating agent occurred quite quickly (20 min) at −78 °C and the final hydrolysis was also performed at this low temperature. The third stereogenic center (C7) of product **5** was formed without any noticeable diastereoselectivity, shown by the isolation of oxacyclopentanespirocyclopropane **5** as a roughly equimolar mixture of diastereoisomers. In addition, when a 6:1 mixture of compound **2** and its diastereoisomer was used as starting material in the reaction with lithium powder, a mixture of four isomers—two major and two minor—was observed, corresponding to products **5** (major isomers) and products **6** and its C7 epimer (minor isomers). Silica gel column chromatography of this crude material gave pure **6** and a mixture of the two major products **5**.

We decided to apply this methodology to other substrates that could eventually lead to oxaspirocyclopropanes with a more elaborate polycyclic structure. The cyclopropanation of norbornene and cyclohexene (see Table 1) with either 2-chloroethoxy(alkenyl)carbene complex **1a** or 3-chloropropoxy(alkenyl)carbene complex **1b** provided tricyclic vinylcyclopropanes **3a**,**b** and bicyclic vinylcyclopropanes **4a**,**b**, each as a single diastereoisomer (a unique set of signals was observed by ^1H and ^{13}C NMR spectroscopy, Table 1, entries 2–5). Further treatment of (2-chloroethoxy)vinylcyclopropanes **3a** and **4a** with either lithium (−20 to 20 °C, overnight) or lithium–naphthalene (−78 °C, 30 min) yielded oxacyclo-

Table 1. Cyclopropanation reactions of electronically neutral alkenes with 2- and 3-chloroalkoxycarbene complexes **1a**,**b**.

Entry	Alkene	Carbene complex	Reaction conditions[a] T [°C]	t [h]	Product	Yield[b] [%]	*de*[c] [%]
1		**1a**	110	4	 **2**[d]	85	72
2		**1a**	130	0.5	 **3a**	80	100
3		**1a**	120	1	 **4a**	88	100
4		**1b**	100	2	 **3b**	75	100
5		**1b**	120	1	 **4b**	67	100

[a] All reactions were conducted in THF in a sealed flask using five equivalents of the corresponding alkene. [b] Yield of isolated product based on the corresponding carbene complex **1a**,**b**. [c] Diastereomeric excess determined by ^1H NMR analysis of the crude products. [d] Only the major diastereoisomer is shown.



Scheme 3. Formation of Spiro compounds **5**–**8**.

Abstract in Spanish: *El tratamiento térmico de complejos 2-haloetoxi- o 3-cloropropoxi(alquenil)carbeno de cromo con alquenos electrónicamente neutros condujo a los correspondientes 1-haloalcoxi-1-vinilciclopropanos con alta diastereoselectividad. Cuando estos compuestos se sometieron a una posterior reacción de intercambio halógeno-litio se aislaron vinilciclopropanoles a partir de los derivados iodados y tert-butillitio, o compuestos que contienen la estructura espiro[ciclopropano-tetrahidrofurano/tetrahidropirano] a partir de los derivados clorados y litio en polvo o una disolución de litionaftaleno. La reacción de hidroxiciclopropanación puede realizarse one-pot de forma más eficiente.*

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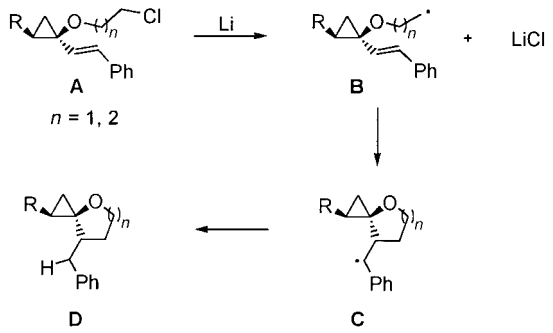
pentanespirocyclopropanes[11] **7a** with a tetracyclic structure and **8a** with a tricyclic framework, respectively (Scheme 3). The analogous reaction with (3-chloropropoxy)vinylcyclopropanes **3b** (Li, −20 to 20 °C, overnight) and **4b** ($Li^+C_{10}H_8^{-\cdot}$, −78 °C, 15 min) gave the corresponding oxacyclohexanespirocyclopropanes[12] **7b** and **8b**. Products **7a**,**b** and **8a**,**b** were all isolated as a single diastereoisomer (in all these cases the stereogenic center created in the last cyclization step gives rise to enantiomers).[13] Stereochemical assignments for compounds **2**, **3a**,**b**, **4a**,**b**, **6**, **7b** and **8a**,**b** are based on either 1D nuclear Overhauser effect (NOE) experiments or 2D nuclear Overhauser enhancement spectroscopy (NOESY) studies (see Supporting Information). The stereochemistry assigned to products **5** and **7a** has been assumed by analogy.

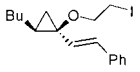
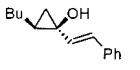
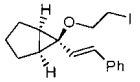
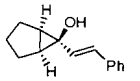
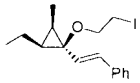
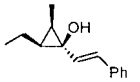
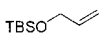
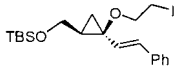
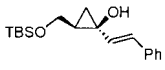
These results clearly discount the formation of the corresponding β-alkoxyorganolithium compounds, unstable intermediates that would spontaneously undergo a β-elimination process more rapidly than an anionic cyclization,[14] and suggest that the cyclization reactions proceed through a mechanism involving free-radical intermediates (Scheme 4). The reaction of chloroalkoxycyclopropanes **A** with either lithium powder or lithium–naphthalene occurs by initial one-electron transfer from the lithium to the alkyl chloride to yield alkyl free radicals **B**.[15] These 3-oxa-5-hexen-1-yl[16] **B** ($n=1$) or 4-oxa-6-hepten-1-yl[17] **B** ($n=2$) radicals go through a favorable cyclization giving 3-oxacyclopentylmethyl radicals **C** ($n=1$) or 3-oxacyclohexylmethyl radicals **C** ($n=2$), respectively, before further one-electron reduction to the primary organolithium takes place. Finally, abstraction of a hydrogen atom from the surrounding medium transforms benzylic radicals **C** into the final oxaspirocyclopropanes **D**. Alternatively, benzylic radicals **C** could be reduced to the anion by a further single-electron transfer from another equivalent of Li or lithium–naphthalene.[18] This possibility seems unlikely taking into account that when D_2O was used to quench experiments carried out with compound **2** and Li–naphthalene at −78 °C, we never observed deuterium incorporation at the benzylic position of products **5** (**D**, R = Bu, $n=1$),[19] unless the carbanions abstract protons from the solvent very rapidly.[20] Furthermore, this cyclization reaction takes place with only a stoichiometric amount of Li–naphthalene. Thus, treatment of **2** with one equivalent of $Li^+C_{10}H_8^{-\cdot}$ at −78 °C for 30 min led after hydrolysis at −78 °C to compound **5** (55 %) together with starting material **2** (7 %). Additionally, product **5** was generated as a nearly equimolar mixture of isomers when the iodine derivative **9** (see below, Table 2) analogous to **2** (I instead of Cl) was treated with tributyltin hydride (3 equiv) and azobisisobutyronitrile (AIBN, 0.3 equiv) in dichloromethane at room temperature for 1.5 h.[21] This outcome could be considered as indirect evidence supporting the proposed radical mechanism.



