α,β-Unsaturated Fischer Carbene Complexes vs. 1,3-Dipoles: Reactions with Nitrones and Nitrilimines

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The reaction of *tert*-butylalkynyl chromium Fischer carbene complex **1** with nitrones **2** affords β-enamino-ketoaldehydes **4** by the light-promoted rearrangement of the corresponding [3+2] cycloadduct carbene complexes **3**. On the other hand, [3+2] cycloaddition of chiral nonracemic Fischer alkenyl carbene complexes **19** with nitrilimines **10** yields enantiomerically pure Δ^2-pyrazolines with high regio- and diastereoselectivity.

Introduction

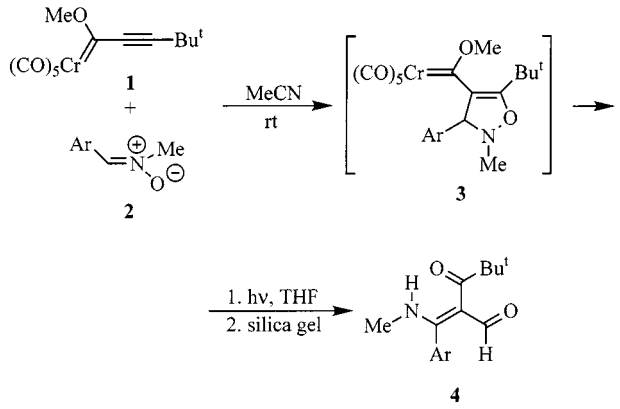
Fischer carbene complexes are nowadays extensively used as reagents in organic synthesis.[1] In this sense, α,β-unsaturated Fischer carbene complexes have been found to behave as good dienophiles and dipolarophiles in [4+2] and [3+2] cycloadditions.[2] Although many examples are known in which both alkenyl[3] and alkynyl[4] carbene complexes undergo [4+2] cycloadditions, their reactivity towards 1,3-dipoles has been much less studied. The first reports in this field refer to the reaction of alkynyl Fischer carbene complexes with diazoderivatives.[5] Subsequently, nitrones[6] and masked 1,3-dipoles[7] have also proved to be successful in their reaction with alkynyl carbene complexes. On the other hand, the reactivity of alkenyl carbene complexes vs 1,3-dipoles is mostly unexplored. Before our study on the diastereoselective cycloaddition of diazo compounds with enantiopure (alkenyl)alkoxy carbene complexes,[8] only some preliminary results had been published on this topic.[9] In this sense, the first part of this paper deals with an attempt to generalize the reaction of nitrones with α,β-unsaturated Fischer carbene complexes,[10] as only arylethynyl Fischer carbene complexes had been formerly used; in the second part we disclose our findings on the reaction of enantiopure alkenyl Fischer carbene complexes vs nitrilimines.[11]

Results and Discussion

1. Fischer Carbene Complexes vs Nitrones

Chan et al. previously showed[6] that phenylethynyl and *p*-tolylethynyl carbene complexes react with *N*-alkyl nitrones to afford the corresponding cycloadducts in a chemo- and regioselective way. Hence, they are the reagents of choice for the synthesis of dihydroisoxazoles, as carbene complexes greatly enhance the regioselectivity and the rate of the reaction when compared with the analogous organic esters. Due to its interest, we have focused our efforts on expanding the scope of this reaction to alkylethynyl complexes.

The reaction of *tert*-butylethynyl carbene complex **1** with *N*-methyl nitrones **2** in acetonitrile at room temperature for five minutes gives rise to the cycloadduct carbene complexes **3** by a chemo- and regioselective 1,3-dipolar cycloaddition. Dihydrooxazoles **3** have been shown to be unstable, decomposing to give compounds **4**. This process takes place within a few days when cycloadducts **3**, which were purified by flash chromatography, are kept in the dark. However, it has been observed that sunlight accelerates the decomposition. So, when THF solutions of cycloadduct carbene complexes **3** are irradiated with a 60 W light bulb, they disappear in 12 h and β-enaminoketoaldehydes **4** are obtained after purification by column chromatography on silica gel (Scheme 1 and Table 1). Compounds **4** are isolated as a single diastereoisomer according to ^{1}H- and ^{13}C-NMR experiments. The presence of a cross peak between the aldehyde proton and the *ortho* aromatic protons in a NOESY experiment for compound **4c** confirms the (*Z*) configuration.



Scheme 1

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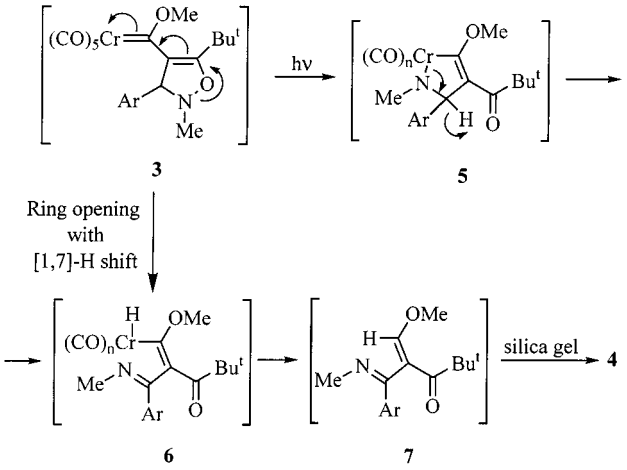
Table 1. Reaction of *tert*-butylethynyl carbene **1** with nitrones **2** to give β-enamino ketoaldehydes **4**

Nitrone	Ar	Product	Yield (%)[a]
2a	Ph	**4a**	32
2b	4-MeC_6H_4	**4b**	31
2c	4-$MeOC_6H_4$	**4c**	37
2d	4-$Me_2NC_6H_4$	**4d**	43

[a] Based on carbene **1**.

This behavior seems to be particular for *tert*-butylethynyl carbene complex **1**, as irradiation of THF solutions of other cycloadducts,[12] with Ph, TMS, or $C(OMe)Me_2$ substituents instead of *tert*-butyl, does not lead to the formation of β-enaminoketoaldehydes. In those cases, aldehydes ArCHO, obtained by the formal hydrolysis of *N*-methyl nitrones **2**, were isolated along with decomposition products.

The transformation of **3** into **4** can be explained by assuming the initial ring opening of cycloadducts **3** by cleavage of the nitrogen–oxygen bond to give metalacycle intermediates **5**,[13] followed by β-hydride elimination and further reductive elimination from intermediates **6**, to afford compounds **7**. The enol ether function would be hydrolyzed during chromatographic purification on silica gel to give rise to β-enaminoketoaldehydes **4** (Scheme 2). An alternative pathway would involve ring opening of cycloadducts **3** with simultaneous [1,7]-hydrogen shift, leading to intermediates **6**.



Scheme 2

It should be pointed out that β-enaminoketoaldehydes **4** can be regarded as precursors of tricarbonyl compounds, bearing three different carbonyl groups attached to the same carbon atom.

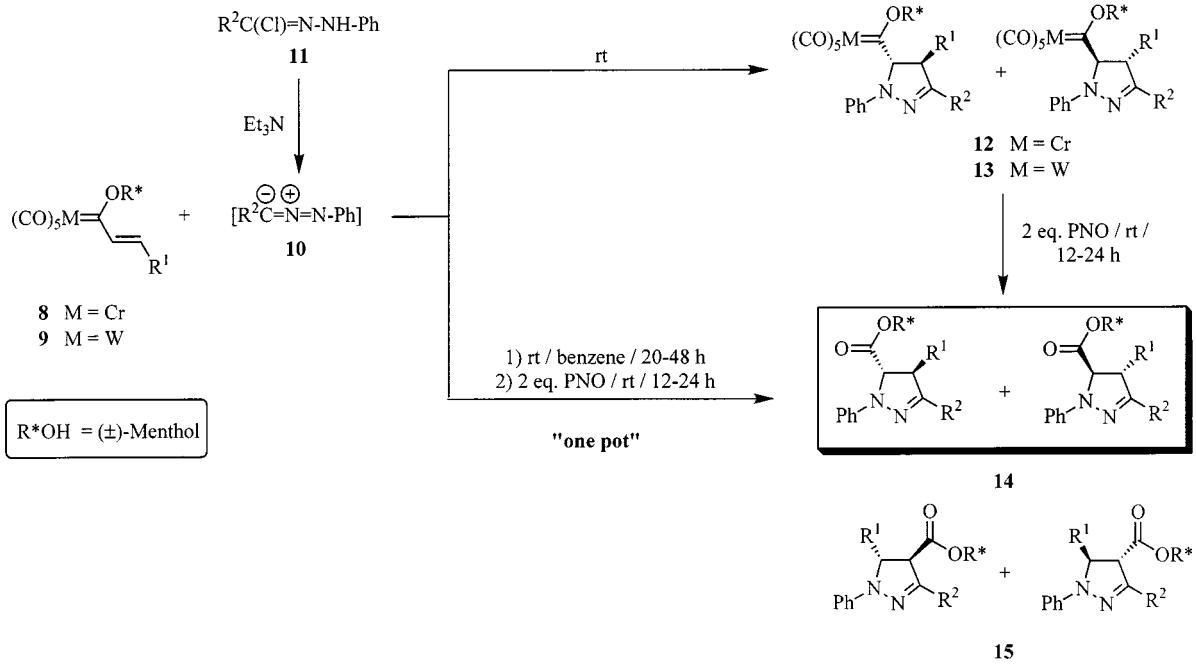
On the other hand, the reactivity of alkenyl Fischer carbene complexes vs nitrones is virtually unknown. Chan et al. showed[6a] that the reaction of methoxy alkenyl complexes with *N*-methyl nitrone **2a** didn't yield the expected cycloadduct but the corresponding esters resulting from the oxidation of the carbene functionality. To our belief, an increase in the steric requirements in the proximity of the metal–carbene carbon bond would hinder the oxidation, facilitating the formation of the isoxazolidine. In this sense, the methoxy group was substituted by (±)-menthyloxy and (–)-8-phenylmenthyloxy, which would, a priori, provide the required bulkiness. However, when those carbenes were treated with *N*-methyl nitrones **2**, only the esters were isolated, whereas no trace of the corresponding cycloadduct could be detected. Those results indicate that the oxidation of the metal–carbon bond is faster than the [3+2] dipolar cycloaddition with nitrones,[14] even when sterically hindered tungsten carbene complexes are employed.[15]

