

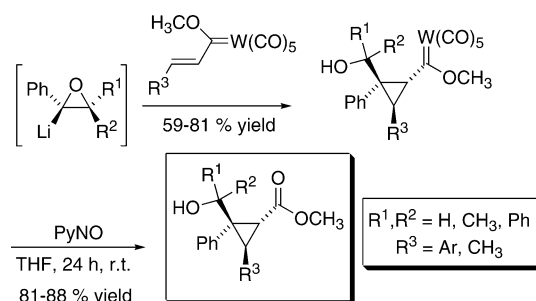
Asymmetric Synthesis of Cyclopropanes from Lithiated Aryloxiranes and α,β -Unsaturated Fischer Carbene Complexes

Vito Capriati,[†] Saverio Florio,^{*,†} Renzo Luisi,[†] Filippo Maria Perna,[†] and José Barluenga[‡]

Dipartimento Farmaco-Chimico, Università di Bari, Via E. Orabona 4, I-70126 Bari, C.N.R.,
Istituto di Chimica dei Composti Organometallici "ICCOM", Sezione di Bari, Italy, and Instituto
Universitario de Química Organometálica "Enrique Moles", Unidad Asociada al C.S.I.C. Julián Clavería,
8, Universidad de Oviedo, 33006 Oviedo, Spain

florio@farmchim.uniba.it

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A diastereo- and enantiospecific formation of tetrasubstituted cyclopropane carbene complexes and cyclopropanecarboxylates from lithiated aryloxiranes and α,β -unsaturated Fischer carbene complexes is described.

Introduction

The utility of lithiated oxiranes as nucleophiles (e.g., oxiranyllithiums) has been long underestimated,¹ though they may provide the organic chemist with a very direct way to assemble substituted epoxides. Only with the beginning of the 1990s has the oxiranyl anion methodology become an efficient synthetic strategy.²

Among metalated oxiranes, α -lithiated aryloxiranes have been investigated only recently.^{1c,f,3,4} There are two aspects of the chemistry of α -lithiated aryloxiranes that make these species significantly important: the configurational stability and the potential as asymmetry inducers. After the seminal papers from Eisch and Galle,³ we

have recently demonstrated that some optically active lithiated aryloxiranes^{1f,5} react with electrophiles in a stereospecific manner with complete retention of configuration at the benzylic carbon atom. However, reactions with aldehydes proceeded with no or very low diastereoselectivity at the newly created stereogenic center, as reported for other oxiranyllithiums.^{1d,2}

We have recently found that lithiated oxazolynyl aryloxiranes couple diastereoselectively with Fischer carbene complexes⁶ providing cyclopropane- γ -butyrolactones and -carboxylates.⁷ These results seemed to be promising for asymmetric induction so that we decided to study the reaction of racemic and optically active α -lithiated aryloxiranes, such as styrene oxides **1**,^{5a} phenylpropylene

[†] Università di Bari.

[‡] Universidad de Oviedo.

(1) (a) Satoh, T. *Chem. Rev.* **1996**, *96*, 3303–3325. (b) Mori, Y. *Rev. Heteroatom Chem.* **1997**, *17*, 183–211. (c) Hodgson, D. M.; Gras, E. *Synthesis* **2002**, 1625–1642. (d) Chemla, F.; Vrancken, E. In *The Chemistry of Organolithium Compounds*; Rappoport, Z., Marek, I., Eds.; John Wiley & Sons: New York, 2004; Vol. 2, Chapter 18, pp 1165–1242. (e) For a special issue on oxiranyl and aziridynyl anions, see: Florio, S., Ed. *Tetrahedron* **2003**, *59*, 9693–9864. (f) For a recent account on α -lithiated aryloxiranes, see: Capriati, V.; Florio, S.; Luisi, R. *Synlett* **2005**, *9*, 1359–1369.

(2) Molander, G. A.; Mautner, K. *Pure Appl. Chem.* **1990**, *62*, 707–712.

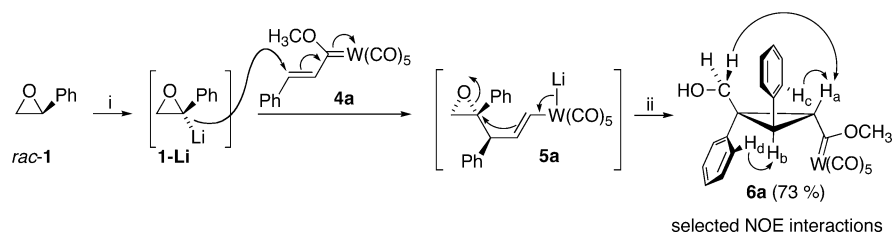
(3) (a) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1976**, *121*, C10–14. (b) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1988**, *341*, 293–313. (c) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1990**, *55*, 4835–4840.

(4) Hodgson, D. M.; Gibbs, A. R.; Lee, G. P. *Tetrahedron* **1996**, *52*, 14361–14384.

(5) (a) Capriati, V.; Florio, S.; Luisi, R.; Salomone, A. *Org. Lett.* **2002**, *4*, 2445–2448. (b) Capriati, V.; Florio, S.; Luisi, R.; Nuzzo, I. *J. Org. Chem.* **2004**, *69*, 3330–3335. (c) Florio, S.; Aggarwal, V. K.; Salomone, A. *Org. Lett.* **2004**, *6*, 4191–4194.

(6) (a) Barluenga, J.; Santamaría, J.; Tomás, M. *Chem. Rev.* **2004**, *104*, 2259–2284. (b) Barluenga, J.; Flórez, J.; Fañanás, F. J. *J. Organomet. Chem.* **2001**, *624*, 5–17. (c) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257–1280. (d) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591–3638. (e) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, p 470.

(7) Florio, S.; Perna, F. M.; Luisi, R.; Barluenga, J.; Fañanás, F. J.; Rodríguez, F. J. *J. Org. Chem.* **2004**, *69*, 9204–9207.

SCHEME 1^a

^a Reagents and conditions: (i) *s*-BuLi/TMEDA, THF, $-98\text{ }^{\circ}\text{C}$; (ii) NH_4Cl .

TABLE 1. Preparation of Cyclopropane Carbenes 6a–k and Cyclopropanecarboxylates 9a–j

oxirane	carbene complex	R ³	R ¹	R ²	compd 6 (% yield) ^a	compd 9 (% yield) ^a
1	4a	Ph	H	H	6a (73)	9a (88)
1	4b	<i>p</i> -MeOC ₆ H ₄	H	H	6b (78)	9b (82)
1	4c	<i>p</i> -ClC ₆ H ₄	H	H	6c (81)	9c (81)
1	4d	1-methylpyrrol-2-yl	H	H	6d (59)	<i>b</i>
1	4e	2-furyl (Fur)	H	H		<i>c</i>
(<i>R</i> [*] , <i>R</i> [*])- 2	4a	Ph	H	Me	6e (71)	9e (88)
(<i>R</i> [*] , <i>R</i> [*])- 2	4f	<i>p</i> -MeC ₆ H ₄	H	Me	6f (68)	
(<i>R</i> [*] , <i>S</i> [*])- 2	4f	<i>p</i> -MeC ₆ H ₄	Me	H	6g (70)	9g (84)
(<i>R</i> [*] , <i>R</i> [*])- 2	4e	2-furyl (Fur)	H	Me	6h (75)	
(<i>R</i> [*] , <i>R</i> [*])- 3^d	4a	Ph	H	Ph	6i (73)	9i (83)
(<i>R</i> [*] , <i>S</i> [*])- 3	4a	Ph	Ph	H	6j (77)	9j (87)
1	4g	Me	H	H	6k (74)	

^a Isolated yield after column chromatography. ^b Lactone **7c** was also detected (<5%) in the crude reaction mixture; see Scheme 2 and text. ^c In this case, lactone **7e** was the only product isolated (48%); see Scheme 3 and text. ^d Reaction temperature: $-60\text{ }^{\circ}\text{C}$.

oxides **2**,^{5b} and stilbene oxides **3**^{5c} with α,β -unsaturated Fischer carbene complexes.