Scheme 4. Proposed mechanism for the generation of spiro compounds **5**–**8**.

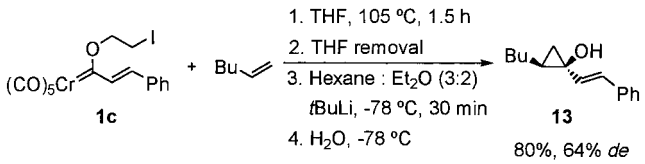
Hydroxycyclopropanation of alkenes: Given the unsuccessful generation of cyclopropanols from the chloro derivatives **2**–**4**, we focused our attention on the reaction with the corresponding iodine derivatives. It is known that the mechanism of the interchange reaction between a primary alkyl iodide and *tert*-butyllithium most likely involves rapid, reversible attack of the alkyllithium on the iodine atom of the substrate,[22] forming ate complex intermediates,[23] rather than a single-

Table 2. Cyclopropanation reactions of alkenes with 2-iodoethoxycarbene complex **1c** and preparation of the corresponding cyclopropanols.

Entry	Alkene	Reaction conditions[a] T [°C]	t [h]	Cyclopropanation product[b]		Yield[c] [%]	*de*[d] [%]	Cyclopropanol derivative[b,e]		Yield[f] [%]
1		110	2		**9**	70	69		**13**	95[g]
2		110	6		**10**	56	100		**14**	96
3		110	5		**11**	65	100		**15**	94
4		110[h]	5		**12**	87	63		**16**	96[i]

[a] All reactions were performed in THF on a sealed flask using five equivalents of the corresponding alkene, unless otherwise noted. [b] Only the major diastereoisomer is shown. [c] Yield of isolated product based on carbene complex **1c**. [d] Diastereomeric excess determined by ^1H NMR analysis of the crude products. [e] Reaction conditions: the corresponding 2-iodoethoxycyclopropane **9**–**12** was treated with two equivalents of *t*BuLi at −78 °C in hexane:Et_2O (3:2) for 30 min, followed by quenching at −78 °C with H_2O. [f] Yield of isolated product based on the corresponding 2-iodoethoxycyclopropane. [g] In this experiment compound **9** as a 4.3:1 (62 % *de*) mixture of isomers was used as starting material producing cyclopropanol **13** as an identical diastereomeric mixture (62 % *de*). [h] Reaction run with one equivalent of alkene (TBS = *t*BuMe$_2$Si). [i] A 9:1 (80 % *de*) mixture of isomers of 2-iodoethoxycyclopropane **12** was used as starting material, which led to cyclopropanol **16** isolated as an identical mixture of diastereoisomers (80 % *de*).

electron-transfer process. Consequently, this method could allow the generation of β-alkoxyorganolithium compounds and therefore provide the corresponding cyclopropanols. 2-Iodoethoxycyclopropanes **9**–**12** were prepared from the corresponding olefin and 2-iodoethoxycarbene complex **1c** using our standard cyclopropanation reaction conditions.[7b] The results are summarized in Table 2. Vinylcyclopropanes **10** and **11**, formed in the cyclopropanation of either a cyclic or acyclic *cis*-1,2-disubstituted olefin, were isolated as a single diastereoisomer[7b] (Table 2, entries 2 and 3), whereas products **9** and **12** produced in the cyclopropanation of a terminal olefin were obtained as diastereomerically enriched compounds[7b] (63–69% *de*; Table 2, entries 1 and 4). In these two latter cases, the major isomer shown in Table 2 was purified by silica gel column chromatography. Finally, the 2-iodoethyl protecting group was efficiently removed by treatment of 2-iodoethoxyvinylcyclopropanes **9**–**12** with two equivalents of *tert*-butyllithium at $-78\,^{\circ}C$ for 30 min, using as solvent a mixture of hexane:diethyl ether (3:2).[22] Further hydrolysis furnished the corresponding vinylcyclopropanols **13**–**16** in almost quantitative yield (Table 2, entries 1–4). Cyclopropanols **13** and **16** were obtained as a mixture of diastereoisomers with the same ratio as that present in the starting material employed in each case (see Table 2, footnotes g,i). Silica gel column chromatography allowed the purification of the major isomer **13**, **16** (Table 2).[24] Furthermore, this overall hydroxycyclopropanation reaction can be carried out in a one-pot fashion as demonstrated by the result presented in Scheme 5.



Scheme 5. One-pot hydroxycyclopropanation reaction.

Thus, after the thermal treatment of carbene complex **1c** with 1-hexene (5 equiv), the solvent, tetrahydrofuran, was removed under vacuum and replaced by a mixture of hexane:diethyl ether (3:2). Subsequent addition of *t*BuLi and final hydrolysis afforded cyclopropanol **13**. The relative configuration of cyclopropanes **9**, **10**,and **14** was elucidated by either 1D NOE or 2D NOESY experiments (see Supporting Information). The same stereochemistry was assumed by analogy for cyclopropanes **11**–**13**, **15**, and **16**.

Conclusion

These results show that 2- and 3-haloalkoxy(alkenyl)carbene complexes of chromium behave as effective reagents to accomplish either the oxaspirocyclopropanation or hydroxycyclopropanation[25] of simple alkenes by appropriate choice of the halogen atom and lithiation reagent employed after an initial thermal treatment. The chloro compounds reacted with lithium or Li–naphthalene to give three-/five- or three-/six-membered spiroheterocyclic subunits through a 5-*exo*-trig or 6-*exo*-trig radical cyclization, respectively.[26] In contrast, the reaction of the iodo-derivatives with *t*BuLi led to vinylcyclopropanols through an unstable β-alkoxyalkyllithium intermediate. The latter reaction can be performed, even more conveniently, in a one-pot procedure.