2. Fischer Carbene Complexes vs Nitrilimines

1,3-Dipolar cycloadditions with nitrilimines is a very well-known process.[16] These synthons[17] are often generated in situ from hydrazonoyl chlorides and trapped with dipolarophiles to give the corresponding Δ^2-pyrazolines as a mixture of regioisomers.[18] Δ^2-Pyrazolines are of interest due to their biological activity (e.g., as anti-inflammatory agents[19]), physical applications (e.g., as optical brighteners[20] and fluorescent switches[21]) and also as starting materials for the synthesis of functionalized cyclic and acyclic compounds;[8a,22] hence procedures to prepare these systems in a regio- and diastereoselective way are of great value.

The first experiments were carried out with (±)-menthol-derived alkenyl carbenes **8** and **9**, which by treatment with nitrilimines **10**, in situ generated from hydrazonoyl chlorides **11**, led to Δ^2-pyrazolines **12** (or **13**) in moderate yields (Scheme 3, Table 2). Compounds **12** were found to be fairly unstable and, moreover, purification from their oxidation products was difficult. For this reason their oxidation to the corresponding esters **14** was promoted in moderate to good yields, by pyridine *N*-oxide (PNO). Better yields of Δ^2-pyrazoline esters **14** were achieved when the cycloaddition–oxidation stepwise sequence was performed one-pot without isolation of adducts **12** (see entries 1 and 8, Table 2). Of the two possible regioisomers **14** and **15,** only **14** was detected; it was obtained as a mixture of two diastereomers (ratio < 2:1, by NMR).

As shown in Table 2, the [3+2] cycloadditions carried out with tungsten carbene complexes **9** provided the corresponding cycloadducts either in lower yield (entries 3, 12) or with worse diastereoselectivity or regioselectivity (entries 3 vs 2) than when starting from chromium carbene complexes **8**. On the other hand, the influence of solvent polarity in the reaction rate is negligible (entries 8–11); this supports a concerted mechanism in the cycloaddition process. The presence of an electron-releasing group in the carbene (entry 1 vs 2 and 4) or an electron-withdrawing group in the nitrilimine (entry 1 vs 8) decreases the reaction rate while an electron-releasing group in the dipole (entry 1 vs 5) accelerates the process. The Frontier Molecular Orbital theory explains these observations if the expected reactivity pattern between Fischer carbenes and nitrilimines is regarded to be HOMO(dipole)–LUMO(dipolarophile) due to the strong electron-withdrawing ability of the metal pentacarbonyl group in **8** (or **9**).[6c,23,24] The results displayed in entries 13 and 14 also agree with this reactivity pattern; thus the



Scheme 3

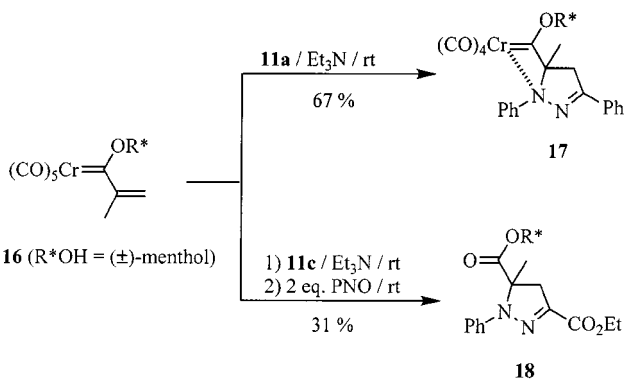
Table 2. Synthesis of Δ^2-pyrazolines **14** from carbenes **8** (or **9**) and nitrilimines **10**

Entry	Carbene	R^1	**10**	R^2	Solvent	Time (h)[a]	Adduct[b]	**14**	*d.r.*[c]	Yield (%)[d]
1	**8a**	Ph	**a**	Ph	THF/acetone 1:1	14	**12a** (67)	**a**	1.7:1	72 (80)[e]
2	**8b**	2-furyl	**a**	Ph	THF/acetone 1:1	84	**12b** (80)	**b**	1.5:1	99
3	**9b**	2-furyl	**a**	Ph	THF/acetone 1:1	14	–	**b**	1.2:1	92[f]
4	**8c**	*p*-anisyl	**a**	Ph	PhH	60	–	**c**	1.5:1	82
5	**8a**	Ph	**b**	*p*-Anisyl	PhH	2	–	**d**	1:1	80
6	**8b**	2-furyl	**b**	*p*-Anisyl	PhH	16	–	**e**	1:1	87[g]
7	**8c**	*p*-anisyl	**b**	*p*-Anisyl	PhH	20	–	**f**	1:1	82
8	**8a**	Ph	**c**	CO_2Et	THF/acetone 1:1	84	**12g** (30)	**g**	1:1	40 (76)[e]
9	**8a**	Ph	**c**	CO_2Et	PhH	84	–	**g**	1:1	55
10	**8a**	Ph	**c**	CO_2Et	hexane	120	–	**g**	1:1	46
11	**8a**	Ph	**c**	CO_2Et	$CHCl_3$	96	–	**g**	1:1	42
12	**9a**	Ph	**c**	CO_2Et	THF/acetone 1:1	96	–	**g**	1:1	27
13	**8b**	2-furyl	**c**	CO_2Et	THF/acetone 1:1	96	– [h]			
14	**9b**	2-furyl	**c**	CO_2Et	THF/acetone 1:1	120	**13** (10)[i]			

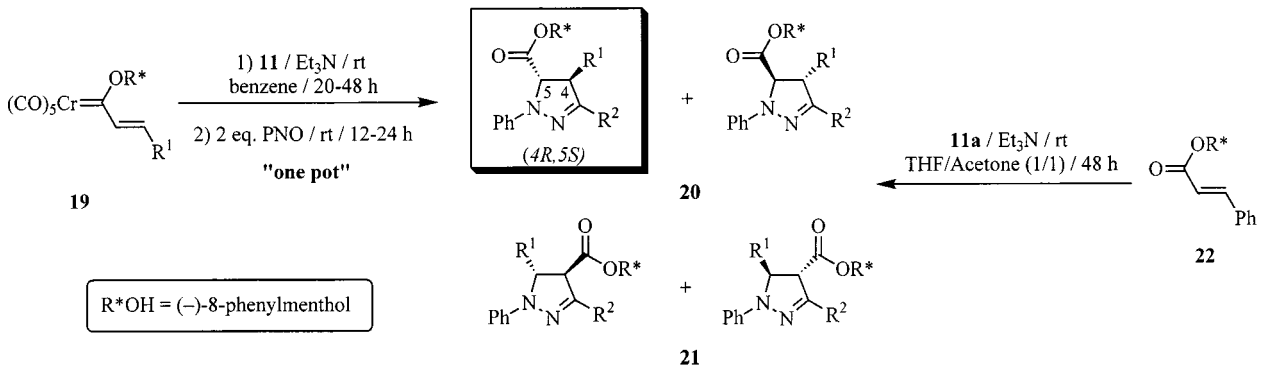
[a] Cycloaddition reaction times monitored by TLC. – [b] The isolated yields are given in parentheses. – [c] Determined by ^{1}H NMR. – [d] Isolated yield from one-pot cycloaddition–oxidation unless otherwise stated. – [e] Yield of the oxidation step. – [f] Regioselectivity 94:6. – [g] Regioselectivity 85:15. – [h] Compound not detected by either TLC or ^{1}H NMR (300 MHz): of the crude residue after the starting material had been consumed. – [i] Compound neither isolated nor purified; diastereomeric ratio 1.1:1; yield was estimated by ^{1}H NMR.

cycloaddition of carbene **8b** with nitrilimine **10c** is slower than carbene decomposition and no cycloadduct was detected when the starting material **8b** was totally consumed. When tungsten carbene **9b**, bearing the same substituents, was reacted with **10c**, a small amount (10%) of cycloadduct **13** was detected, probably due to the higher strength of the carbon–tungsten bond that allows some cycloaddition to proceed before carbene decomposition.

When a [3+2] cycloaddition reaction was performed between α-methyl-substituted alkenylcarbene **16** and diphenylnitrilimine **10a**, compound **17** was isolated as a 1:1 mixture of diastereomers (Scheme 4). Carbene **17** bears only four carbonyl ligands; this is supported by the tetracarbonyl ligand pattern observed in the ^{13}C-NMR and FT-IR spectra of **17**. This result is particularly interesting, as it allows the proposed regiochemistry of compound **17** to be



Scheme 4



Scheme 5

assigned; the other regioisomer should necessarily be a pentacarbonyl derivative, as N coordination to chromium wouldn't be feasible in that case. Also, the one-pot reaction between **16** and nitrilimine **10c**, followed by PNO-oxidation yielded Δ^2-pyrazolinecarboxylate derivative **18** as a 1:1 mixture of diastereomers.