Results and Discussion

Treatment of *rac*-**1** with *s*-BuLi/TMEDA in THF at $-98\text{ }^{\circ}\text{C}$ (10 min) produced α -lithium styrene oxide **1-Li** (Scheme 1): addition to the α,β -unsaturated tungsten carbene complex **4a** resulted in the formation of cyclopropane derivative **6a** as the sole diastereomer upon quenching with NH_4Cl after 1 h at $-98\text{ }^{\circ}\text{C}$ and warming to rt (73%, Table 1). The relative configuration of **6a** was deduced from 2D-NOESY correlations. Significant NOE interactions, detected either between the two cyclopropane ring protons H_a and H_b and the two ortho aromatic ring protons H_c and H_d or between one of the two methylenic carbinol protons and H_a , as depicted in Scheme 1, were diagnostic of a close proximity relationship. Moreover, the coupling constant value (5.8 Hz) between H_a and H_b was in agreement with a *trans* arrangement of these two protons, as analogously reported for other diastereomeric cyclopropanes.⁸

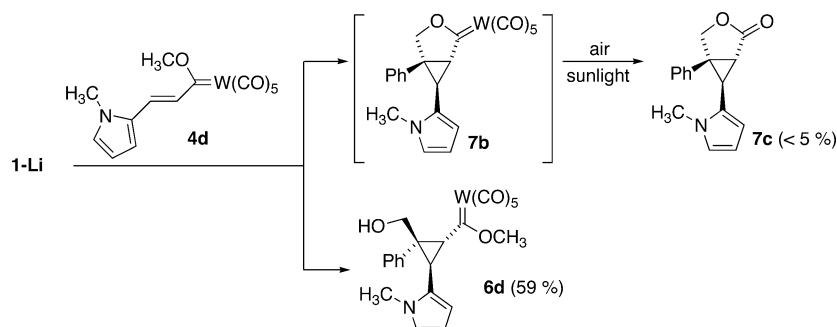
The stereochemical outcome of the above reaction might reasonably be accounted for with a diastereoselective nucleophilic 1,4-addition of **1-Li** to **4a** (similar to that reported for β -lithiated oxazolinylloxiranes)⁷ leading to the lithium derivative **5a** in which the appropriate orbital alignment allows the overlap of the carbanion lone pair on the β -carbon (with respect to the oxirane ring) with the antibonding orbital of the oxirane C–O bond, thus promoting cyclopropanation simultaneously with the oxirane ring-opening. Comparable results were obtained when **1-Li** was reacted with complexes **4b** and **4c** to give **6b** (78%) and **6c** (81%), respectively (Table 1).

The addition of lithiated *rac*-**1** to heteroaryl carbene complexes **4d** and **4e** (Table 1) was also investigated. The pyrrole carbene complex **4d** reacted with **1-Li** likewise to **4a–c** leading diastereoselectively to the cyclopropane derivative **6d** as the main product (59% yield) (Scheme 2). A minor compound, identified as the cyclopropane- γ -butyrolactone **7c**, likely generated by air oxidation of the related organometallic precursor **7b**, was also detected by NMR and GC–MS in the crude reaction mixture; it formed only in traces (<5%) and was not isolated (Scheme 2).

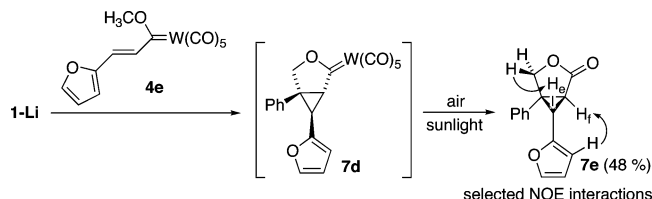
Something particularly interesting happened when we used the Fischer carbene complex **4e**. Indeed, in contrast to **4a–d**, the furyl carbene complex **4e** proved to be unreactive toward **1-Li** at $-98\text{ }^{\circ}\text{C}$. Only upon warming to rt, after 1 h at $-98\text{ }^{\circ}\text{C}$, did it react, leading exclusively, through **7d** (not isolated), to the cyclopropane- γ -butyrolactone **7e** (single diastereomer) (48% yield) (Scheme 3).

(8) (a) Capriati, V.; Florio, S.; Luisi, R.; Rocchetti, M. T. *J. Org. Chem.* **2002**, *67*, 759–763. (b) Vicinal coupling constants between protons of cyclopropanes exhibit a strong dependence on the stereochemistry of the two protons and depend also on the nature and the electronegativities of the substituents, decreasing as the latter increase. The relationship J_{cis} (6–12 Hz) > J_{trans} (2–9 Hz) is always observed, and there are no known exceptions (see: Pretsch, E.; Bühlmann, P.; Affolter, C. In *Structure Determination of Organic Compounds*, 3rd ed.; Tables of Spectral Data; Springer Publishing: New York, 2004; pp 176–178).

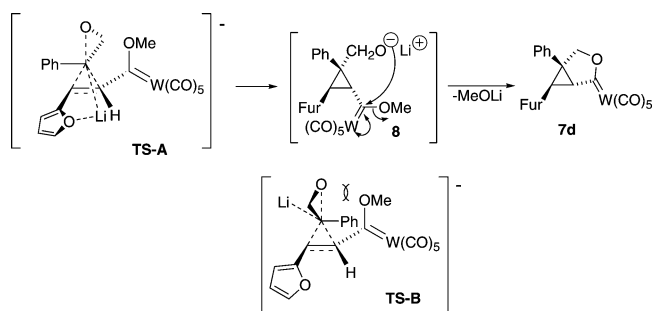
SCHEME 2



SCHEME 3



SCHEME 4

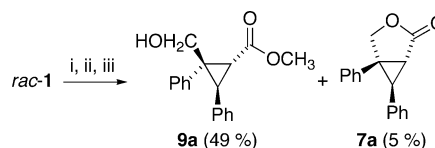


Also in this case, the relative configuration was established by 2D-NOESY correlations, the H_e and H_f coupling constant value (3.3 Hz) indicating a *trans* relationship (Scheme 3).^{sb}

A tentative mechanistic explanation for the formation of **7e** might be given by considering that **4e** contains a Lewis basic heteroatom and that styrene oxide **1-Li**, as reported,^{5a} can exhibit a *carbenoid* character even at low temperature! Now, assuming that lactone **7d** would likely result from a stereochemistry which puts the alkoxy group and the metal fragment *cis* to each other on the cyclopropane ring, to justify this geometry it could be reasonable to suppose that in the presence of a preliminary coordination between the lithium and the furyl oxygen, the π bond of **4e** might act as a nucleophile causing an S_N2-like epoxide ring-opening⁹ (i.e., a concerted S_N2-type pathway with backside attack of the C=C bond at the oxirane C–O bond) according to the transition state TS-A (transition state TS-B should be more sterically congested and without any possibility to chelate the lithium) to give first the alkoxide **8** and, soon after, the lactone **7d** whose formation should be the driving force of the reaction (Scheme 4). Indeed, the furyl cyclopropane, deriving from the protonation of alkoxide **8**, was never isolated.