Experimental Section

General: All reactions involving organometallic species were carried out under an atmosphere of dry N_2 using oven-dried glassware and syringes. THF, hexane and Et_2O were distilled from sodium benzophenone ketyl under N_2 immediately prior to use, and CH_2Cl_2 from P_2O_5. The solvents used in column chromatography, hexane and EtOAc were distilled before use. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator (Scharlau). Flash column chromatography was carried out on silica gel 60, 230–240 mesh. ^1H NMR (200, 300, 400 MHz) and ^{13}C NMR (50.5, 75.5, 100 MHz) spectra were measured at room temperature on Bruker AC-200, AC-300 and AMX-400 instruments, respectively, with tetramethylsilane ($\delta = 0.0$, ^1H NMR) or $CDCl_3$ ($\delta = 77.00$, ^{13}C NMR) as internal standard. Carbon multiplicities were assigned by DEPT techniques. Low-resolution electron impact mass spectra (EI-MS) were obtained at 70 eV on a HP 5987 A instrument, and the intensities are reported as a percentage relative to the base peak after the corresponding *m*/*z* value. High-resolution mass spectra (HRMS) were determined on a Finnigan MAT 95 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 microanalyzer.

Materials: 2-Chloro-1-ethanol, 3-chloro-1-propanol, 2-iodo-1-ethanol, all the olefins, and common reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. 3-(*tert*-Butyldimethylsilyloxy)-1-propene was prepared according to literature methods.[27] Lithium–naphthalene was prepared by adding lithium powder (0.41 g, 58 mmol) to a solution of naphthalene (7.5 g, 58 mmol) in THF (50 mL) at $0\,^{\circ}C$. After addition, the ice–water bath was removed and the mixture was stirred for 10 h at room temperature. The resulting solution was filtered and checked by double titration with hydrochloric acid.[28]

General procedure for the synthesis of carbene complexes 1a–c: *Method A*: *t*BuLi (1.5 M in pentane, 80 mL, 120 mmol) was added dropwise to a solution of β-bromostyrene (7.7 mL, 60 mmol) in Et_2O (100 mL) cooled to $-60\,^{\circ}C$. The mixture was stirred for 0.5 h at $-60\,^{\circ}C$ and then for 0.5 h at room temperature. The resulting red solution was slowly added by cannula to a well-stirred suspension of hexacarbonylchromium (11.44 g, 52 mmol) in Et_2O (200 mL) at $-40\,^{\circ}C$. After addition, the cold bath was removed and the mixture stirred for 1 h at room temperature. The solvents were removed under vacuum. The residue obtained was dissolved in deoxygenated H_2O (200 mL), treated with Me_4NBr (8.80 g, 57.2 mmol) for 10 min, and extracted with CH_2Cl_2. The organic phase was dried and concentrated under reduced pressure. After crystallization in CH_2Cl_2:Et_2O (10:1) pentacarbonyl[(*E*)-3-phenyl-1-{(tetramethylammonio)oxy}-2-propenylidene]chromium was obtained as a brown solid (20.6 g, 90%). Freshly distilled pivaloyl chloride (1.4 mL, 11 mmol) was added dropwise at $-45\,^{\circ}C$ to a solution of this ammonium salt (3.97 g, 10 mmol) in dry CH_2Cl_2 (100 mL). After the mixture had been stirred at $-45\,^{\circ}C$ for 45 min, the corresponding alcohol (2-chloro-1-ethanol, 2-iodo-1-ethanol or 3-chloro-1-propanol, 11 mmol) was added and the resulting solution was stirred for 10 h and allowed to warm slowly to room temperature without removing the cold bath. The reaction was quenched with deoxygenated water (10 mL), stirred for 5 min, and extracted with CH_2Cl_2. The organic phase was dried with anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the resulting residue was purified by silica gel column chromatography using hexane as the eluant to give carbene complexes **1a–c** as dark garnet crystalline solids. Yields are reported in Scheme 2. *Method B*: Acetyl bromide (4.1 mL, 55 mmol) was added dropwise to a solution of freshly prepared pentacarbonyl[1-{(tetramethylammonio)oxy}ethylidene]-chromium[29] (15.45 g, 50 mmol) in dry CH_2Cl_2 (200 mL) cooled at $-45\,^{\circ}C$. After stirring for 45 min at this temperature, the corresponding haloalcohol (55 mmol), was added.[9] The solution was stirred for 10 h and allowed to warm slowly to room temperature without removing the cold bath. The reaction was quenched with water (30 mL), stirred for 5 min, and extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the

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residue purified by silica gel column chromatography using hexane as the eluant to give pentacarbonyl[1-(2-chloroethoxy)ethylidene]chromium (7.46 g, 50%), pentacarbonyl[1-(3-chloropropoxy)ethylidene]chromium[30] (8.12 g, 52%), or pentacarbonyl[1-(2-iodoethoxy)ethylidene]chromium (9.36 g, 48%) as orange oils. The corresponding oil (25 mmol) was dissolved in dry Et_2O (100 mL) and treated with benzaldehyde (7.6 mL, 75 mmol), triethylamine (10.4 mL, 65 mmol), and chlorotrimethylsilane (6.9 mL, 50 mmol) at 0 °C.[31] The resulting mixture was stirred at room temperature for 10 h. After removal of the volatiles, the residue was purified by column chromatography on silica gel, eluting with hexane to give the corresponding carbene complexes **1a** (5.79 g, 60%), **1b** (5.50 g, 55%), and **1c** (6.57 g, 55%).

Pentacarbonyl[(*E*)-1-(2-chloroethoxy)-3-phenyl-2-propenylidene]chromium (1a): Dark garnet solid; $R_f = 0.16$ (hexane); m.p. 83–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.10$ (t, $J = 5.3$ Hz, 2H), 5.30 (t, $J = 5.3$ Hz, 2H), 7.07 (d, $J = 15.4$ Hz, 1H), 7.43–7.45 (m, 3H), 7.62–7.65 (m, 2H), 8.02 (d, $J = 15.4$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 42.0$, 78.4, 129.0, 129.6, 130.1, 131.0, 134.2, 139.5, 216.3, 224.0, 332.3; MS (70 eV, EI): *m*/*z* (%): 386, (5) $[M]^+$, 246 (20), 190 (98), 131 (100), 103 (55), 84 (38); HRMS calcd for $[M]^+$, $C_{16}H_{11}ClCrO_6$, 385.9650, found 385.9660; elemental analysis calcd (%) for $C_{16}H_{11}ClCrO_6$ (386.71): C 49.70, H 2.87; found: C 49.71, H 3.16.