To improve the diastereoselectivity of the cycloaddition process, (–)-8-phenylmenthol-derived carbenes **19** were used in view of the excellent results obtained in related reactions of Fischer carbene complexes.[8,25] The reaction of carbenes **19** with nitrilimines followed by one-pot oxidation with PNO affords Δ^2-pyrazolines **20** in moderate yields (Scheme 5, Table 3). Only regioisomer **20** was obtained as a sole diastereomer in most of the cases. However, the cycloaddition of carbene **19a** with nitrilimine **10c** did not proceed at all (entry 6, Table 3), probably due to a combination of steric (originated by the 8-phenylmenthyloxy group) and electronic (electron-withdrawing group in **10c**) effects.

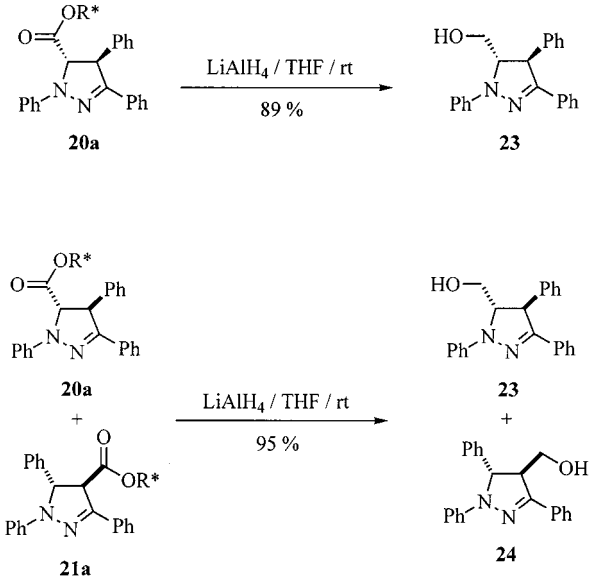
Table 3. One-pot synthesis of Δ^2-pyrazolines **20** from carbenes **19** and nitrilimines **10**

Entry	19	R^1	10	R^2	20/21[a]	Yield (%)[b]	*dr*[a]
1	**a**	Ph	**a**	Ph	**a** (>95:5)	55	92:8[c]
2[d]	**b**	2-furyl	**a**	Ph	**b** (>95:5)	35	>95:5
3	**a**	Ph	**b**	*p*-anisyl	**c** (>95:5)	40	>95:5
4	**b**	2-furyl	**b**	*p*-anisyl	**d** (>95:5)	73	>95:5
5	**c**	*p*-anisyl	**b**	*p*-anisyl	**e** (>95:5)	69	>95:5
6	**a**	Ph	**c**	CO_2Et	–	–[e]	

[a] Regio- and diastereomeric ratio determined by ^1H NMR (300 MHz): of the crude mixture. – [b] Isolated yields. – [c] Diastereomers not separated. – [d] Reaction carried out at 40 °C. – [e] Compound not detected by either TLC or ^1H NMR (300 MHz): of the crude residue after the starting material had been consumed.

To check the usefulness of Fischer carbene complexes in 1,3-dipolar cycloadditions with nitrilimines, (1*R*,3*R*,4*S*)-phenylmenthyl cinnamate **22** was also reacted with nitrilimine **10a**. In this case, both regioisomers **20a** and **21a** were obtained in quantitative yield in a 38:62 ratio as a mixture of diastereomers (*d.r.* = 32:68 for **20a** and 71:29 for **21a**) (Scheme 5). When the two methods for the synthesis of **20a**, starting from carbene **19a** or cinnamate **22**, are compared, the advantages of Fischer carbene complexes **19** in the preparation of Δ^2-pyrazolines **20** are obvious. The role of the metal pentacarbonyl moiety was, once more, crucial for the regio-[5a] and diastereoselectivity[8] of the [3+2] cycloaddition process.

To confirm the regiochemistry of the cycloaddition for α-unsubstituted (–)-8-phenylmenthol-derived carbene complexes **19**, Δ^2-pyrazoline **20a**, obtained from **19a** and diphenylnitrilimine **10a**, was converted into its alcohol derivative **23** by reduction with lithium aluminum hydride. In a separate reaction, a mixture of pyrazolines **20a** and **21a**, obtained from cinnamate **22** and diphenylnitrilimine **10a**, was also reduced to give a mixture of regioisomeric alcohols **23** and **24** (Scheme 6). ^1H,^{13}C-HMQC and ^1H,^{13}C-HMBC experiments, performed on **23** and on the mixture of **23** and **24**, helped to unequivocally ascertain the regiochemistry of **23**.



Scheme 6

The experiment that allows differentiation between the regioisomers is the ^1H,^{13}C-HMBC. Thus, the spectrum for compound **23** has no cross-peak for the CH_2 protons at δ = 3.86 and the *C*=N moiety (δ = 150.1), as would be expected for compound **23**; this is due to the four-bond distance between these nuclei, not present in regioisomer **24**

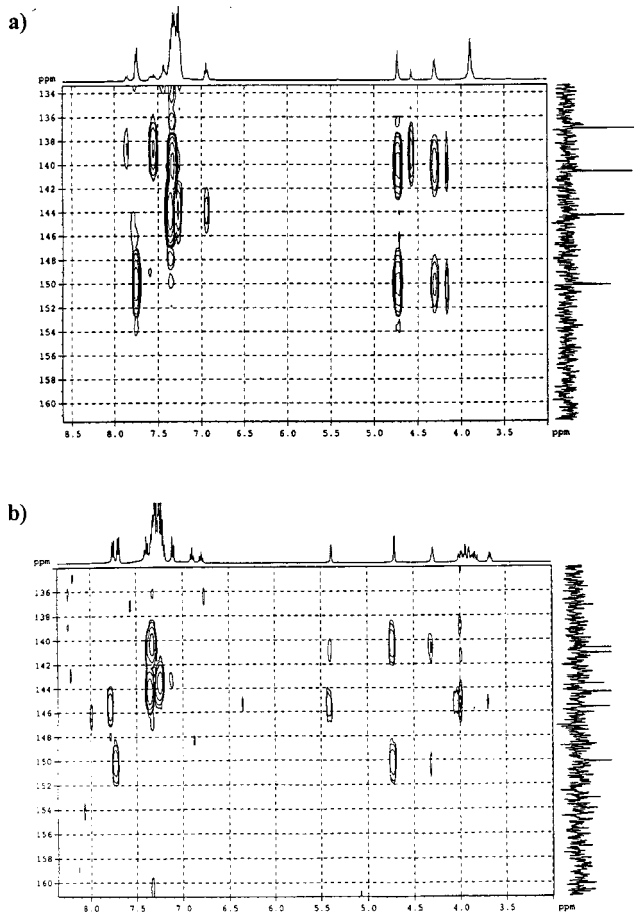
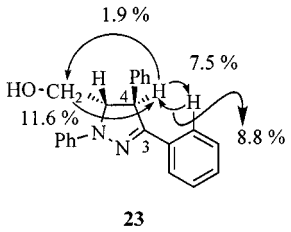


Figure 1. (a) $^{1}H,^{13}C$-HMBC spectrum for compound **23**; (b) $^{1}H,^{13}C$-HMBC spectrum for the mixture of **23** and **24**

(Figure 1, a). This is confirmed by the $^{1}H,^{13}C$-HMBC spectrum for the mixture of **23** and **24**. In effect, the correlation observed in Figure 1 (b) between the signals corresponding to the CH_2 protons (at δ = 4.00–3.68) and the *C*=N moiety (at δ = 145.8) is in good agreement with structure **24**, as it presents a $^{3}J_{CH}$ correlation peak between those nuclei. On the other hand, as pointed out before, the $^{4}J_{CH}$ correlation peak between those nuclei in structure **23** is usually too small to be observed.

NOE difference experiments performed on **23** also confirmed the proposed regiochemistry. Thus, upon irradiation of the hydrogen on C4 or the *ortho*-hydrogen atoms of the phenyl group at C3, reciprocal NOE enhancements were observed (Figure 2).



23

Figure 2. Representative NOE enhancements for compound **23**

The relative configuration in the Δ^2-pyrazoline ring of both adducts and esters was assigned to be *trans* on the basis of the values of the ^{1}H-NMR coupling constants for adduct **12a**, menthyl ester **14g** and (1*R*,3*R*,4*S*)-phenylmenthyl esters **20**.[26] This was later confirmed by the reciprocal NOE enhancements between the hydrogen on C4 and the exocyclic CH_2 on alcohol **23** (Figure 2). Thus, the cycloaddition is suprafacial as the stereochemical information of the dipolarophile is completely transferred to the cycloadduct.[27]

Several attempts to obtain crystals, to determine the absolute stereochemistry of the cycloadducts, either carbenes or esters, by X-ray structural analysis, were unsuccessful. Also, derivatization of compounds **20** or **23** did not lead to good crystalline samples. However, the absolute stereochemistry of cycloadducts **20** was proposed to be (4*R*,5*S*), on the basis of the model that assumes that, in the reactive conformation of **19**, the phenyl group on the chiral auxiliary shields the double bond upper face, inducing the dipole to selectively approach from the (*Si,Si*)-bottom face (Figure 3). This approach has been demonstrated by X-ray analysis for prior nucleophilic additions[25] and [3+2] dipolar cycloadditions[8a] to carbenes **19**.