(9) The LUMO of the carbenoid could be, in this case, a strongly polarized $\sigma^*_{\text{C-O}}$ orbital. For an exhaustive review on the electrophilic character of carbenoids, see: Boche, G.; Lohrenz, C. W. *Chem. Rev.* **2001**, *101*, 697–756.

SCHEME 5^a



^a Reagents and conditions: (i) *s*-BuLi/TMEDA, THF, -98 °C; (ii) **4a** and quick warming to rt; (iii) air and sunlight.

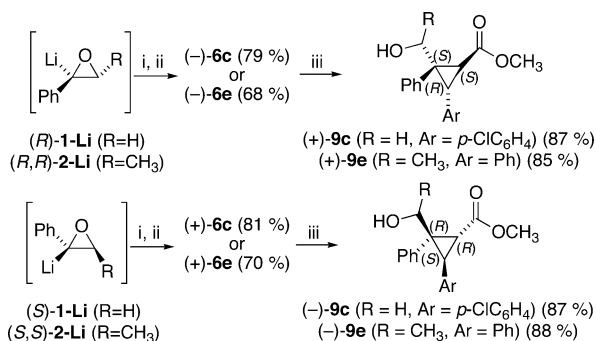
In this context, the formation of the cyclopropane- γ -butyrolactone **7a** besides **9a** in the reaction of **1-Li** with **4a** (Scheme 5), when the reaction mixture was warmed to rt after 5 min from the reactants mixing, could be similarly rationalized with the carbenoid character of lithiated styrene oxide; indeed, it has been demonstrated that the electrophilic character (vs the carbanionic character) of lithiated styrene oxide tends to increase with the temperature.^{5a}

Lithiated phenylpropylene oxides (R^*,R^*)-**2-Li** and (R^*,S^*)-**2-Li**^{5b} reacted with carbenes **4a** and **4f** to give cyclopropane carbenes **6e–g** in good yields (Table 1). It is worth pointing out that (R^*,R^*)-**2-Li**, in contrast to **1-Li**, reacted with **4e** to give **6h** (75% yield, Table 1). This different behavior might be justified considering that lithiated phenylpropylene oxide would have a more pronounced *carbanionic* character at low temperature;^{5b} indeed, it is known that it survives for more than 2 h at $-98\text{ }^{\circ}\text{C}$, whereas lithiated styrene oxide **1-Li**, under the same conditions, has a lifetime of only 30 min. It is, therefore, reasonable that lithiated species **1-Li** may exhibit a different reactivity (*carbanionic* and/or *carbenoid*) depending upon the electrophile and the temperature. However, more work is needed to support this mechanistic viewpoint.¹⁰

The addition of lithiated stilbene oxides (*R**,*R**)-**3-Li** and (*R**,*S**)-**3-Li**^{5c} to **4a** resulted in the formation of carbenes **6i** (73%) and **6j** (77%) (Table 1), respectively (dr > 98:2): the relative configuration of **6i** was secured by an X-ray analysis.¹¹ This was a clear confirmation that the lithiated aryloxirane retains the configuration in the Michael addition step but inverts at the α-carbon in the oxirane ring-opening.

(10) A computational and an NMR spectroscopic study on lithiated styrene- and phenylpropylene oxides is underway, and results will be reported in due course.

(11) Crystallographic data for compound **6i** have been deposited at the Cambridge Crystallographic Data Centre (deposition no. CCDC-259218). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: (int.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

SCHEME 6^a

^a Reagents and conditions: (i) **4a** or **4c**; (ii) NH₄Cl; (iii) PyNO, rt, THF, 24 h.

All of the above cyclopropane carbenes (**6a–c,e,g,i,j**) could be easily oxidized to the corresponding cyclopropanecarboxylates (**9a–c,e,g,i,j**) with pyridine *N*-oxide (PyNO)¹² in THF (rt, 24 h) (Table 1).

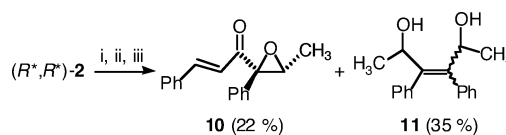
Next, we studied the addition of lithiated optically active styrene oxides (*R*)-**1** and (*S*)-**1** to the complex **4c**: the addition of (*R*)-**1-Li** resulted in the formation of tetrasubstituted arylcyclopropane (1*S*,2*S*,3*R*)-(-)-**6c** (79% yield, dr > 98/2), whereas the addition of (*S*)-**1-Li** furnished the enantiomeric arylcyclopropane (1*R*,2*R*,3*S*)-(+)-**6c** (81% yield, dr > 98/2) (Scheme 6). The (*S*)-(+)- α -methoxy- α -trifluoromethylphenylacetyl chloride (MTPA-Cl) was used to ascertain, via NMR,¹³ the enantiomeric purity of the above-cited cyclopropanecarboxylates, by comparing the two MTPA esters formed with those deriving from a sample of *rac*-**1**. A cascade process involving the stereospecific Michael addition (retention of configuration at the α -carbon) of (*R*)- or (*S*)-**1-Li** to **4c** (according to that described in Scheme 1), followed by the oxirane ring-opening-promoted cyclopropanation (inversion of configuration at the α -carbon), might likely explain the formation of (-)- and (+)-**6c**. Taking into account the stereochemical features of the entire process, it has been possible to determine also the absolute configuration of all three stereocenters of these cyclopropane carbenes by 2D-NOESY experiments.

Similarly, lithiated optically active phenylpropylene oxides (*R,R*)-**2-Li** and (*S,S*)-**2-Li**^{5b} (Scheme 6), generated by deprotonation of (*R,R*)-**2** and (*S,S*)-**2**, reacted smoothly with **4a** to furnish cyclopropane carbenes (1'*S*,1*R*,2*R*,3*S*)-(-)-**6e** (68%) and (1'*R*,1*S*,2*S*,3*R*)-(+)-**6e** (70%), respectively, in both cases highly enantiomerically enriched [er > 98:2, via (*S*)-MTPA chloride].

The absolute configuration of the four stereocenters was determined by 2D-NOESY experiments considering that there is retention of configuration at the β -carbon and inversion at the α -benzylic carbon of the starting epoxide. Compounds (-)-/(+)-**6c** and (-)-/(+)-**6e** could be easily oxidized with PyNO to give the corresponding cyclopropanecarboxylates (+)-/(-)-**9c**, (87% yield) and (+)-**9e** (85% yield) and (-)-**9e** (88% yield), respectively (Scheme 6). The configuration remained unaffected.

(12) (a) Barluenga, J.; Bernad, P. L.; Concellón, J. M.; Piñera-Nicolás, A.; García-Granda, S. *J. Org. Chem.* **1997**, *62*, 6870–6875 and references cited therein. (b) Herndon, J. W. *Coord. Chem. Rev.* **2002**, *248*, 3–79.