Pentacarbonyl[(*E*)-1-(3-chloropropoxy)-3-phenyl-2-propenylidene]chromium (1b): Dark garnet solid; $R_f = 0.16$ (hexane); m.p. 88–89 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.54$ (quintet, $J = 6.1$ Hz, 2H), 3.83 (t, $J = 6.3$ Hz, 2H), 5.20 (t, $J = 6.0$ Hz, 2H), 6.98 (d, $J = 15.4$ Hz, 1H), 7.42–7.44 (m, 3H), 7.59–7.62 (m, 2H), 7.96 (d, $J = 15.4$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 32.7$, 41.4, 76.6, 129.5, 129.8, 131.1, 131.3, 134.7, 139.7, 216.9, 224.6, 332.9; MS (70 eV, EI): *m*/*z* (%): 400 (3) $[M]^+$, 260 (20), 173 (100), 131 (68), 115 (38); HRMS calcd for $[M]^+$, $C_{17}H_{13}ClCrO_6$ 399.9806, found 399.9811; elemental analysis calcd (%) for $C_{17}H_{13}ClCrO_6$ (400.74): C 50.95, H 3.27; found: C 50.75, H 3.26.

Pentacarbonyl[(*E*)-1-(2-iodoethoxy)-3-phenyl-2-propenylidene]chromium (1c): Dark garnet solid; $R_f = 0.17$ (hexane); m.p. 92–93 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.69$ (t, $J = 6.3$ Hz, 2H), 5.33 (t, $J = 6.3$ Hz, 2H), 7.14 (d, $J = 15.4$ Hz, 1H), 7.44–7.46 (m, 3H), 7.64–7.66 (m, 2H), 8.02 (d, $J = 15.4$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 0.13$, 78.6, 129.0, 129.6, 130.3, 131.0, 134.2, 139.4, 216.3, 224.0, 331.5; MS (70 eV, EI): *m*/*z* (%): 478 (8) $[M]^+$, 338 (35), 282 (98), 131 (67), 84 (100); HRMS calcd for $[M]^+$, $C_{16}H_{11}CrIO_6$ 477.9006, found 477.8979; elemental analysis calcd (%) for $C_{16}H_{11}CrIO_6$ (478.16): C 40.19, H 2.32; found: C 40.15, H 2.24.

General procedure for the cyclopropanation reactions: A mixture of the appropriate carbene complex **1a**, **1b**, or **1c** (1 mmol) and the corresponding alkene (5 or 1 mmol) in THF (15 mL) was introduced in a sealed flask and heated in an oil bath at 100–120 °C until disappearance of the color of the starting carbene complex (reaction times are given in Tables 1 and 2). The reaction mixture was cooled to room temperature, the solvent removed under reduced pressure, and the residue taken up in hexane and exposed to sunlight and air for 0.5–1 h to remove the coordinated metal species. The resulting suspension was filtered through a short pad of Celite and the volatiles then evaporated. The remaining oil was purified by column chromatography on silica gel to give the corresponding pure cyclopropanes **2**, **3a**,**b**, **4a**,**b**, and **9**–**12**. Yields are listed in Tables 1 and 2. The major diastereoisomer of **2**, **9**, and **12** was each separated by this procedure.

(1*R,2*S**)-2-Butyl-1-(2-chloroethoxy)-1-[(*E*)-2-phenylethenyl]cyclopropane (2)**: Colorless oil; $R_f = 0.44$ (hexane/EtOAc, 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.74$ (dd, $J = 6.6$, 5.6 Hz, 1H), 0.92 (t, $J = 7.2$ Hz, 3H), 0.98 (dd, $J = 9.4$, 5.2 Hz, 1H), 1.02–1.10 (m, 1H), 1.32–1.55 (m, 5H), 1.66–1.73 (m, 1H), 3.64–3.74 (m, 3H), 3.90–4.00 (m, 1H), 6.01 (d, $J = 16.2$ Hz, 1H), 6.52 (d, $J = 16.2$ Hz, 1H), 7.15–7.48 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$, 19.2, 22.4, 27.3, 28.5, 31.7, 43.3, 65.1, 68.5, 125.9, 126.7, 127.0, 128.5, 132.1, 136.9; MS (70 eV, CI with ammonia) *m*/*z* (%): 296 (100) $[M + NH_4]^+$, 279 (68) $[M + 1]^+$, 221 (62), 216 (84), 199 (75), 131 (23); HRMS calcd for $[M + 1]^+$, $C_{17}H_{24}ClO$ 279.1516, found 279.1516; elemental analysis calcd (%) for $C_{17}H_{23}ClO$ (278.82): C 73.23, H 8.31; found: C 73.31, H 8.27.

***meso*-(1*R*,2*S*,3*S*,4*R*,5*S*)-3-(2-Chloroethoxy)-3-[(*E*)-2-phenylethenyl]tricyclo[3.2.1.0^{2,4}]octane (3a)**: Colorless oil; $R_f = 0.35$ (hexane/EtOAc, 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.85$ (d, $J = 10.0$ Hz, 1H), 1.05 (s, 2H), 1.33 (dd, $J = 6.8$, 2.4 Hz, 2H), 1.59 (d, $J = 8.3$ Hz, 2H), 1.99 (d, $J = 10.0$ Hz, 1H), 2.70 (s, 2H), 3.69–3.78 (m, 4H), 5.77 (d, $J = 16.1$ Hz, 1H), 6.61 (d, $J = 16.1$ Hz, 1H), 7.24–7.40 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 29.6$, 30.8, 32.7, 36.9, 43.1, 67.2, 67.5, 125.9, 126.6, 126.9, 128.4, 132.3, 136.9; MS (70 eV, EI): *m*/*z* (%): 287 (100) $[M - 1]^+$, 209 (74), 131 (62), 103 (78), 91 (73); HRMS calcd for $[M]^+$, $C_{18}H_{21}ClO$ 288.1292, found 288.1281.