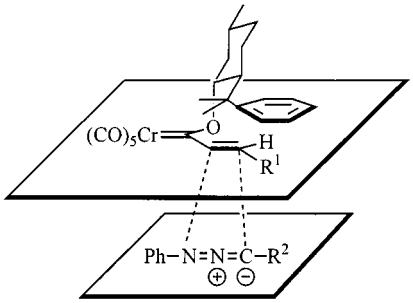


Figure 3. Postulated reactive conformation of **19**, in which the chiral auxiliary phenyl group shields the (*Re,Re*)-face of the double bond, inducing selective attack from the (*Si,Si*)-face

In summary, it should be pointed out that alkynyl Fischer carbene complexes react with nitrones to afford 2,3-dihydroisoxazoles which, in the case of *tert*-butyl alkynyl complexes, photochemically rearrange to yield β-enamino ketoaldehydes. For the alkenyl carbene complexes, oxidation is favored over cycloaddition, even when bulky substituents are introduced in the metal's coordination sphere. Finally, the [3+2] cycloaddition of enantiomerically pure Fischer alkenyl carbene complexes and nitrilimines described herein is a convenient synthesis of Δ^2-pyrazolines, in a highly regio- and diastereoselective manner.

Experimental Section

General Considerations: All reactions involving air-sensitive compounds were carried out under a N_2 atmosphere. – All common reagents and solvents were obtained from commercial suppliers and were used without any further purification unless otherwise indicated. *N*-methyl nitrones **2**[28] and hydrazonoyl halides **11**,[29] precursors of nitrilimines **10**, were prepared according to previously described procedures. Fischer carbene complexes **1**,[30] **8a**,[25b] **8b**,[31] **8c**,[8a] **16**,[8a] and **19a**,**b**[25b] were prepared as described. – Solvents were dried by standard methods. Hexane, ethyl acetate, and triethylamine were distilled before use. – TLC was performed on alu-

minum-backed plates coated with silica gel 60 with F_{254} indicator; the chromatograms were visualized under ultraviolet light and/or by staining with a Ce/Mo reagent [prepared by dissolving phosphomolybdic acid (2 g), cerium(IV) sulfate (1 g) and conc. sulfuric acid (10 mL) in H_2O (90 mL)] and subsequent heating. – Flash column chromatography was carried out on silica gel 60, 230–240 mesh. – Routine NMR measurements were recorded on Bruker AC-200 or AC-300 spectrometers. ^{1}H NMR: splitting pattern abbreviations are: s, singlet; br. s, broad singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet. ^{13}C NMR: multiplicities were determined by DEPT, abbreviations are: q, CH_3; t, CH_2; d, CH; s, quaternary carbons. In the cases where a mixture of diastereomers was observed, the abbreviation "min" refers to the signals assigned to the minor diastereomer and the abbreviation "maj" to the signals belonging to the major one; in the cases where nothing is specified, either it hasn't been possible to assign the signal to any of the diastereomers or it belongs to both of them. NOESY, HMQC, and HMBC experiments were carried out on a Bruker AMX-400 spectrometer. Standard pulse sequences were employed for the DEPT, ^{1}H,^{13}C-HMQC and ^{1}H,^{13}C-HMBC experiments. – FT-IR spectroscopy was performed with a Mattson 3000 FT-IR spectrometer. – High resolution mass spectra (HRMS) were obtained with a Finnigan Mat95 Mass Spectrometer. – Elemental analyses were carried out with a Perkin–Elmer 240 B microanalyzer.

Synthesis of β-Enaminoketoaldehydes 4. – General Procedure: Nitrone **2** (3.4 mmol) was added to a solution of *tert*-butylethynyl carbene complex **1** (2 mmol) in acetonitrile (20 mL) at room temperature and the mixture was stirred for five minutes. Solvent was evaporated and the residue was chromatographed on silica gel, with 30% (v/v) ethyl acetate in hexane as eluent. The red fraction was collected, solvents were evaporated under vacuum and the residue was dissolved in THF (50 mL). The solution was irradiated for 12 h with a bulb lamp and THF was removed under reduced pressure. Hexane was added and the suspension was filtered through celite. After the hexane was removed, the residue was purified by column chromatography on silica gel, with a 7:3 hexane/ethyl acetate mixture as eluent, to give compounds **4**.

2-*tert*-Butylcarbonyl-3-methylamino-3-phenyl-2-propenal (4a): Pale yellow oil; yield 32%. – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.04 (br s, 1 H, NH), 8.92 (s, 1 H), 7.60–7.45 (m, 5 H), 2.75 (d, J = 4.1 Hz, 3 H), 1.25 (s, 9 H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 208.6 (s), 185.5 (d), 171.0 (s), 132.5 (s), 129.8 (d), 128.8 (d), 128.1 (d), 113.0 (s), 44.2 (s), 31.8 (q), 27.1 (q). – MS (EI, 70 eV): *m*/*z* (%): 245 [M$^+$] (3), 188 (100), 160 (14), 118 (35). – $C_{15}H_{19}NO_2$: C 73.44, H 7.81, N 5.71; found: C 73.52, H 7.72, N 5.66.

2-*tert*-Butylcarbonyl-3-methylamino-3-(4-methylphenyl)-2-propenal (4b): Pale yellow oil; yield 31%. – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.05 (br s, 1 H, NH), 8.92 (s, 1 H), 7.45 (d, J = 7.0 Hz, 2 H), 7.33 (d, J = 7.0 Hz, 2 H), 2.75 (d, J = 5.0 Hz, 3 H), 2.47 (s, 3 H), 1.25 (s, 9 H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 208.7 (s), 185.5 (d), 172.3 (s), 139.6 (s), 129.3 (d), 128.2 (d), 113.1 (s), 44.2 (s), 31.8 (q), 27.1 (q), 20.9 (q). – MS (EI, 70 eV): *m*/*z* (%): 259 [M$^+$] (3), 202 (100), 174 (22), 132 (62), 115 (11). – $C_{16}H_{21}NO_2$: C 74.10, H 8.16, N 5.40; found: C 74.21, H 8.05, N 5.48.

2-*tert*-Butylcarbonyl-3-(4-methoxyphenyl)-3-methylamino-2-propenal (4c): Pale yellow oil; yield 37%. – ^{1}H NMR ([D$_6$]DMSO, 200 MHz): δ = 10.95 (br s, 1 H, NH), 8.92 (s, 1 H), 7.42 (d, J = 8.5 Hz, 2 H), 7.18 (d, J = 8.5 Hz, 2 H), 3.94 (s, 3 H), 2.81 (d, J = 4.9 Hz, 3 H), 1.25 (s, 9 H). – ^{13}C NMR ([D$_6$]DMSO, 50 MHz): δ = 209.0 (s), 185.4 (d), 171.2 (s), 160.4 (s), 130.2 (d), 124.4 (s), 114.1 (d), 113.3 (s), 55.3 (q), 44.2 (s), 31.8 (q), 27.1 (q). – MS (EI, 70 eV): *m*/*z* (%): 275 [M$^+$] (4), 218 (100), 190 (25), 148 (58). – $C_{16}H_{21}NO_3$: C 69.79, H 7.69, N 5.09; found: C 69.88, H 7.60, N 4.99.

2-*tert*-Butylcarbonyl-3-(4-dimethylaminophenyl)-3-methylamino-2-propenal (4d): Pale yellow oil; yield 43%. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.40 (br s, 1 H, NH), 8.95 (s, 1 H), 7.03 (d, J = 8.8 Hz, 2 H), 6.60 (d, J = 8.8 Hz, 2 H), 2.92 (s, 6 H), 2.77 (d, J = 5.1 Hz, 3 H), 1.05 (s, 9 H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 210.4 (s), 186.0 (d), 172.15 (s), 151.1 (s), 129.8 (d), 118.8 (s), 113.6 (s), 111.0 (d), 44.4 (s), 39.7 (q), 31.6 (q), 27.2 (q). – MS (EI, 70 eV): *m*/*z* (%): 288 [M$^+$] (10), 231 (100), 203 (25), 161 (12), 148 (18). – $C_{17}H_{24}N_2O_2$: C 70.80, H 8.39, N 9.71; found: C 70.86, H 8.32, N 9.76.

Synthesis of Carbene Complexes 9 and 19c: These compounds were prepared according to previously described methodology.[25b]

Pentacarbonyl{1-[(1*R,3*R**,4*S**)-menthyloxy]-*trans*-3-phenyl-2-propenylidene}tungsten(0) (9a):** Purple syrup; yield 62%. – R_f = 0.61 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 2957, 2063, 1977, 1927. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.92 (d, 1 H, J = 15.3 Hz), 7.61–7.55 (m, 2 H), 7.42–7.32 (m, 3 H), 7.04 (d, 1 H, J = 15.3 Hz), 4.95 (m, 1 H), 2.19–0.75 (m, 18 H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 302.6 (s), 203.3 (s), 197.6 (s), 144.5 (d), 134.5 (s), 131.6 (d), 130.7 (d), 129.1 (d), 93.6 (d), 48.1 (d), 42.0 (t), 34.1 (t), 31.1 (d), 26.8 (d), 24.1 (t), 21.9 (q), 21.4 (q), 17.2 (q).

Pentacarbonyl{*trans*-3-(2-furyl)-1-[(1*R,3*R**,4*S**)-menthyloxy]-2-propenylidene}tungsten(0) (9b):** Purple syrup; yield 65%. – R_f = 0.49 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 2958, 2062, 1927. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.86 (d, 1 H, J = 15.1 Hz), 7.62 (d, 1 H, J = 1.6 Hz), 6.88 (d, 1 H, J = 15.1 Hz), 6.86 (d, 1 H, J = 4.4 Hz), 6.54 (dd, 1 H, J = 4.4 and 1.6 Hz), 4.97 (m, 1 H), 2.21–2.14 (m, 1 H), 1.99–0.83 (m, 17 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 300.1 (s), 203.5 (s), 197.7 (s), 151.1 (s), 146.0 (d), 141.9 (d), 118.7 (d), 117.6 (d), 113.2 (d), 93.1 (d), 48.1 (d), 42.0 (t), 34.0 (t), 31.1 (d), 26.7 (d), 24.1 (t), 21.9 (q), 21.4 (q), 17.2 (q).