(13) Seco, J. M.; Quiñoá, E.; Riguera, R. *Chem. Rev.* **2004**, *104*, 17–117.

SCHEME 7^a

^a Reagents and conditions: (i) *s*-BuLi/TMEDA, THF, -98 °C; (ii) methyl *trans*-cinnamate; (iii) NH₄Cl.

As observed for α - and β -lithiated oxazolinylloxiranes,⁷ the use of complexes **4** was necessary for the formation of cyclopropane carbenes. Indeed, lithiated racemic styrene oxide **1-Li** did not react with methylcinnamate, and *trans*-phenylpropylene oxide (*R*^{*},*R*^{*})-**2-Li** gave a mixture of the 1,2-addition product **10** (22% yield) and a chromatographically separable mixture of hex-3-en-2,5-diols **11** (35% overall yield, 2.9:1 *E/Z* ratio),¹⁴ which likely originates from the carbenoid dimerization of the starting lithiated oxirane (Scheme 7).

Finally, we could prove that the addition of lithiated aryloxiranes to α,β -unsaturated Fischer carbene complexes takes place also with β -alkyl- α,β -unsaturated Fischer carbene complexes other than with the aryl-substituted ones. Indeed, the addition of **1-Li** to the Fischer carbene complex **4g** gave the cyclopropane derivative **6k** in good yield and with high diastereoselectivity (74%, dr > 98:2, Table 1).

In conclusion, lithiated styrene, phenylpropylene, and stilbene oxides react diastereo- and, when optically active, enantiospecifically with α,β -unsaturated Fischer carbene complexes to give stereodefined tetrasubstituted cyclopropane carbenes and cyclopropanecarboxylates,¹⁵ which are potentially useful intermediates in organic synthesis.¹⁶ These are, to the best of our knowledge, the first examples of optically active lithiated aryloxiranes capable of inducing asymmetry in the coupling reaction with prochiral substrates.

Experimental Section

Preparation of Carbene Complexes 6a–k and Phenylpropenone 10. General Procedure. A solution of *s*-BuLi (1.2 mmol, 0.92 mL of a 1.3 N solution in cyclohexane), under N₂ and stirring, was added to a solution of oxirane **1**, **2**, or **3** (1.0 mmol) and TMEDA (3.0 mmol) in THF (6 mL) previously cooled to -98 °C (methanol–liquid nitrogen bath) [-60 °C in the case of (*R*^{*},*R*^{*})-**3**]. After 15 min [60 min for (*R*^{*},*R*^{*})-**2**,

(14) The *Z* or *E* configuration to diastereomeric enediols **11** could be assigned on the basis of the methine and methyl protons chemical shifts: 5.12 and 1.29 vs 4.31 and 1.03 δ , respectively. In fact, if bulky substituent groups exist on the double bond *gem* to aromatic rings these will adopt a twist conformation and a shielding of the protons in “*cis* positions” will occur, as reported (Gaudemar, A. In *Stereochemistry: Fundamentals and Methods*; Kagan, H. B., Ed.; Georg Thieme Publishers: Stuttgart, 1977; Vol. 1. Determination of configurations by spectrometric methods, pp 48–50). A PM3 semiempirical geometry optimization of the *Z* and *E* diastereomers showed that the phenyl ring was indeed twisted with respect to the plane of the C=C double bond of about 86° and 73°, respectively, thus supporting the above conclusions.

(15) For other routes to diastereomerically pure cyclopropanes, see also: Avery, T. D.; Taylor, D. K.; Tiekink, E. R. T. *J. Org. Chem.* **2000**, *65*, 5531–5546.

(16) (a) Reissig, H. U. Organic synthesis via cyclopropanes: principles and applications. In *The Chemistry of the Cyclopropyl Group*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1987; Chapter 8. (b) Liu, H. W.; Walsh, C. T. Biochemistry of the cyclopropyl group. In *The Chemistry of the Cyclopropyl Group*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1987; Chapter 16.

(*R**,*S**)-**2**, (*R**,*R**)-**3**] at the above temperature, a solution of the tungsten complex **4** (0.9 mmol) (or a solution of methyl *trans*-cinnamate in the case of synthesis of **10**) in THF (3 mL) was added dropwise. The resulting mixture was stirred for 1 h, allowed to warm to rt, and quenched with saturated aqueous NH₄Cl. Then, it was poured into 20 mL of satd brine, extracted with Et₂O (3 × 15 mL), dried (Na₂SO₄), and concentrated in vacuo. The crude residue was flash chromatographed (silica gel; petroleum ether/Et₂O 4/1) to give the compounds **6a–k** and **10**, which showed the following data:

Pentacarbonyl{[(1*R,2*R**,3*S**)-2-hydroxymethyl-2,3-diphenylcyclopropyl]methoxymethylene}tungsten (**6a**):** yellow solid; mp 63–64 °C (Et₂O), 73%; ¹H NMR (300 MHz) δ 2.61 (br s, exchanges with D₂O, 1 H), 3.52 (d, *J* = 11.9 Hz, 1 H), 3.95 (d, *J* = 5.8 Hz, 1 H), 3.98 (s, 3 H), 4.05 (d, *J* = 11.9 Hz, 1 H), 4.33 (d, *J* = 5.8 Hz, 1 H), 7.33–7.46 (m, 10 H); ¹³C NMR (75.4 MHz, DEPT) δ 40.5 (CH), 54.9 (C_q), 59.2 (CH), 66.3 (CH₂), 68.5 (CH₃), 127.4 (CH), 127.6 (CH), 128.4 (2 × CH), 128.8 (2 × CH), 128.9 (2 × CH), 130.4 (2 × CH), 135.8 (C_q), 137.6 (C_q), 197.7 (4 × C=O), 204.9 (C=O), 323.3 (C=W); GC–MS (70 eV) *m/z* 266 [M⁺ – W(CO)₅, 43], 205 (100), 191 (40), 176 (49), 115 (27), 105 (31), 91 (53), 77 (23); FT-IR (film, cm^{–1}) 3422, 2925, 2066, 1934, 1447, 1277, 700. Anal. Calcd for C₂₃H₁₈O₇W: C, 46.80; H, 3.07. Found: C, 47.14; H, 3.08.

Pentacarbonyl{[(1*R,2*R**,3*S**)-2-hydroxymethyl-3-(4-methoxyphenyl)-2-phenylcyclopropyl]methoxymethylene}tungsten (**6b**):** yellow solid; mp 54–55 °C (Et₂O), 78%; ¹H NMR (300 MHz) δ 3.11 (br s, exchanges with D₂O, 1 H), 3.49 (d, *J* = 11.9 Hz, 1 H), 3.81 (s, 3 H), 3.90 (d, *J* = 5.9 Hz, 1 H), 3.97 (s, 3 H), 4.04 (d, *J* = 11.9 Hz, 1 H), 4.24 (d, *J* = 5.8 Hz, 1 H), 6.96–7.04 (m, 2 H), 7.30–7.55 (m, 7 H); ¹³C NMR (75.4 MHz, DEPT) δ 40.4 (CH), 51.3 (CH₃), 55.0 (C_q), 59.2 (CH), 66.0 (CH₂), 68.5 (CH₃), 115.1 (2 × CH), 127.7 (CH), 127.9 (2 × CH), 128.5 (2 × CH), 129.3 (2 × CH), 135.8 (C_q), 137.6 (C_q), 156.9 (C_q), 197.7 (4 × C=O), 204.9 (C=O), 324.1 (C=W); GC–MS (70 eV) *m/z* 296 [M⁺ – W(CO)₅, 21], 235 (100), 204 (38), 115 (27), 105 (13), 91 (31), 77 (29); FT-IR (film, cm^{–1}) 3412, 2926, 2066, 1924, 1447, 1271, 804, 703. Anal. Calcd for C₂₄H₂₀O₈W: C, 46.47; H, 3.25. Found: C, 46.18; H, 3.14.