***meso*-(1*R*,2*S*,3*S*,4*R*,5*S*)-3-(3-Chloropropoxy)-3-[(*E*)-2-phenylethenyl]tricyclo[3.2.1.0^{2,4}]octane (3b)**: White solid; $R_f = 0.36$ (hexane/EtOAc, 95:5); m.p. 49–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.85$ (d, $J = 9.9$ Hz, 1H), 1.09 (s, 2H), 1.33 (d, $J = 7.4$ Hz, 2H), 1.58 (d, $J = 7.4$ Hz, 2H), 1.93 (d, $J = 9.9$ Hz, 1H), 2.09 (quintet, $J = 6.2$ Hz, 2H), 2.69 (s, 2H), 3.64 (t, $J = 5.9$ Hz, 2H), 3.75 (t, $J = 6.4$ Hz, 2H), 5.75 (d, $J = 15.8$ Hz, 1H), 6.52 (d, $J = 15.8$ Hz, 1H), 7.21–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 29.6$, 30.7, 32.7, 32.8, 36.9, 41.8, 63.2, 67.1, 125.9, 126.1, 126.8, 128.4, 132.8, 137.0; MS (70 eV, EI): *m*/*z* (%): 301 (100) $[M - 1]^+$, 235 (18), 225 (27), 209 (32), 49 (16); HRMS calcd for $[M]^+$ $C_{19}H_{23}ClO$ 302.1429, found 302.1437; elemental analysis calcd (%) for $C_{19}H_{23}ClO$ (302.84): C 75.36, H 7.66; found: C 75.12, H 7.48.

***meso*-(1*R*,6*S*,7*S*)-7-(2-Chloroethoxy)-7-[(*E*)-2-phenylethenyl]bicyclo[4.1.0]heptane (4a)**: Colorless oil; $R_f = 0.51$ (hexane/EtOAc, 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.18–1.21$ (m, 2H), 1.28–1.48 (m, 4H), 1.72–1.92 (m, 4H), 3.72 (t, $J = 5.9$ Hz, 2H), 3.93 (t, $J = 5.9$ Hz, 2H), 6.16 (d, $J = 16.1$ Hz, 1H), 6.45 (d, $J = 16.1$ Hz, 1H), 7.15–7.42 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 18.5$, 21.6, 21.7, 43.1, 65.2, 67.3, 125.8, 126.8, 126.9, 128.4, 132.7, 136.9; MS (70 eV, EI): *m*/*z* (%): 275 (70) $[M - 1]^+$, 197 (80), 131 (100), 103 (98), 91 (87); HRMS calcd for $[M]^+$, $C_{17}H_{21}ClO$ 276.1281, found 276.1268; elemental analysis calcd (%) for $C_{17}H_{21}ClO$ (276.81): C 74.37, H 7.97; found: C 74.33, H 7.93.

***meso*-(1*R*,6*S*,7*S*)-7-(3-Chloropropoxy)-7-[(*E*)-2-phenylethenyl]bicyclo[4.1.0]heptane (4b)**: Colorless oil; $R_f = 0.42$ (hexane/EtOAc, 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.10–1.20$ (m 2H), 1.32–1.45 (m, 4H), 1.72–2.82 (m, 2H), 1.84–1.93 (m, 2H), 2.10 (quintet, $J = 6.2$ Hz, 2H), 3.74 (t, $J = 6.4$ Hz, 2H), 3.79 (t, $J = 6.0$ Hz, 2H), 6.12 (d, $J = 16.1$ Hz, 1H), 6.39 (d, $J = 16.1$ Hz, 1H), 7.17–7.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.6$, 21.8, 21.9, 33.2, 42.0, 63.3, 64.8, 125.9, 126.3, 126.8, 128.4, 133.4, 137.1; MS (70 eV, EI): *m*/*z* (%): 289 (68)$[M - 1]^+$, 197 (66), 131 (100), 103 (92), 91 (64); HRMS calcd for $[M]^+$, $C_{18}H_{23}ClO$ 290.1437, found 290.1433; elemental analysis calcd (%) for $C_{18}H_{23}ClO$ (290.83): C 74.37, H 7.97; found: C 74.36, H 7.94.

(1*R,2*S**)-2-Butyl-1-(2-iodoethoxy)-1-[(*E*)-2-phenylethenyl]cyclopropane (9)**: Colorless oil; $R_f = 0.57$ (hexane/EtOAc, 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.73$ (dd, $J = 6.6$, 5.2 Hz, 1H), 0.92 (t, $J = 7.1$ Hz, 3H), 0.97–1.01 (m, 1H), 1.05 (dd, $J = 9.4$, 6.6 Hz, 1H), 1.33–1.47 (m, 4H), 1.48–1.56 (m, 1H), 1.67 (dt, $J = 13.6$, 6.6 Hz, 1H), 3.25–3.34 (m, 2H), 3.64 (dt, $J = 10.6$, 7.0 Hz, 1H), 3.96 (dt, $J = 10.6$, 6.1 Hz, 1H), 6.02 (d, $J = 16.0$ Hz, 1H), 6.49 (d, $J = 16.0$ Hz, 1H), 7.18–7.36 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 3.6$, 14.1, 19.1, 22.5, 27.4, 28.6, 31.7, 65.0, 68.9, 125.9, 126.7, 127.0, 128.5, 132.2, 136.9; MS (70 eV, CI with ammonia): *m*/*z* (%): 387 (38) $[M + NH_3]^+$, NH_3 232 (100), 215 (53), 173 (70), 105 (52); elemental analysis calcd (%) for $C_{17}H_{23}IO$ (370.27): C 55.15, H 6.26; found: C 55.19, H 6.28.

***meso*-(1*R*,5*S*,6*S*)-6-(2-Iodoethoxy)-6-[(*E*)-2-phenylethenyl]bicyclo[3.1.0]hexane (10)**: Colorless oil; $R_f = 0.34$ (hexane/EtOAc, 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.53$ (s, 2H), 1.59–1.65 (m, 2H), 1.88–2.00 (m, 4H), 3.21(t, $J = 6.9$ Hz, 2H), 3.75 (t, $J = 6.9$ Hz, 2H), 5.94 (d, $J = 16.2$ Hz, 1H), 6.35 (d, $J = 16.2$ Hz, 1H), 7.09–7.31 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 3.1$, 25.2, 26.5, 33.1, 68.6, 68.8, 125.9, 126.6, 127.0, 128.4, 131.6, 136.8.