Pentacarbonyl{*trans*-3-(4-methoxyphenyl)-1-[(1*R*,3*R*,4*S*)-8-phenylmenthyloxy]-2-propenylidene}chromium(0) (19c): Purple syrup; yield 10%. – R_f = 0.21 (hexane/CH_2Cl_2 = 9:1). – FT-IR (neat, cm^{-1}): 2052, 1929. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.64 (d, 1 H, J = 15.2 Hz), 7.42–7.39 (m, 2 H), 7.30–7.27 (m, 2 H), 7.20–7.15 (m, 2 H), 6.94–6.88 (m, 3 H), 6.14 (d, 1 H, J = 15.2 Hz), 5.23 (m, 1 H), 3.88 (s, 3 H), 2.55 (m, 1 H), 2.15–2.10 (m, 1 H), 1.92–1.70 (m, 3 H), 1.42–0.89 (m, 3 H), 1.38 (s, 3 H), 1.33 (s, 3 H), 0.97 (d, 3 H, J = 6.2 Hz). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 325.0 (s), 223.9 (s), 217.1 (s), 161.7 (s), 151.0 (s), 139.3 (d), 131.4 (d), 128.6 (d), 128.0 (d), 126.9 (s), 125.4 (d), 125.0 (d), 114.4 (d), 91.4 (d), 55.3 (q), 52.6 (d), 43.5 (t), 39.6 (s), 34.5 (t), 31.2 (d), 28.0 (q), 26.6 (t), 25.2 (q), 21.7 (q). – MS (EI, 70 eV): *m*/*z* (%): 568 [M$^+$] (<5), 428 [M$^+$– 5 CO] (<5), 178 (35), 119 (100). – HRMS for $C_{26}H_{32}CrO_2$ [M – 5 CO]: calcd. 428.1808; found 428.1802.

Preparation of Δ^2-Pyrazolidine Carbenes 12, 13, or 17 by [3+2] Cycloaddition of Fischer Carbene Complexes 8, 9, or 16 with Nitrilimines 10. – General Procedure: Hydrazonoyl chloride **11** (1.8 equiv) and NEt_3 (1.4 mL, 10 mmol) were sequentially added to an approximately 0.2 M solution of alkenylcarbene **8**, **9**, or **16** (2 mmol). The resulting mixture was stirred at room temperature till disappearance of starting material was observed by TLC (see Table 2 for solvent employed and time required). SiO_2 (1 g) was then added, the solvent was evaporated under vacuum, and the residue was purified by flash chromatography over silica gel with hexane/AcOEt (50:1) as eluent. Adducts **12**, **13**, or **17**, orange syrups, were

isolated as mixtures of diastereoisomers that could not be separated.

Pentacarbonyl{[(4*R,5*S**)-4,5-dihydro-1,3,4-triphenyl-1*H*-pyrazol-5-yl][(1*R**,3*R**,4*S**)-menthyloxy]methylidene}chromium(0) (12a):** Orange syrup; yield 67%. – R_f = 0.43 (hexane/AcOEt = 50:1). – FT-IR (neat, cm^{-1}): 2060, 1946, 1925, 1599. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.69–7.66 (m, 4 H), 7.36–7.07 (m, 24 H), 6.90–6.83 (m, 2 H), 6.13 (d, 1 H, *J* = 2.6 Hz, min.), 6.03 (d, 1 H, *J* = 3.6 Hz, maj.), 5.17–5.02 (m, 2 H); 4.39 (d, 1 H, *J*= 2.6 Hz, min.), 4.34 (d, 1 H, *J* = 3.6 Hz, maj.), 2.33–0.26 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 347.6 (s, maj.), 346.0 (s, min.), 221.8 (s), 216.0 (s), 147.8 (s, min.), 147.2 (s, maj.), 144.7 (s, min.), 143.7 (s, maj.), 138.7 (s, maj.), 138.4 (s, min.), 131.5 (s, maj.), 131.2 (s, min.), 129.2 (d), 129.1 (d), 128.8 (d), 128.3 (d), 128.0 (d), 127.7 (d), 127.5 (d), 127.3 (d), 126.3 (d), 126.0 (d, maj.), 125.8 (d, min.), 119.8 (d, min.), 119.5 (d, maj.), 113.8 (d, min.), 112.6 (d, maj.), 92.9 (d, maj.), 92.7 (d, min.), 90.9 (d, min.), 90.7 (d, maj.), 55.8 (d, min.), 55.5 (d, maj.), 47.1 (d, min.), 46.7 (d, maj.), 40.7 (t, maj.), 39.7 (t, min.), 33.3 (t), 30.8 (d, maj.), 30.4 (d, min.), 25.4 (d, min.), 24.4 (d, maj.), 22.1 (t), 21.8 (q, maj.), 21.7 (q, min.), 21.1 (q, maj.), 20.0 (q, min.), 15.3 (q). – MS (EI, 70 eV): *m*/*z* (%): 628 [M^+– CO] (<5), 572 [M^+– 3 CO] (5), 516 [M^+– 5 CO] (6), 297 [$C_{21}H_{17}N_2$] (100). – $C_{37}H_{36}CrN_2O_6$: C 67.67, H 5.53, N 4.27; found: C 67.88, H 5.44, N 4.21.

Pentacarbonyl{[(4*R,5*S**)-4-(2-furyl)-4,5-dihydro-1,3-diphenyl-1*H*-pyrazol-5-yl]-[(1*R**,3*R**,4*S**)-menthyloxy]methylidene}chromium(0) (12b):** Orange syrup; yield 80%. – R_f = 0.62 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 2060, 1950, 1941. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.82–7.64 (m, 4 H), 7.46–6.82 (m, 18 H), 6.33–6.18 (m, 6 H), 5.08–5.05 (m, 2 H), 4.59–4.52 (m, 2 H), 2.32–0.29 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 347.3 (s, maj.), 345.7 (s, min.), 221.9 (s), 215.7 (s), 150.6 (s), 144.5 (s), 144.2 (s), 143.5 (s), 143.2 (s), 142.7 (d, maj.), 142.4 (d, min.), 131.4 (s, maj.), 131.2 (s, min.), 129.2 (d, maj.), 129.0 (d, min.), 128.4 (d), 126.2 (d), 126.0 (d), 125.8 (d), 125.6 (d), 119.9 (d), 119.6 (d), 113.7 (d, min.), 112.5 (d, maj.), 110.7 (d), 108.3 (d, maj.), 108.0 (d, min.), 92.9 (d), 88.3 (d, min.), 88.0 (d, maj.), 48.9 (d), 47.1 (d, min.), 46.7 (d, maj.), 40.7 (t, maj.), 39.8 (t, min.), 33.9 (t), 30.7 (d, maj.), 30.4 (d, min.), 25.4 (d, min.), 24.4 (d, maj.), 22.2 (t), 21.7 (q), 21.1 (q, maj.), 20.1 (q, min.), 15.4 (q). – $C_{34}H_{34}CrN_2O_7$: C 64.35, H 5.40, N 4.41; found: C 64.49, H 5.28, N 4.33.

Pentacarbonyl{[(4*R,5*S**)-3-ethoxycarbonyl-4,5-dihydro-1,4-diphenyl-1*H*-pyrazol-5-yl]-[(1*R**,3*R**,4*S**)-menthyloxy]methylidene}-chromium(0) (12g):** Orange syrup; yield 30%. – R_f = 0.30 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 2062, 1948, 1925, 1730, 1705. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.41–6.94 (m, 20 H), 6.21 (m, 2 H), 5.11 (m, 2 H), 4.35–4.12 (m, 6 H), 2.31–0.42 (m, 42 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 342.5 (s, maj.), 341.8 (s, min.), 221.4 (s), 215.5 (s, maj.), 215.4 (s, min.), 161.2 (s, maj.), 161.0 (s, min.), 142.6 (s, min.), 141.8 (s, maj.), 139.7 (s, min.), 139.1 (s, maj.), 138.6 (s, maj.), 138.4 (s, min.), 129.3 (d), 129.2 (d), 129.0 (d), 128.9 (d), 128.2 (d), 127.5 (d), 122.0 (d, min.), 121.7 (d, maj.), 114.8 (d, min.), 113.8 (d, maj.), 93.2 (d, maj.), 92.8 (d, min.), 90.8 (d, min.), 90.7 (d, maj.), 61.0 (t), 55.0 (d, min.), 54.3 (d, maj.), 47.1 (d, min.), 46.6 (d, maj.), 40.7 (t, maj.), 39.9 (t, min.), 33.4 (t, maj.), 33.3 (t, min.), 30.9 (d, maj.), 30.4 (d, min.), 25.8 (d, min.), 24.5 (d, maj.), 22.5 (t, min.), 22.2 (t, maj.), 21.9 (q, maj.), 21.6 (q, min.), 20.9 (q, maj.), 20.8 (q, min.), 15.9 (q, min.), 15.3 (q, maj.), 14.0 (q, maj.), 13.6 (q, min.). – MS (EI, 70 eV): *m*/*z* (%): 652 [M^+] (<5), 568 [M^+– 4 CO] (16), 512 [M^+– 5 CO] (27), 476 (69), 293 [$C_{18}H_{17}N_2O_2$] (100). – HRMS for $C_{29}H_{36}CrN_2O_3$ [*M* – 5 CO]: calcd. 512.2132; found 512.2139.