Pentacarbonyl{[(1*R,2*R**,3*S**)-3-(4-chlorophenyl)-2-hydroxymethyl-2-phenylcyclopropyl]methoxymethylene}tungsten (**6c**):** yellow solid; mp 55–56 °C (Et₂O), 81%; ¹H NMR (300 MHz) δ 2.48 (br s, exchanges with D₂O, 1 H), 3.42 (d, *J* = 12.0 Hz, 1 H), 3.84 (d, *J* = 6.0 Hz), 3.93 (s, 3 H), 4.05 (d, *J* = 12.0 Hz, 1 H), 4.20 (d, *J* = 6.0 Hz, 1 H), 7.26–7.32 (m, 3 H), 7.34–7.41 (m, 6 H); ¹³C NMR (75.4 MHz, DEPT) δ 39.7 (CH), 54.6 (C_q), 59.2 (CH), 65.4 (CH₂), 68.5 (CH₃), 127.6 (CH), 128.3 (2 × CH), 128.9 (2 × CH), 130.4 (4 × CH), 130.5 (C_q), 133.3 (C_q), 137.3 (C_q), 197.6 (4 × C=O), 203.3 (C=O), 322.1 (C=W); GC–MS (70 eV) *m/z* 300 [M⁺ – W(CO)₅, 1], 241 (28), 239 (84), 204 (70), 175 (100), 91 (15); FT-IR (film, cm^{–1}) 3406, 2067, 1916, 1494, 1447, 1277, 1089, 700. Anal. Calcd for C₂₃H₁₇ClO₇W: C, 44.22; H, 2.74. Found: C, 44.54; H, 2.55. (+)-(1*R*,2*R*,3*S*)-**6c**: 81%; [α]_D²⁰ = +205 (c 1, CHCl₃). (–)-(1*S*,2*S*,3*R*)-**6c**: 79%; [α]_D²⁰ = –206 (c 1, CHCl₃).

Pentacarbonyl{[(1*R,2*R**,3*S**)-2-hydroxymethyl-2-phenyl-3-(1-methyl-1*H*-pyrrol-2-yl)cyclopropyl]methoxymethylene}tungsten (**6d**):** yellow oil, 59%; ¹H NMR (300 MHz) δ 3.58–3.61 (m, 2 H), 3.63 (br s, exchanges with D₂O, 1 H), 3.73 (s, 3 H), 3.94 (s, 3 H), 4.18–4.21 (m, 2 H), 6.06–6.12 (m, 2 H), 6.62–6.66 (m, 1 H), 7.28–7.41 (m, 5 H); ¹³C NMR (75.4 MHz) δ 31.8, 34.2, 54.3, 59.2, 65.8, 68.6, 107.0, 108.6, 122.9, 127.5, 127.7, 128.6, 130.2, 137.3, 197.7 (4 × C=O), 203.4 (C=O), 323.1 (C=W); GC–MS (70 eV) *m/z* 207 [M⁺ – W(CO)₅, 100], 190 (10), 165 (16), 103 (9), 77 (7); FT-IR (film, cm^{–1}) 3427, 3031, 2929, 2066, 1934, 1449, 1261, 1172, 751, 700.

Pentacarbonyl{[(1*R,1*S**,2*S**,3*R**)-2-[1-hydroxyethyl]-2,3-diphenylcyclopropyl]methoxymethylene}tungsten (**6e**):** yellow oil, 71%; ¹H NMR (500 MHz) δ 0.75 (d, *J* = 6.5 Hz, 3 H), 1.72 (br s, exchanges with D₂O, 1 H), 3.42 (q, *J* = 6.5 Hz, 1 H), 3.81 (d, *J* = 6.0 Hz, 1 H), 3.93 (s, 3 H), 4.57 (d, *J* = 6.0 Hz, 1 H), 7.27–7.38 (m, 10 H); ¹³C NMR (125 MHz) δ

20.4, 41.7, 59.5, 60.6, 68.5, 71.3, 127.2, 127.3, 127.9, 128.4, 128.7, 131.7, 135.2, 136.1, 197.8 (4 × C=O), 203.4 (C=O), 324.2 (C=W); GC–MS (70 eV) *m/z* 280 [M⁺ – W(CO)₅, 18], 264 (8), 220 (60), 205 (100), 192 (45), 115 (37), 77 (13); FT-IR (film, cm^{–1}) 3473, 3028, 2948, 2928, 2067, 1917, 1496, 1448, 1269, 1089, 755, 701. (+)-(1*S*,1*R*,2*R*,3*S*)-**6e**: 70%; [α]_D²⁰ = +189 (c 1, CHCl₃). (–)-(1*R*,1*S*,2*S*,3*R*)-**6e**: 68%; [α]_D²⁰ = –187 (c 1, CHCl₃).

Pentacarbonyl{[(1*R,1*S**,2*S**,3*R**)-2-[1-hydroxyethyl]-3-(4-methylphenyl)-2-phenylcyclopropyl]methoxymethylene}tungsten (**6f**):** yellow oil, 68%; ¹H NMR (500 MHz) δ 0.76 (d, *J* = 6.5 Hz, 3 H), 1.99 (br s, exchanges with D₂O, 1 H), 2.36 (s, 3 H), 3.42 (q, *J* = 6.5 Hz, 1 H), 3.76 (d, *J* = 6.0 Hz, 1 H), 3.93 (s, 3 H), 4.53 (d, *J* = 6.0 Hz, 1 H), 7.16–7.34 (m, 9 H); ¹³C NMR (125 MHz) δ 20.4, 21.0, 41.6, 59.7, 60.8, 68.4, 71.3, 127.2, 127.9, 128.2, 129.3, 131.7, 132.1, 136.2, 136.9, 197.8 (4 × C=O), 203.4 (C=O), 324.4 (C=W); GC–MS (70 eV) *m/z* 294 [M⁺ – W(CO)₅, 10], 278 (11), 234 (60), 205 (100), 192 (45), 77 (13); FT-IR (film, cm^{–1}) 3473, 3461 3032, 2948, 2928, 2066, 1917, 1448, 1263, 1080, 701.