(1*R,2*S**,3*R**)-2-Ethyl-1-(2-iodoethoxy)-3-methyl-1-[(*E*)-2-phenylethenyl]cyclopropane (11)**: Colorless oil; $R_f = 0.35$ (hexane/EtOAc, 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.92–1.05$ (m, 1H), 1.10 (td, $J = 7.4$, 2.0 Hz, 3H), 1.17–1.29 (m, with s at 1.23, 4H), 1.52–1.76 (m, 2H), 3.34 (t, $J = 6.7$ Hz, 2H), 3.82 (t, $J = 6.7$ Hz, 2H), 6.23 (d, $J = 16.2$ Hz, 1H), 6.47 (d, $J = 16.2$ Hz, 1H), 7.22–7.43 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 3.3$, 7.1, 14.1, 15.8, 22.7, 30.7, 65.1, 68.2, 125.9, 126.9, 127.0, 128.5, 133.0, 136.9; MS (70 eV, CI with ammonia): *m*/*z* (%): 374 (100)$[M + NH_4]^+$, 220 (85), 202 (74), 185 (81), 131 (64); HRMS calcd for $[M + 1]^+$, $C_{16}H_{22}O$ 357.0503, found 357.0715.

(1*S,2*R**)-2-(*tert*-Butyldimethylsilyloxymethyl)-1-(2-iodoethoxy)-1-[(*E*)-2-phenylethenyl]cyclopropane (12)**: Colorless oil; $R_f = 0.43$ (hexane/EtOAc, 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.11$, 0.12 (2s, 6H), 0.86–0.94 (m with s at 0.93, 10H), 1.03 (dd, $J = 9.6$, 6.1 Hz, 1H), 1.37–1.47 (m, 1H), 3.26–3.32 (m, 2H), 3.69–4.02 (m, 4H), 6.09 (d, $J = 16.0$ Hz, 1H), 6.54 (d, $J = 16.0$ Hz, 1H), 7.23–7.39 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta =$

−5.1, 3.4, 17.4, 18.3, 26.0, 29.7, 61.8, 64.9, 68.8, 126.0, 127.2, 128.1, 128.5, 130.7, 136.6; MS (70 eV, EI): *m*/*z* (%) : 401 (3) $[M-t\mathrm{Bu}]^+$, 171 (52), 159 (62), 131 (65), 75 (100); HRMS calcd for $[M-t\mathrm{Bu}]^+$, $C_{16}H_{22}IO_2Si$ 401.0434, found 401.0453; elemental analysis calcd (%) for $C_{20}H_{31}IO_2Si$ (458.45): C 52.40, H 6.81; found: C 52.39, H 6.79.

General procedure for the synthesis of oxaspirocyclopropanes 5, 6, 7a,b, and 8a,b: *Method A*: Lithium powder (70 mg, 10 mmol) was added at −10 °C to a solution of the corresponding 2-chloroethoxy or 3-chloropropoxycyclopropane **2**, **3a**, or **3b** (1 mmol) in THF (15 mL), and the mixture stirred for 10 h at room temperature. The obtained dark red mixture was filtered through a plug of Celite, to eliminate the excess of lithium, and the filtrate was quenched with water at 0 °C. The solvent was removed and the residue extracted with hexane. The organic phase was dried (anhydrous Na_2SO_4) and concentrated under reduced pressure. Column chromatography on silica gel of the resulting oil afforded pure compounds **5**, **6**, and **7a**,**b**. Yields are reported in Scheme 3. Compound **5** was isolated as a 1:1 mixture of diastereoisomers, which could not be separated by column chromatography. When compound **2** (as a 6:1 mixture of isomers) was used as starting material, a mixture of four diastereoisomers—two major and two minor—was isolated, from which the pure compound **6** and a mixture of the two major products **5** were separated by column chromatography.

Method B: Lithium–naphthalene (1.1 M in THF, 1.8 mL, 2 mmol) was added at −78 °C to a colorless solution of the corresponding 2-chloroethoxy or 3-chloropropoxycyclopropane **2** or **4a**,**b** (1 mmol) in THF (15 mL). The solution became red, then dark red when allowed to stir for 30 min at the same temperature. The reaction was then quenched with water (0.2 mL) at −78 °C or deuterium oxide (0.2 mL; used in the experiments with compound **2**). The cold bath was removed and the mixture stirred for 30 min at room temperature resulting in a yellow solution. The solvent was removed under reduced pressure and the residue extracted with hexane. The organic phase was dried and the volatiles evaporated. The resulting oil was purified by column chromatography on silica gel to give pure compounds **5**, and **8a**,**b**. Yields are reported in Scheme 3.

(1*S,3*S**)-7-Benzyl-1-butyl-4-oxaspiro[2.4]heptane (5)**: Data taken from a 1.5:1 mixture of diastereoisomers. Colorless oil; $R_f = 0.55$ (hexane/EtOAc, 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.39$ (t, $J = 6.1$ Hz, 1H, major isomer), 0.41 (t, $J = 6.1$ Hz, 1H, minor isomer), 0.57 (dd, $J = 9.6$, 5.4 Hz, 1H), 0.61–0.69 (m, 1H), 0.80 (dd, $J = 9.6$, 6.1 Hz, 1H), 0.84–0.99 (m, 7H), 1.25–1.55 (m, 12H), 1.65–1.84 (m, 2H), 1.95–2.12 (m, 2H), 2.14–2.16 (m, 1H), 2.28–2.37 (m, 1H), 2.41 (dd, $J = 13.5$, 10.5 Hz, 1H, minor isomer), 2.47 (dd, $J = 13.5$, 10.5 Hz, 1H, major isomer), 2.64 (dd, $J = 12.9$, 4.1 Hz, 1H, minor isomer), 2.72 (dd, $J = 13.5$, 4.8 Hz, 1H, minor isomer), 3.82–3.99 (m, 4H), 7.15–7.35 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 12.4$, 14.1, 22.4, 22.6, 27.5, 31.4, 32.1, 38.0, 44.4, 66.4, 70.2, 125.8, 128.3, 128.8, 140.7; resolvable resonances of the minor isomer: $\delta = 15.1$, 18.6, 27.7, 31.8, 32.2, 37.7, 43.9, 66.2, 70.0, 125.9, 128.7, 140.6.