Pentacarbonyl{[(4*R,5*S**)-3-ethoxycarbonyl-4-(2-furyl)-4,5-dihydro-1-phenyl-1*H*-pyrazol-5-yl][(1*R**,3*R**,4*S**)-menthyloxy]methylidene}-tungsten(0) (13):** Compound not fully characterized; data obtained from the crude reaction mixture. – ^1H NMR (200 MHz, $CDCl_3$) δ = 7.69–7.61 (m, 2 H), 7.49–6.91 (m, 10 H), 6.47–6.22 (m, 4 H), 5.68–5.62 (m, 2 H), 4.83–4.65 (m, 2 H), 4.45–4.20 (m, 6 H), 2.09–0.69 (m, 42 H).

Tetracarbonyl{(4,5-dihydro-5-methyl-1,3-diphenyl-1*H*-pyrazol-5-yl)[(1*R,3*R**,4*S**)-menthyloxy]methylidene}chromium(0) (17):** Orange syrup; yield 60%. – R_f = 0.24 (hexane/AcOEt = 50:1). – FT-IR (neat, cm^{-1}): 2016, 1941, 1915, 1858, 1599, 1491, 1451, 1362, 1292; ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.97–7.15 (m, 20 H), 5.00 (m, 2 H), 3.42–3.05 (m, 4 H), 2.53–0.84 (m, 42 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 342.8 (s), 342.3 (s), 233.2 (s), 233.1 (s), 230.5 (s), 223.7 (s), 223.0 (s), 218.2 (s), 217.5 (s), 160.4 (s), 160.0 (s), 144.8 (s), 144.5 (s), 131.2 (d), 128.8 (d), 128.6 (d), 127.4 (d), 127.3 (d), 126.0 (d), 94.2 (s), 91.3 (d), 90.6 (d), 47.4 (d), 45.1 (t), 44.7 (t), 40.7 (t), 34.0 (t), 31.3 (d), 31.2 (d), 26.3 (d), 25.9 (d), 22.9 (t), 22.1 (q), 20.9 (q), 20.8 (q), 20.6 (q), 15.8 (q), 15.6 (q). – MS (EI, 70 eV): *m*/*z* (%): 566 [M^+] (<5), 538 [M^+– CO] (<5), 510 [M^+– 2 CO] (7), 482 [M^+– 3 CO] (<5), 454 [M^+– 4 CO] (8), 235 (100). – HRMS for $C_{31}H_{34}CrN_2O_5$: calcd. 566.1875; found 566.1873.

Preparation of Δ^2-Pyrazolidinecarboxylates 14, 18, or 20 by [3+2] Cycloaddition of Fischer Carbene Complexes 8, 9, 16, or 19 with Nitrilimines 10 Followed By One-Pot Oxidation. – General Procedure: Hydrazonoyl chloride **11** (1.8 equiv.) and NEt_3 (0.7 mL, 5 mmol) were sequentially added to an approximately 0.2 M solution of alkenylcarbene **8**, **9**, **16**, or **19** (1 mmol) and the resulting mixture was stirred at room temperature till disappearance of starting material was observed by TLC (see Table 2 and 3 and Schemes 3 and 5 for solvent employed and time required). Pyridine *N*-oxide (0.19 g, 2 mmol) was then added and the solution was stirred at room temperature for a 12–24 h period, till disappearance of the initially formed cycloadduct was observed by TLC. Solvents were then evaporated, the residue was dissolved in hexane/AcOEt (3:1, 20 mL) and exposed to sunlight till the solution turned almost colorless. The solution was then filtered through celite and the solvents were evaporated. The residue was purified by flash chromatography over silica gel with hexane/AcOEt = 50:1, 20:1, and 9:1 as sequential eluents. Esters **14**, **18**, or **20** were isolated as fluorescent syrups.[32,20,21] Optical rotations of these compounds could not be determined due to the fluorescence, as the solutions were not permeable to sodium lamp irradiation.

(1*R,3*R**,4*S**)-Menthyl (4*R**,5*S**)-4,5-Dihydro-1,3,4-triphenyl-1*H*-pyrazole-5-carboxylate (14a):** Fluorescent syrup; yield 80%. – R_f = 0.12 (hexane/AcOEt = 50:1). – FT-IR (neat, cm^{-1}): 1728, 1599, 1503. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.73–7.71 (m, 4 H), 7.34–7.19 (m, 24 H), 6.98–6.90 (m, 2 H), 4.85–4.75 (m, 6 H), 2.36–0.64 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.4 (s, maj.), 170.1 (s, min.), 148.8 (s, min.), 148.4 (s, maj.), 144.0 (s), 139.4 (s, maj.), 139.2 (s, min.), 131.4 (s), 129.2 (d), 129.1 (d), 129.0 (d), 128.3 (d), 127.8 (d), 127.3 (d), 126.3 (d), 126.2 (d), 119.7 (d), 113.1 (d), 112.9 (d), 75.8 (d, maj.), 75.7 (d, min.), 71.4 (d, maj.), 71.1 (d, min.), 57.3 (d, maj.), 57.2 (d, min.), 46.6 (d, min.), 46.4 (d, maj.), 40.2 (t), 33.9 (t), 31.2 (d), 26.1 (d, min.), 25.4 (d, maj.), 23.0 (t, min.), 22.8 (t, maj.), 21.9 (q), 20.7 (q, maj.), 20.5 (q, min.), 15.9 (q, min.), 15.6 (q, maj.). – MS (EI, 70 eV): *m*/*z* (%): 480 [M^+] (68), 342 (29), 297 [$C_{21}H_{17}N_2$] (100). – $C_{32}H_{36}N_2O_2$: C 79.97, H 7.55, N 5.83; found: C 80.06, H 7.42, N 5.91.

(1*R,3*R**,4*S**)-Menthyl (4*R**,5*S**)-4-(2-Furyl)-4,5-dihydro-1,3-diphenyl-1*H*-pyrazole-5-carboxylate (14b):** Fluorescent syrup; yield

99%. – R_f = 0.39 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 1728, 1599, 1503. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.92–7.82 (m, 4 H), 7.48–7.27 (m, 16 H), 7.03–6.96 (m, 2 H), 6.36–6.35 (m, 2 H), 6.26–6.24 (m, 2 H), 5.12–5.01 (m, 4 H), 4.95–4.78 (m, 2 H), 2.39–0.71 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 169.9 (s, maj.), 169.6 (s, min.), 150.8 (s), 145.8 (s, min.), 145.3 (s, maj.), 144.0 (s, min.), 143.9 (s, maj.), 142.4 (d), 131.2 (s), 128.9 (d), 128.8 (d), 128.4 (d), 128.2 (d), 125.9 (d), 119.7 (d), 113.0 (d, min.), 112.9 (d, maj.), 110.5 (d), 107.6 (d), 75.8 (d), 68.6 (d, maj.), 68.4 (d, min.), 50.2 (d, maj.), 50.0 (d, min.), 46.4 (d, min.), 46.3 (d, maj.), 40.0 (t, maj.), 39.9 (t, min.), 33.7 (t), 31.0 (d), 25.9 (d, min.), 25.2 (d, maj.), 22.8 (t, min.), 22.6 (t, maj.), 21.7 (q), 20.5 (q, maj.), 20.4 (q, min.), 15.7 (q, min.), 15.4 (q, maj.). – MS (EI, 70 eV): *m/z* (%): 470 [M^+] (42), 332 (28), 287 [$C_{19}H_{15}N_2O$] (100). – HRMS for $C_{30}H_{34}N_2O_3$: calcd. 470.2569; found 470.2562.

(1*R,3*R**,4*S**)-Menthyl (4*R**,5*S**)-4,5-Dihydro-4-(4-methoxyphenyl)-1,3-diphenyl-1*H*-pyrazole-5-carboxylate (14c):** Fluorescent syrup; yield 82%. – R_f = 0.19 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 1726, 1599, 1505. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.76–7.72 (m, 4 H), 7.36–7.22 (m, 18 H), 6.94–6.85 (m, 6 H), 4.82–4.71 (m, 6 H), 3.78 (s, 6 H), 2.09–0.67 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.4 (s, maj.), 170.1 (s, min.), 159.0 (s), 149.0 (s, min.), 148.6 (s, maj.), 144.2 (s, min.), 144.1 (s, maj.), 131.4 (s, maj.), 131.2 (s, min.), 129.0 (d), 128.9 (d), 128.3 (d), 128.2 (d), 126.2 (d), 126.1 (d), 119.5 (d), 114.5 (d), 113.0 (d, min.), 112.8 (d, maj.), 75.7 (d, maj.), 75.6 (d, min.), 71.4 (d, maj.), 71.2 (d, min.), 56.53 (d, maj.), 56.5 (d, min.), 55.0 (q), 46.6 (d, min.), 46.4 (d, maj.), 40.1 (t), 33.9 (t), 31.2 (d), 26.0 (d, min.), 25.4 (d, maj.), 23.0 (t, min.), 22.7 (t, maj.), 21.8 (q), 20.6 (q, maj.), 20.4 (q, min.), 15.8 (q, min.), 15.6 (q, maj.). – MS (EI, 70 eV): *m/z* (%): 510 [M^+] (50), 372 (16), 327 [$C_{22}H_{19}N_2O$] (100). – HRMS for $C_{33}H_{38}N_2O_3$: calcd. 510.2882; found 510.2892.