Pentacarbonyl{[(1*R,1*R**,2*R**,3*S**)-2-[1-hydroxyethyl]-3-(4-methylphenyl)-2-phenylcyclopropyl]methoxymethylene}tungsten (**6g**):** yellow solid; mp 51–52 °C (Et₂O), 70%; ¹H NMR (500 MHz) δ 1.20 (d, *J* = 6.5 Hz, 3 H), 1.58 (br s, exchanges with D₂O, 1 H), 2.34 (s, 3 H), 3.57 (q, *J* = 6.5 Hz, 1 H), 3.71 (d, *J* = 5.7 Hz, 1 H), 3.98 (s, 3 H), 4.33 (d, *J* = 5.7 Hz, 1 H), 7.07–7.36 (m, 9 H); ¹³C NMR (125 MHz) δ 21.0, 32.2, 43.0, 58.8, 59.4, 68.6, 70.3, 127.2, 127.3, 127.9, 128.5, 129.5, 132.1, 136.0, 137.1, 197.7 (4 × C=O), 203.2 (C=O), 324. (C=W); GC–MS (70 eV) *m/z* 294 [M⁺ – W(CO)₅, 11], 278 (20), 219 (100), 115 (37), 77 (13); FT-IR (film, cm^{–1}) 3564, 3453, 3026, 2970, 2948, 2066, 1926, 1446, 1271, 1046, 763, 701. Anal. Calcd for C₂₅H₂₂O₇W: C, 48.57; H, 3.59. Found: C, 48.29; H, 3.40.

Pentacarbonyl{[(1*R,1*S**,2*S**,3*R**)-3-(2-furyl)-2-[1-hydroxyethyl]-2-phenylcyclopropyl]methoxymethylene}tungsten (**6h**):** yellow oil, 75%; ¹H NMR (500 MHz) δ 0.85 (d, *J* = 6.2 Hz, 3 H), 3.56 (d, *J* = 5.2 Hz, 1 H), 3.62 (q, *J* = 6.2 Hz, 1 H), 3.91 (s, 3 H), 4.40 (d, *J* = 5.2 Hz, 1 H), 6.25 (d, *J* = 3.1 Hz), 6.34 (dd, *J* = 3.1, 1.8 Hz, 1 H), 7.22–7.37 (m, 7 H, 6 H after exchange with D₂O); ¹³C NMR (125 MHz) δ 20.5, 33.5, 58.1, 61.1, 68.5, 71.6, 108.0, 110.5, 127.4, 127.9, 131.6, 135.2, 142.1, 150.2, 197.6 (4 × C=O), 203.0 (C=O), 324.9 (C=W); GC–MS (70 eV) *m/z* 270 [M⁺ – W(CO)₅, 11], 195 (100), 115 (23), 91 (14), 77 (7); FT-IR (film, cm^{–1}) 3477, 3033, 2927, 2066, 1936, 1537, 1260, 753, 700.

Pentacarbonyl{[(1*R,1*S**,2*S**,3*R**)-2-[hydroxy(phenyl)methyl]-2,3-diphenylcyclopropyl]methoxymethylene}tungsten (**6i**):** yellow oil, 73%; ¹H NMR (500 MHz) δ 2.12 (br s, exchanges with D₂O, 1 H), 3.77 (d, *J* = 6.0 Hz, 1 H), 3.94 (s, 3 H), 4.54 (s, 1 H), 4.83 (d, *J* = 6.0 Hz, 1 H), 6.05–6.07 (m, 2 H), 6.86–7.03 (m, 4 H), 7.22–7.41 (m, 9 H); ¹³C NMR (125 MHz) δ 42.1, 59.7, 60.0, 65.8, 68.5, 126.8, 127.1, 127.2, 127.3, 127.4, 127.5, 128.6, 128.8, 132.2, 135.1, 136.2, 140.2, 197.7 (4 × C=O), 203.5 (C=O), 324.4 (C=W); GC–MS (70 eV) *m/z* 342 [M⁺ – W(CO)₅, 6], 326 (10), 281 (60), 207 (100), 191 (25), 115 (39), 77 (13); FT-IR (film, cm^{–1}) 3404, 3028, 2928, 2067, 1916, 1494, 1365, 753, 700.

Pentacarbonyl{[(1*R,1*R**,2*R**,3*S**)-2-[hydroxy(phenyl)methyl]-2,3-diphenylcyclopropyl]methoxymethylene}tungsten (**6j**):** yellow oil, 77%; ¹H NMR (500 MHz) δ 3.77 (d, *J* = 6.0 Hz, 1 H), 3.89 (s, 3 H), 4.54 (s, 1 H), 4.75 (d, *J* = 6.0 Hz, 1 H), 6.79 (br s, exchanges with D₂O, 1 H), 6.85–6.89 (m, 2 H), 7.05–7.20 (m, 8 H), 7.32–7.57 (m, 5 H); ¹³C NMR (125 MHz) δ 43.8, 58.4, 60.1, 68.6, 76.5, 127.0, 127.1, 127.2, 127.5, 127.7, 127.8, 128.7, 128.8, 132.4, 135.6, 135.8, 140.2, 197.5 (4 × C=O), 203.0 (C=O), 325.0 (C=W); GC–MS (70 eV) *m/z* 342 [M⁺ – W(CO)₅, 11], 326 (9), 281 (53), 207 (100), 191 (30), 115 (43), 77 (13); FT-IR (film, cm^{–1}) 3365, 303, 2930, 2065, 1917, 1511, 1444, 756, 704.

Pentacarbonyl{[(1*R,2*R**,3*R**)-2-hydroxymethyl-3-methyl-2-phenylcyclopropyl]methoxymethylene}tungsten (**6k**):** yellow oil, 77%; ¹H NMR (500 MHz) δ 0.95 (d, *J* = 6.5 Hz, 3 H), 1.72 (br s, exchanges with D₂O, 1 H), 3.42 (q, *J* = 6.5 Hz, 1 H), 3.81 (d, *J* = 6.0 Hz, 1 H), 3.93 (s, 3 H), 4.57 (d, *J* = 6.0 Hz, 1 H), 7.27–7.38 (m, 10 H); ¹³C NMR (125 MHz) δ

tungsten (6k): yellow oil, 74%; ^1H NMR (400 MHz) δ 1.38 (d, $J = 6.4$ Hz, 3 H), 1.42 (br s, exchanges with D_2O , 1 H), 2.60–2.64 (m, 1 H), 3.53 (d, $J = 5.2$ Hz, 1 H), 3.75 (d, $J = 12.0$ Hz, 1 H), 3.82 (s, 3 H), 4.25 (d, $J = 12.0$ Hz, 1 H), 7.13–7.28 (m, 5 H); ^{13}C NMR (100 MHz) δ 13.4, 31.3, 55.0, 63.1, 66.4, 68.3, 127.4, 128.3, 130.4, 138.4, 197.7 ($4 \times \text{C}=\text{O}$), 203.5 ($\text{C}=\text{O}$), 324.3 ($\text{C}=\text{W}$); GC–MS (70 eV) m/z 204 [$\text{M}^+ - \text{W}(\text{CO})_5$, 11], 143 (100), 115 (22), 77 (10); FT-IR (film, cm^{-1}) 3406, 3028, 2933, 2066, 1938, 1446, 1268, 1063, 759, 700.

1-[(2R*,3R*)-3-Methyl-2-phenyloxiran-2-yl]-3-phenylprop-2-en-1-one (10): white solid; mp 57–58 °C (Et_2O), 22%; ^1H NMR (500 MHz) δ 1.41 (d, $J = 6.0$ Hz, 3 H), 3.29 (q, $J = 6.0$ Hz, 1 H), 6.56 (d, $J = 12.6$ Hz, 1 H), 6.89 (d, $J = 12.6$ Hz, 1 H), 7.26–7.42 (m, 6 H), 7.48–7.59 (m, 4 H); ^{13}C NMR (125 MHz) δ 15.8, 62.8, 67.9, 122.8, 128.0, 128.3, 128.4, 128.5, 128.7, 128.8, 134.3, 135.4, 145.4, 194.9; GC–MS (70 eV) m/z 264 (M^+ , 16), 248 (21), 157 (12), 131 (100), 105 (29), 77 (25); FT-IR (film, cm^{-1}) 3031, 2967, 1685, 1541, 1260, 753, 702.