(1*S,3*R**,7*R**)-7-Benzyl-1-butyl-4-oxaspiro[2.4]heptane (6)**: Colorless oil; $R_f = 0.54$ (hexane/EtOAc, 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.27$ (dd, $J = 6.5$, 6.0 Hz, 1H), 0.85–0.95 (m, with t at 0.91, $J = 7.0$ Hz, 4H), 0.98 (dd, $J = 9.9$, 6.0 Hz, 1H), 1.12–1.30 (m, 2H), 1.32–1.41 (m, 4H), 1.73–1.87 (m, 1H), 1.95–2.09 (m, 1H), 2.25–2.38 (m, 1H), 2.54 (dd, $J = 13.4$, 12.9 Hz, 1H), 2.78 (dd, $J = 13.4$, 4.7 Hz, 1H), 3.69 (q, $J = 7.9$ Hz, 1H), 3.91 (q, $J = 7.9$ Hz, 1H), 7.17–7.22 (m, 3H), 7.26–7.31 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 12.8$, 14.1, 22.5, 22.8, 29.5, 31.6, 32.2, 38.3, 39.7, 65.9, 70.5, 125.9, 128.3, 128.9, 140.8; MS (70 eV, EI): *m*/*z* (%): 244 (18) $[M]^+$, 187 (93), 159 (24), 91 (100), 84 (21); HRMS calcd for $[M]^+$, $C_{17}H_{24}O$ 244.1827, found 244.1828; elemental analysis calcd (%) for $C_{17}H_{24}O$ (244.38): C 83.55, H 9.90; found: C 83.57, H 9.91.

(1*R,2*S**,3*S**,4*R**,5*S**)-Tricyclo[3.2.1.0^{2,4}]octane-3-spiro-2′-(2′*S**)-3′-benzyltetrahydrofuran (7a)**: Colorless oil; $R_f = 0.35$ (hexane/EtOAc, 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.65$ (dd, $J = 9.5$, 7.1 Hz, 2H), 0.94 (d, $J = 7.6$ Hz, 1H), 1.16–1.24 (m, 2H), 1.39–1.47 (m, 2H), 1.52–1.59 (m, 1H), 1.81–1.88 (m, 1H), 1.89–1.95 (m, 2H), 2.35 (dd, $J = 13.7$, 11.4 Hz, 1H), 2.42 (s, 1H), 2.50 (s, 1H), 2.71 (dd, $J = 13.7$, 3.8 Hz, 1H), 3.71–3.77 (m, 1H), 3.88–3.93 (m, 1H), 7.07–7.14 (m, 3H), 7.19–7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 26.2$, 29.6, 29.7, 29.8, 29.9, 31.0, 36.7, 36.8, 37.5, 46.8, 66.4, 73.2, 125.8, 128.3, 128.9, 140.9; MS (70 eV, EI): *m*/*z* (%): 254 (9) $[M]^+$, 187 (27), 91 (74), 84 (100), 51 (57); HRMS calcd for $[M]^+$, $C_{18}H_{22}O$ 254.1671, found 254.1669.

(1*R,2*S**,3*S**,4*R**,5*S**)-Tricyclo[3.2.1.0^{2,4}]octane-3-spiro-2′-(2′*S**)-3′-benzyltetrahydropyran (7b)**: Colorless oil; $R_f = 0.47$ (hexane/EtOAc, 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.64$–0.70 (m, 3H), 0.95–0.98 (m, 1H), 1.20–1.26 (m, 2H), 1.33–1.38 (m, 1H), 1.42–1.54 (m, 3H), 1.60–1.69 (m, 1H), 1.89–2.00 (m, 2H), 2.52 (s, 2H), 2.87–2.91 (m, 2H), 3.43 (td, $J = 12.2$, 2.6 Hz, 1H), 3.86 (dd, $J = 10.7$, 4.9 Hz, 1H), 7.14–7.19 (m, 3H), 7.25–7.28 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 21.0$, 24.7, 29.7, 30.1, 30.5, 31.2, 31.5, 35.4, 36.4, 36.9, 43.7, 67.1, 69.3, 125.6, 128.1, 129.0, 141.5; MS (70 eV, EI): *m*/*z* (%): 268 (62) $[M]^+$, 173 (100), 117 (90), 91 (93), 79 (81); HRMS calcd for $[M]^+$, $C_{19}H_{24}O$ 268.1827, found 268.1816; elemental analysis calcd (%) for $C_{19}H_{24}O$ (268.40): C 85.07, H 9.03; found: C 85.06, H 9.07.

(1*R,6*S**,7*S**)-Bicyclo[4.1.0]heptane-7-spiro-2′-(2′*S**)-3-benzyltetrahydrofuran (8a)**: Colorless oil; $R_f = 0.27$ (hexane/EtOAc, 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.78$ (ddd, $J = 10.1$, 8.6, 2.6 Hz, 1H), 0.98–1.05 (m, 1H), 1.15–1.19 (m, 1H), 1.20–1.48 (m, 3H), 1.49–1.60 (m, 1H), 1.62–1.72 (m, 1H), 1.73–1.90 (m, 3H), 2.00–2.12 (m, 1H), 2.17–2.26 (m, 1H), 2.49 (dd, $J = 13.6$, 10.6 Hz, 1H), 2.76 (dd, $J = 13.6$, 4.8 Hz, 1H), 3.80–3.89 (m, 1H), 3.98–4.05 (m, 1H), 7.15–7.30 (m, 3H), 7.31–7.42 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 12.8$, 16.2, 18.2, 18.7, 21.8, 22.1, 31.0, 38.1, 44.8, 66.1, 71.1, 125.8, 128.2, 128.8, 140.9.

(1*R,6*S**,7*S**)-Bicyclo[4.1.0]heptane-7-spiro-2′-(2′*S**)-3-benzyltetrahydropyran (8b)**: Colorless oil; $R_f = 0.40$ (hexane/EtOAc, 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.57$–0.62 (m, 1H), 0.74–0.79 (m, 1H), 1.10–1.45 (m, 7H), 1.50–1.66 (m, 3H), 1.67–1.76 (m, 1H), 1.77–1.87 (m, 1H), 1.88–2.15 (m, 1H), 2.75 (dd, $J = 13.4$, 10.3 Hz, 1H), 2.88 (dd, $J = 13.4$, 5.2 Hz, 1H), 3.62 (td, $J = 11.2$, 7.8 Hz, 1H), 3.90 (d, $J = 11.0$ Hz, 1H), 7.11–7.19 (m, 3H), 7.22–7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.8$, 17.9, 18.6, 19.3, 21.5, 22.1, 22.2, 25.3, 35.5, 43.6, 65.4, 67.1, 125.5, 128.1, 129.0, 141.6; MS (70 eV, EI): *m*/*z* (%): 256 (11) $[M]^+$, 173 (22), 165 (100), 117 (14), 91 (37); HRMS calcd for $[M]^+$, $C_{18}H_{24}O$ 256.1823, found 256.1827.