(1*R,3*R**,4*S**)-Menthyl (4*R**,5*S**)-4,5-Dihydro-3-(4-methoxyphenyl)-1,4-diphenyl-1*H*-pyrazole-5-carboxylate (14d):** Fluorescent syrup; yield 80%. – R_f = 0.22 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 1726, 1599, 1501, 1389. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.67 (d, 4 H, *J* = 8.5 Hz), 7.37–7.19 (m, 18 H), 6.96–6.88 (m, 2 H), 6.86 (d, 4 H, *J* = 8.5 Hz), 4.84–4.74 (m, 6 H), 3.80 (s, 6 H), 2.42–0.67 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.5 (s, maj.), 170.2 (s, min.), 159.8 (s), 148.7 (s, min.), 148.4 (s, maj.), 144.4 (s, maj.), 144.3 (s, min.), 139.5 (s, maj.), 139.3 (s, min.), 129.2 (d), 129.0 (d), 128.9 (d), 127.7 (d), 127.3 (d), 124.1 (s), 119.3 (d), 113.7 (d), 112.9 (d, min.), 112.8 (d, maj.), 75.8 (d, maj.), 75.6 (d, min.), 71.3 (d, maj.), 71.1 (d, min.), 57.5 (d, maj.), 57.4 (d, min.), 55.0 (q), 46.6 (d, min.), 46.4 (d, maj.), 40.2 (t), 33.9 (t), 31.2 (d), 26.1 (d, min.), 25.4 (d, maj.), 23.0 (t, min.), 22.8 (t, maj.), 21.8 (q), 20.6 (q, maj.), 20.5 (q, min.), 15.9 (q, min.), 15.6 (q, maj.). – MS (EI, 70 eV): *m/z* (%): 510 [M^+] (27), 372 (15), 327 [$C_{22}H_{19}N_2O$] (100). – HRMS for $C_{33}H_{38}N_2O_3$: calcd. 510.2882; found 510.2873.

(1*R,3*R**,4*S**)-Menthyl (4*R**,5*S**)-4-(2-Furyl)-4,5-dihydro-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (14e):** Fluorescent syrup; yield 87% (*d.r.* ca. 1:1). – R_f = 0.19 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 1728, 1599, 1501, 1387, 1256. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.70–7.66 (m, 4 H), 7.38–7.16 (m, 12 H), 6.92–6.87 (m, 4 H), 6.30 (m, 2 H), 6.18 (m, 2 H), 4.98–4.70 (m, 6 H), 3.83 (s, 6 H), 2.08–0.57 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.2 (s), 169.9 (s), 159.9 (s), 151.1 (s), 145.9 (s), 145.5 (s), 144.5 (s), 144.3 (s), 142.4 (d), 129.0 (d), 128.9 (d), 127.5 (d), 124.0 (s), 119.6 (d), 113.8 (d), 113.1 (d), 112.9 (d), 110.6 (d), 107.7 (d), 75.9 (d), 68.7 (d), 68.6 (d), 55.1 (q), 50.6 (d), 50.4 (d), 46.5 (d), 46.4 (d), 40.2 (t), 40.1 (t), 33.9 (t), 31.2 (d), 26.1 (d), 25.4 (d), 23.0 (t), 22.8 (t), 21.8 (q), 20.6 (q), 15.9 (q), 15.6 (q). – MS (EI, 70 eV): *m/z* (%): 500 [M^+] (47), 362 (19), 317 [$C_{20}H_{17}N_2O_2$] (100). – HRMS for $C_{31}H_{36}N_2O_4$: calcd. 500.2675; found 500.2665.

(1*R,3*R**,4*S**)-Menthyl (4*R**,5*S**)-4,5-Dihydro-3,4-bis(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (14f):** Fluorescent syrup; yield 82% (*d.r.* ca. 1:1). – R_f = 0.16 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 1726, 1599, 1512, 1501, 1254, 1177. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.65 (d, 4 H, *J* = 8.4 Hz), 7.36–7.10 (m, 12 H), 6.90–6.83 (m, 10 H), 4.75–4.68 (m, 6 H), 3.79 (s, 12 H), 2.15–0.64 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.6 (s), 170.3 (s), 159.7 (s), 159.0 (s), 149.0 (s), 148.7 (s), 144.5 (s), 144.4 (s), 131.5 (s), 131.4 (s), 129.0 (d), 128.4 (d), 127.8 (d), 124.1 (s), 119.3 (d), 114.5 (d), 113.7 (d), 112.9 (d), 112.8 (d), 75.7 (d), 75.6 (d), 71.4 (d), 71.2 (d), 56.8 (d), 55.0 (q), 46.6 (d), 46.4 (d), 40.2 (t), 33.9 (t), 31.2 (d), 26.1 (d), 25.4 (d), 23.0 (t), 22.8 (t), 21.8 (q), 20.6 (q), 20.5 (q), 15.9 (q), 15.6 (q). – MS (EI, 70 eV): *m/z* (%): 540 [M^+] (36), 402 (14), 357 [$C_{23}H_{21}N_2O_2$] (100). – HRMS for $C_{34}H_{40}N_2O_4$: calcd. 540.2988; found 540.2984.

3-Ethyl 5-(1*R,3*R**,4*S**)-Menthyl (4*R**,5*S**)-4,5-Dihydro-1,4-diphenyl-1*H*-pyrazole-3,5-dicarboxylate (14g):** Fluorescent syrup; yield 55%. – R_f = 0.25 (hexane/AcOEt = 9:1). – FT-IR (neat, cm^{-1}): 1728, 1707, 1601, 1557, 1503. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.38–7.18 (m, 18 H), 7.02–6.97 (m, 2 H), 4.87 (d, 1 H, *J* = 5.0 Hz, maj.), 4.84 (d, 1 H, *J* = 4.4 Hz, min.), 4.74 (m, 1 H, min.), 4.69 (m, 1 H, maj.), 4.61 (d, 1 H, *J* = 5.0 Hz, maj.), 4.58 (d, 1 H, *J* = 4.4 Hz, min.), 4.27–4.21 (t, 4 H, *J* = 7.0 Hz), 2.32–0.56 (m, 42 H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.0 (s, maj.), 168.7 (s, min.), 161.5 (s), 142.0 (s), 141.0 (s, min.), 140.7 (s, maj.), 139.3 (s, maj.), 139.2 (s, min.), 129.1 (d, min.), 129.0 (d, maj.), 127.9 (d), 127.0 (d), 121.8 (d), 114.1 (d, min.), 114.0 (d, maj.), 76.2 (d, maj.), 76.1 (d, min.), 71.6 (d, maj.), 71.2 (d, min.), 61.0 (t), 55.7 (d, maj.), 55.5 (d, min.), 46.5 (d, min.), 46.4 (d, maj.), 40.2 (t, maj.), 40.1 (t, min.), 33.9 (t), 31.2 (d, maj.), 31.2 (d, min.), 26.2 (d, min.), 25.3 (d, maj.), 23.0 (t, min.), 22.7 (t, maj.), 21.8 (q, min.), 20.6 (q, maj.), 15.9 (q, min.), 15.5 (q, maj.), 14.0 (q). – MS (EI, 70 eV): *m/z* (%): 476 [M^+] (80), 249 (81), 221 [$C_{15}H_{13}N_2$] (100). – HRMS for $C_{29}H_{36}N_2O_4$: calcd. 476.2675; found 476.2669.

3-Ethyl 5-(1*R,3*R**,4*S**)-Menthyl 4,5-Dihydro-5-methyl-1-phenyl-1*H*-pyrazole-3,5-dicarboxylate (18):** Fluorescent syrup; yield 31%. – R_f = 0.50 (hexane/AcOEt = 9:1). – FT-IR (neat, cm^{-1}): 1730, 1703, 1601, 1564. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.29–6.95 (m, 10 H), 4.78–4.55 (m, 2 H), 4.42–4.30 (dq, 4 H), 3.52 (d, 2 H, *J* = 17.6 Hz), 3.18 (d, 1 H, *J* = 17.6 Hz), 3.16 (d, 1 H, *J* = 17.6 Hz), 2.10–0.48 (m, 48 H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 172.1 (s), 171.9 (s), 162.5 (s), 141.34 (s), 141.3 (s), 136.0 (s), 128.9 (d), 128.85 (d), 122.1 (d), 121.8 (d), 115.7 (d), 115.0 (d), 73.6 (d), 70.8 (s), 70.5 (s), 61.3 (t), 47.1 (t), 46.9 (t), 46.6 (d), 46.4 (d), 40.2 (t), 39.8 (t), 34.0 (t), 33.9 (t), 31.3 (d), 31.2 (d), 26.2 (d), 25.1 (d), 23.0 (t), 22.7 (t), 21.9 (q), 21.5 (q), 20.7 (q), 20.6 (q), 15.8 (q), 15.6 (q), 14.3 (q). – MS (EI, 70 eV): *m/z* (%): 414 [M^+] (10), 231 (100), 185 (78). – HRMS for $C_{24}H_{34}N_2O_4$: calcd. 414.2519; found 414.2522.