Preparation of Cyclopropanecarboxylates 9a–j and Lactone 7e. General Procedure. A solution of the carbene complex **6a–c,e,g,i,j** (or the crude reaction mixture of **7b**, obtained from the reaction of **1-Li** with **4e** according to the general procedure described above) (0.8 mmol) in hexane (10 mL) was subjected to air oxidation under sunlight. After 24 h, the mixture was filtered off on Celite, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (Et_2O /petroleum ether 1/4) to give the corresponding cyclopropanecarboxylate. Alternatively, the oxidation could be carried out with pyridine *N*-oxide (3 equiv) in THF (5 mL) at rt overnight.^{12a}

(1R*,5S*,6R*)-6-(2-Furyl)-5-phenyl-3-oxabicyclo[3.1.0]-hexan-2-one (7e): white solid; mp 55–56 °C (Et_2O), 48%; ^1H NMR (300 MHz) δ 2.80 (d, $J = 3.3$ Hz, 1 H), 2.90 (d, $J = 3.3$ Hz, 1 H), 4.40 (d, $J = 9.3$ Hz, 1 H), 4.68 (d, $J = 9.3$ Hz, 1 H), 5.87 (d, $J = 3.2$ Hz, 1H), 6.16 (dd, $J = 3.2$, 1.9 Hz, 1H), 7.15–7.31 (m, 6 H), 7.31–7.56 (m, 7 H); ^{13}C NMR (75.4 MHz, DEPT) δ 28.7 (CH), 39.4 (CH), 45.5 (C_q), 74.7 (CH_2), 107.7 (CH), 110.4 (CH), 128.1 (CH), 128.6 ($2 \times \text{CH}$), 128.9 ($2 \times \text{CH}$), 133.3 (C_q), 141.9 (CH), 148.1 (C_q), 170.9 ($\text{C}=\text{O}$); GC–MS (70 eV) m/z 240 (M^+ , 7), 196 (100), 195 (57), 181 (47), 91 (10), 77 (12); FT-IR (film, cm^{-1}) 3044, 2927, 1732, 1448, 1247, 1035, 700. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_3$: C, 74.99; H, 5.03. Found: C, 74.68; H, 4.87.

(1R*,2R*,3S*)-Methyl-2-(hydroxymethyl)-2,3-diphenylcyclopropanecarboxylate (9a): white solid; mp 45–46 °C (Et_2O), 88%; ^1H NMR (300 MHz) δ 2.11 (br s, exchanges with D_2O , 1 H), 2.53 (d, $J = 5.9$ Hz, 1 H), 3.30 (d, $J = 11.8$ Hz, 1 H), 3.42 (d, $J = 5.9$ Hz, 1 H), 3.55 (s, 3 H), 3.71 (d, $J = 11.8$ Hz, 1 H), 7.22–7.42 (m, 10 H); ^{13}C NMR (75.4 MHz, DEPT) δ 29.5 (CH), 33.6 (CH), 43.5 (C_q), 51.8 (CH_3), 66.7 (CH_2), 127.5 (CH), 127.6 ($2 \times \text{CH}$), 128.0 ($2 \times \text{CH}$), 128.2 (CH), 128.5 ($2 \times \text{CH}$), 128.7 ($2 \times \text{CH}$), 134.2 (C_q), 138.3 (C_q), 170.3 ($\text{C}=\text{O}$); GC–MS (70 eV) m/z 282 (M^+ , 11), 264 (25), 205 (100), 146 (43), 91 (71), 77 (32); FT-IR (film, cm^{-1}) 3429, 2923, 1737, 1516, 1441, 753, 700. Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3$: C, 76.57; H, 6.43. Found: C, 76.78; H, 6.28.

(1R*,2R*,3S*)-Methyl-2-(hydroxymethyl)-3-(4-methoxyphenyl)-2-phenylcyclopropanecarboxylate (9b): white solid; mp 53–54 °C (Et_2O), 82%; ^1H NMR (300 MHz) δ 2.20 (br s, exchanges with D_2O , 1 H), 2.50 (d, $J = 5.8$ Hz, 1 H), 3.40 (d, $J = 5.8$ Hz, 1 H), 3.44 (d, $J = 11.9$ Hz, 1 H), 3.55 (s, 3 H), 3.75 (d, $J = 11.9$ Hz, 1 H), 3.84 (s, 3 H), 6.86–6.95 (m, 2 H), 7.31–7.56 (m, 7 H); ^{13}C NMR (75.4 MHz, DEPT) δ 29.4 (CH), 33.6 (CH), 43.5 (C_q), 51.7 (CH_3), 55.2 (CH_3), 66.6 (CH_2), 114.0 ($2 \times \text{CH}$), 127.5 (CH), 128.5 ($2 \times \text{CH}$), 129.7 ($2 \times \text{CH}$), 129.9 ($2 \times \text{CH}$), 133.0 (C_q), 138.6 (C_q), 158.6 (C_q), 170.9 ($\text{C}=\text{O}$); GC–MS (70 eV) m/z 312 (M^+ , 2), 294 (30), 235 (100), 221 (42), 176 (62), 137 (83), 121 (45), 91 (53), 77 (15); FT-IR (film, cm^{-1}) 3422, 2927, 1732, 1514, 1445, 1247, 1035, 700. Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_4$: C, 73.06; H, 6.45. Found: C, 73.16; H, 6.49.

(1R*,2R*,3S*)-Methyl-2-(hydroxymethyl)-3-(4-chlorophenyl)-2-phenylcyclopropanecarboxylate (9c): white solid; mp 48–49 °C (Et_2O), 81%; ^1H NMR (300 MHz) δ 2.03 (br s, exchanges with D_2O , 1 H), 2.49 (d, $J = 5.9$ Hz, 1 H), 3.34 (d, $J = 11.8$ Hz, 1 H), 3.40 (d, $J = 5.9$ Hz, 1 H), 3.55 (s, 3 H), 3.70 (d, $J = 11.8$ Hz, 1 H), 7.32–7.42 (m, 9 H); ^{13}C NMR (75.4 MHz, DEPT) δ 29.5 (CH), 33.8 (CH), 43.6 (C_q), 51.9 (CH_3), 66.4 (CH_2), 127.7 (CH), 128.6 (C_q), 128.8 ($2 \times \text{CH}$), 129.7 ($2 \times \text{CH}$), 130.5 ($2 \times \text{CH}$), 133.0 ($2 \times \text{CH}$), 134.2 (C_q), 138.3 (C_q), 170.7 ($\text{C}=\text{O}$); GC–MS (70 eV) m/z 318 ($\text{M}^+ + 2$, 2), 316 (M^+ , 6), 298 (20), 241 (31), 239 (100), 180 (65), 137 (83), (31), 91 (53), 77 (15); FT-IR (film, cm^{-1}) 3407, 2927, 1739, 1447, 1277, 760, 700. Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{ClO}_3$: C, 68.25; H, 5.41. Found: C, 68.48; H, 5.28. (–)-(1R*,2R*,3S)-**9c**: 87%; $[\alpha]_D^{20} = -41.3$ (c 1, CHCl_3). (+)-(1S,2S,3R)-**9c**: 87%; $[\alpha]_D^{20} = +41.8$ (c 1, CHCl_3).