General procedure for the synthesis of cyclopropanols 13–16: The corresponding 2-iodoethoxycyclopropane **9**–**12** (1 mmol) was dissolved in a 3:1 mixture of hexane:diethyl ether (15 mL), cooled at −78 °C, and treated with *t*BuLi (1.5 M in pentane, 1.3 mL, 2 mmol). The reaction mixture was stirred for 30 min at −78 °C and quenched with H_2O (0.2 mL) at the same temperature. Then the cold bath was removed and the mixture stirred for 30 min at room temperature. The resulting solution was extracted with hexane, the organic phase dried, and the volatiles evaporated. The obtained oil was purified by column chromatography on silica gel to give pure compounds **13**–**16**. The major diastereoisomer of **13** and **16** was separated by this technique. Yields are reported in Table 2.

(1*R,2*S**)-2-Butyl-1-[(*E*)-2-phenylethenyl]-1-cyclopropanol (13)**: Colorless oil; $R_f = 0.52$ (hexane/EtOAc, 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.76$–0.78 (m, 1H), 0.93 (t, $J = 7.2$ Hz, 3H), 1.01–1.03 (m, 2H), 1.34–1.48 (m, 4H), 1.52–1.62 (m, 2H), 2.06 (br s, 1H), 5.95 (d, $J = 15.9$ Hz, 1H), 6.63 (d, $J = 15.9$ Hz, 1H), 7.17–7.23 (m, 1H), 7.26–7.37 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 14.1$, 21.8, 22.5, 27.2, 27.6, 31.9, 59.0, 125.0, 125.9, 126.8, 128.5, 135.7, 137.1; MS (70 eV, EI): *m*/*z* (%): 215 (8) $[M-1]^+$, 105 (100), 91 (42), 77 (34), 55 (35); HRMS calcd for $[M]^+$, $C_{15}H_{20}O$ 216.1512, found 216.1514; elemental analysis calcd (%) for $C_{15}H_{20}O$ (216.32): C 83.29, H 9.32; found: C 83.29, H 9.33.

***meso*-(1*R*,5*S*,6*S*)-6-[(*E*)-2-phenylethenyl]bicyclo[3.1.0]hexan-6-ol (14)**: Colorless oil; $R_f = 0.48$ (hexane/EtOAc, 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.59$ (dd, $J = 3.6$, 1.4 Hz, 2H), 1.65–1.80 (m, 2H), 1.85–1.97 (m, 3H), 1.99–2.10 (m, 2H), 5.89 (d, $J = 16.0$ Hz, 1H), 6.56 (d, $J = 16.0$ Hz, 1H), 7.15–7.20 (m, 1H), 7.25–7.38 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 25.7$, 25.9, 33.2, 62.8, 124.4, 125.8, 126.6, 128.4, 135.0, 137.2.

(1*R,2*S**,3*R**)-2-Ethyl-3-methyl-1-[(*E*)-2-phenylethenyl]-1-cyclopropanol (15)**: Colorless oil; $R_f = 0.50$ (hexane/EtOAc, 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.85$–0.98 (m, 1H), 1.02 (t, $J = 7.5$ Hz, 3H), 1.08–1.13 (m, with s at 1.12, 4H), 1.21–1.27 (m, 1H), 1.45–1.55 (m, 2H), 5.95 (d, $J = 16.0$ Hz, 1H), 6.61 (d, $J = 16.0$ Hz, 1H), 7.18–7.40 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 6.2$, 13.9, 15.2, 22.8, 30.5, 59.1, 124.1, 125.7, 126.5, 128.4, 137.0, 137.2; MS (70 eV, EI): *m*/*z* (%): 202 (5) $[M]^+$, 131 (80), 86 (68), 84 (100), 77 (65); HRMS calcd for $[M]^+$, $C_{14}H_{18}O$ 202.1358, found 202.1351.

(1*S,2*R**)-2-(*tert*-Butyldimethylsilyloxymethyl)-1-[(*E*)-2-phenylethenyl]-1-cyclopropanol (16)**: Yellow oil; $R_f = 0.51$ (hexane/EtOAc, 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.11$ (s, 6H), 0.92 (s, 9H), 1.03 (dd, $J = 9.7$, 5.7 Hz, 1H), 1.08–1.14 (m, 1H), 1.29–1.39 (m, 1H), 3.35 (br s, 1H), 3.85 (dd, $J = 10.8$, 7.4 Hz, 1H), 4.17 (dd, $J = 11.1$, 4.8 Hz, 1H), 5.93 (d, $J = 15.7$ Hz, 1H),

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6.70 (d, $J = 15.7$ Hz, 1H), 7.16–7.39 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = -5.4$, -5.3, 18.2, 19.8, 25.8, 27.6, 59.0, 62.6, 125.9, 126.0, 126.8, 128.4, 134.3, 137.2; MS (70 eV, EI): m/z (%): 247 (10) $[M - t\mathrm{Bu}]^+$, 131 (24), 105 (44), 83 (100), 75 (90); HRMS calcd for $[M - t\mathrm{Bu}]^+$, $C_{14}H_{19}O_2Si$ 247.1154, found 247.1146.

One-pot hydroxycyclopropanation reaction: Preparation of compound 13: A mixture of carbene complex **1c** (0.48 g, 1 mmol) and 1-hexene (0.6 mL, 5 mmol) in THF (15 mL) was introduced in a sealed flask and heated at 105 °C for 1.5 h. The reaction mixture was then cooled to room temperature and the solvent removed under reduced pressure and replaced by a 3:1 mixture of hexane: diethyl ether (15 mL). *t*BuLi (1.5 M in pentane, 1.3 mL, 2 mmol) at −78 °C was added to the resulting solution; the mixture was stirred for 30 min at −78 °C and then quenched with water (0.2 mL) at the same temperature. The cold bath was removed and the solution was stirred for 30 min at room temperature. The mixture was extracted with hexane and the organic phase dried. The volatiles were evaporated and the resulting oil filtered on silica gel to give pure cyclopropanol **13** (173 mg, 80%) as a 4.6:1 mixture of diastereoisomers.

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