(1R*,1S*,2S*,3R*)-Methyl 2-[1-hydroxyethyl]-2,3-diphenylcyclopropanecarboxylate (9e): colorless oil, 88%; ^1H NMR (500 MHz) δ 0.85 (d, $J = 6.5$ Hz, 3 H), 1.95 (br s, exchanges with D_2O , 1 H), 2.86 (d, $J = 6.2$ Hz, 1 H), 3.29 (q, $J = 6.5$ Hz, 1 H), 3.47 (d, $J = 6.2$ Hz, 1 H), 3.93 (s, 3 H), 7.35–7.52 (m, 10 H); ^{13}C NMR (125 MHz) δ 20.2, 30.4, 35.2, 47.1, 51.9, 70.7, 127.0, 127.5, 128.0, 128.5, 128.6, 130.8, 135.0, 136.5, 171.0; GC–MS (70 eV) m/z 296 (M^+ , 1), 278 (48), 219 (95), 190 (100), 158 (46), 134 (47), 91 (53), 77 (22); FT-IR (film, cm^{-1}) 3415, 3031, 2929, 1723, 1480, 1261, 754, 702. (–)-(1'S,1R,2R,3S)-**9e**: 88%; $[\alpha]_D^{20} = -55.0$ (c 1, CHCl_3). (+)-(1'R,1S,2S,3R)-**9e**: 85%; $[\alpha]_D^{20} = +54.3$ (c 1, CHCl_3).

(1R*,1R*,2R*,3S*)-Methyl 2-[1-hydroxyethyl]-3-(4-methylphenyl)-2-diphenylcyclopropanecarboxylate (9g): colorless oil, 84%; ^1H NMR (500 MHz) δ 1.15 (d, $J = 6.5$ Hz, 3 H), 2.05 (br s, exchanges with D_2O , 1 H), 2.35 (s, 3 H), 2.41 (d, $J = 6.0$ Hz, 1 H), 2.74 (q, $J = 6.5$ Hz, 1 H), 3.30 (d, $J = 6.0$ Hz, 1 H), 3.57 (s, 3 H), 7.08–7.36 (m, 9 H); ^{13}C NMR (125 MHz) δ 20.4, 21.1, 29.7, 35.7, 46.7, 51.8, 69.6, 127.4, 127.9, 128.8, 129.3, 131.2, 132.2, 136.1, 136.8, 171.0; GC–MS (70 eV) m/z 310 (M^+ , 1), 292 (41), 233 (86), 190 (100), 158 (46), 134 (42), 105 (51); FT-IR (film, cm^{-1}) 3421, 3036, 2973, 2941, 1716, 1478, 1261, 841, 751, 702.

(1R*,1S*,2S*,3R*)-Methyl-2-[hydroxy(phenyl)methyl]-2,3-diphenylcyclopropanecarboxylate (9i): white solid; mp 75–76 °C (Et_2O), 83%; ^1H NMR (500 MHz) δ 3.05 (d, $J = 6.1$ Hz, 1 H), 3.37 (d, $J = 6.1$ Hz, 1 H), 3.55 (s, 3 H), 3.79 (br s, exchanges with D_2O , 1 H), 4.40 (s, 1 H), 6.08–6.11 (m, 2 H), 6.88–6.91 (m, 2 H), 7.03–7.39 (m, 11 H); ^{13}C NMR (125 MHz) δ 29.7, 35.7, 47.7, 51.9, 76.4, 126.7, 127.2, 127.4, 127.5, 128.0, 128.2, 128.5, 129.0, 131.2, 135.1, 136.8, 140.3, 171.0; GC–MS (70 eV) m/z 358 (M^+ , 20), 281 (42), 252 (100), 220 (89), 191 (85), 165 (33), 105 (70), 77 (64); FT-IR (film, cm^{-1}) 3583, 3406, 2954, 2915, 1731, 1455, 1377, 1168, 1025, 754, 699.

(1R*,1R*,2R*,3S*)-Methyl 2-[hydroxy(phenyl)methyl]-2,3-diphenylcyclopropanecarboxylate (9j): white solid; mp 69–70 °C (Et_2O), 87%; ^1H NMR (500 MHz) δ 2.86 (d, $J = 6.0$ Hz, 1 H), 3.03 (br s, exchanges with D_2O , 1 H), 3.40 (d, $J = 6.0$ Hz, 1 H), 3.46 (s, 3 H), 4.27 (s, 1 H), 6.80–6.95 (m, 4 H), 7.15–7.44 (m, 9 H), 7.56–7.59 (m, 2 H); ^{13}C NMR (125 MHz) δ 35.4, 47.9, 51.8, 67.6, 75.5, 126.3, 127.2, 127.3, 127.4, 127.7, 128.8, 128.9, 129.0, 131.5, 135.4, 135.5, 140.9, 170.4; GC–MS (70 eV) m/z 358 (M^+ , 18), 281 (32), 249 (59), 220 (55), 196 (100), 165 (30), 105 (74), 77 (63); FT-IR (film, cm^{-1}) 3570, 3425, 3059, 2955, 2921, 1735, 1448, 1237, 1166, 1013, 756, 700.

3,4-Diphenylhex-3-ene-2,5-diol (11). (*E*, major diastereomer): white solid; mp 102–103 °C (Et_2O); 26%; R_f 0.46 (Et_2O , silica gel); ^1H NMR (400 MHz) δ 1.03 (d, $J = 6.4$ Hz, 6 H), 1.65 (br s, exchanges with D_2O , 2 H), 4.31 (q, $J = 6.4$ Hz, 2 H), 7.22–7.39 (m, 10 H); ^{13}C NMR (100 MHz) δ 22.2, 67.5, 127.3, 128.1, 129.9, 136.3, 141.8; GC–MS (70 eV) m/z 268 (M^+ , 4), 250 (15), 207 (100), 178 (51), 129 (58), 91 (26); FT-IR (film, cm^{-1}) 3281, 2967, 2925, 1600, 1442, 1370, 1113, 1065, 748, 700. (*Z*, minor diastereomer): colorless oil; 9%; R_f 0.38 (Et_2O , silica gel); ^1H NMR (400 MHz) δ 1.29 (d, $J = 6.4$ Hz, 6 H), 1.62 (br s, exchanges with D_2O , 2 H), 5.12 (q, $J = 6.4$ Hz, 2 H), 6.93–7.09 (m, 10 H); ^{13}C NMR (100 MHz) δ 23.0, 67.2, 126.2, 127.4,

130.2, 138.5, 142.7; GC–MS (70 eV) m/z 268 (M^+ , 2), 250 (21), 207 (100), 178 (43), 129 (15), 77 (18); FT-IR (film, cm^{-1}) 3356, 2922, 1657, 1598, 1442, 1115, 752, 700.

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Supporting Information Available: General experimental methods; copies of ^1H or ^{13}C NMR spectra for compounds **6d–f, h–k, 9e, g, i, j, 10**, and (*E*)- and (*Z*)-**11**; ORTEP view and CIF file for compound **6i**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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