(1*R*,3*R*,4*S*)-8-Phenylmenthyl (4*R*,5*S*)-4,5-Dihydro-1,3,4-triphenyl-1*H*-pyrazole-5-carboxylate (20a): Fluorescent syrup; yield 55%. – R_f = 0.26 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 1744, 1724, 1599, 1503. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.87–6.83 (m, 20 H), 4.86 (m, 1 H), 4.52 (d, 1 H, *J* = 4.0 Hz), 4.12 (d, 1 H, *J* = 4.0 Hz), 2.34–0.82 (m, 8 H), 1.31 (s, 3 H), 1.25 (s, 3 H), 0.89 (d, 3 H, *J* = 6.4 Hz). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 169.1 (s), 150.9 (s), 148.3 (s), 144.1 (s), 139.4 (s), 131.5 (s), 129.1 (d), 128.9 (d), 128.3 (d), 127.9 (d), 127.6 (d), 127.3 (d), 126.2 (d), 125.2 (d), 119.6 (d), 113.3 (d), 76.3 (d), 70.5 (d), 56.4 (d), 49.9 (d), 41.1 (t), 39.6 (s), 34.3 (t), 31.1 (d), 27.2 (q), 26.5 (t), 26.0 (q), 21.6 (q). – MS

(EI, 70 eV): *m/z* (%): 556 [M^+] (23), 342 (42), 297 [$C_{21}H_{17}N_2$] (100). – HRMS for $C_{38}H_{40}N_2O_2$: calcd. 556.3090; found 556.3092. – $C_{38}H_{40}N_2O_2$: C 81.98, H 7.24, N 5.03; found: C 82.09, H 7.12, N 4.96.

(1*R*,3*R*,4*S*)-8-Phenylmenthyl (4*R*,5*S*)-4-(2-Furyl)-4,5-dihydro-1,3-diphenyl-1*H*-pyrazole-5-carboxylate (20b): Fluorescent syrup; yield 35%. – R_f = 0.26 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 1744, 1724, 1599, 1505, 1497. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.69–6.91 (m, 16 H), 6.32 (m, 1 H), 6.11 (m, 1 H), 4.84 (m, 1 H), 4.66 (d, 1 H, *J* = 4.3 Hz), 4.35 (d, 1 H, *J* = 4.3 Hz), 2.65–0.75 (m, 8 H), 1.29 (s, 3 H), 1.24 (s, 3 H), 0.84 (d, 3 H, *J* = 6.5 Hz). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 168.9 (s), 151.2 (s), 150.9 (s), 145.6 (s), 144.1 (s), 142.3 (d), 131.4 (s), 128.9 (d), 128.5 (d), 128.3 (d), 127.9 (d), 126.0 (d), 125.2 (d), 125.1 (d), 119.8 (d), 113.5 (d), 110.6 (d), 107.5 (d), 76.5 (d), 68.1 (d), 49.8 (d), 49.5 (d), 41.0 (t), 39.7 (s), 34.2 (t), 31.1 (d), 27.0 (q), 26.6 (t), 26.4 (q), 21.6 (q). – MS (EI, 70 eV): *m/z* (%): 546 [M^+] (41), 332 (49), 287 [$C_{19}H_{15}N_2O$] (100). – HRMS for $C_{36}H_{38}N_2O_3$: calcd. 546.2882; found 546.2883. – $C_{36}H_{38}N_2O_3$: C 79.09, H 7.01, N 5.12; found: C 79.18, H 7.12, N 4.97.

(1*R*,3*R*,4*S*)-8-Phenylmenthyl (4*R*,5*S*)-4,5-Dihydro-3-(4-methoxyphenyl)-1,4-diphenyl-1*H*-pyrazole-5-carboxylate (20c): Fluorescent syrup; yield 40%. – FT-IR (neat, cm^{-1}): 1742, 1724, 1599, 1501, 1454, 1254. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.56 (d, 2 H, *J* = 8.7 Hz), 7.31–7.10 (m, 13 H), 6.92–6.84 (m, 2 H), 6.78 (d, 2 H, *J* = 8.7 Hz), 4.82 (m, 1 H), 4.47 (d, 1 H, *J* = 3.6 Hz), 4.09 (d, 1 H, *J* = 3.6 Hz), 3.76 (s, 3 H), 2.06–0.78 (m, 8 H), 1.28 (s, 3 H), 1.22 (s, 3 H), 0.85 (d, 3 H, *J* = 6.8 Hz). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.3 (s), 159.7 (s), 150.9 (s), 148.4 (s), 144.4 (s), 139.5 (s), 129.1 (d), 128.9 (d), 127.9 (d), 127.7 (d), 127.6 (d), 127.3 (d), 125.1 (d), 124.2 (s), 119.2 (d), 113.7 (d), 113.2 (d), 76.2 (d), 70.5 (d), 56.7 (d), 55.1 (q), 49.9 (d), 41.1 (t), 39.7 (s), 34.3 (t), 31.1 (d), 27.1 (q), 26.6 (t), 26.3 (q), 21.6 (q). – MS (EI, 70 eV): *m/z* (%): 586 [M^+] (41), 372 (43), 327 [$C_{22}H_{19}N_2O$] (100). – HRMS for $C_{39}H_{42}N_2O_3$: calcd. 586.3195; found 586.3195. – $C_{39}H_{42}N_2O_3$: C 79.83, H 7.21, N 4.77; found: C 80.02, H 7.34, N 4.65.

(1*R*,3*R*,4*S*)-8-Phenylmenthyl (4*R*,5*S*)-4-(2-Furyl)-4,5-dihydro-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (20d): Fluorescent syrup; yield 73%. – R_f = 0.14 (hexaneAcOEt = 20:1). – FT-IR (neat, cm^{-1}): 1744, 1724, 1599, 1501, 1391, 1254, 1179. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.68 (d, 2 H, *J* = 8.9 Hz), 7.42–6.81 (m, 13 H), 6.36 (dd, 1 H, *J* = 3.2 and 1.9 Hz), 6.15 (d, 1 H, *J* = 3.2 Hz), 4.88 (m, 1 H), 4.70 (d, 1 H, *J* = 4.4 Hz), 4.40 (d, 1 H, *J* = 4.4 Hz), 3.83 (s, 3 H), 2.36–0.87 (m, 8 H), 1.35 (s, 3 H), 1.29 (s, 3 H), 0.89 (d, 3 H, *J* = 6.4 Hz). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 169.0 (s), 159.9 (s), 151.3 (s), 150.8 (s), 145.6 (s), 144.4 (s), 142.2 (d), 128.8 (d), 127.9 (d), 127.5 (d), 125.2 (d), 125.1 (d), 124.1 (s), 119.5 (d), 113.7 (d), 113.3 (d), 110.6 (d), 107.4 (d), 76.4 (d), 68.1 (d), 55.1 (q), 49.74 (d), 49.7 (d), 40.9 (t), 39.7 (s), 34.2 (t), 31.0 (d), 26.8 (q), 26.5 (q), 26.5 (t), 21.5 (q). – MS (EI, 70 eV): *m/z* (%): 576 [M^+] (52), 362 (76), 317 [$C_{20}H_{17}N_2O_2$] (100). – HRMS for $C_{37}H_{40}N_2O_4$: calcd. 576.2988; found 576.2990. – $C_{37}H_{40}N_2O_4$: C 77.06, H 6.99, N 4.86; found: C 77.17, H 6.88, 4.97.

(1*R*,3*R*,4*S*)-8-Phenylmenthyl (4*R*,5*S*)-4,5-Dihydro-3,4-bis(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (20e): Fluorescent syrup; yield 69%. – R_f = 0.27 (hexane/AcOEt = 9:1). – FT-IR (neat, cm^{-1}): 1742, 1724, 1599, 1501, 1252. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.58 (d, 2 H, *J* = 8.5 Hz), 7.38–6.78 (m, 16 H), 4.83 (m, 1 H), 4.48 (d, 1 H, *J* = 3.9 Hz), 4.14 (d, 1 H, *J* = 3.9 Hz), 3.82 (s, 3 H), 3.78 (s, 3 H), 2.12–0.82 (m, 8 H), 1.29 (s, 3 H), 1.25 (s, 3 H), 0.86 (d, 3 H, *J* = 6.4 Hz). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 169.4 (s), 159.7 (s), 159.0 (s), 150.8 (s), 148.6 (s), 144.5 (s), 131.6 (s), 128.8 (d), 128.4 (d), 127.8 (d), 127.7 (d), 125.2 (d), 125.1 (d), 124.2 (s), 119.2 (d), 114.4 (d), 113.7 (d), 113.2 (d), 76.3 (d), 70.7 (d), 56.0 (d), 55.2 (q), 55.1 (q), 49.9 (d), 41.1 (t), 39.7 (s), 34.3 (t), 31.1 (d), 26.7 (q), 26.6 (t), 21.6 (q). – MS (EI, 70 eV): *m/z* (%): 616 [M^+] (77), 402 (41), 357 [$C_{23}H_{21}N_2O_2$] (100). – $C_{40}H_{44}N_2O_4$: C 77.89, H 7.19, N 4.54; found: C 77.96, H 7.08, N 4.45.

Preparation of Δ²-Pyrazolidine Esters 14a,g by Oxidation of Carbenes 12a,g: Pyridine *N*-oxide (0.19 g, 2 mmol) was added to a solution of carbene **12a** or **12g** (1 mmol) in dry THF (10 mL); the reaction mixture was stirred at room temperature for a 12–24 h period, till disappearance of the carbene was observed by TLC. Solvents were then evaporated, the residue was dissolved in hexane/AcOEt (3:1, 20 mL) and the solution was exposed to sunlight until it turned almost colorless. The solution was then filtered through celite and solvents were evaporated. The residue was purified as described before to give esters **14a** or **14g** in the yields reported in Table 2.

Cycloaddition of (1*R*,3*R*,4*S*)-8-Phenylmenthyl Cinnamate 22 with Diphenylnitrilimine 10a: A solution of (1*R*,2*S*,5*R*)-8-phenylmenthyl cinnamate **22** (0.36 g, 1 mmol) and diphenylnitrilimine – generated in situ by treatment of hidrazonoyl chloride **11a** (0.42 g, 1.8 mmol) with NEt_3 (0.7 mL, 5 mmol), as described previously – in THF/acetone (1:1, 5 mL) was stirred for 48 h at room temperature. After solvents were evaporated and the residue was purified by flash chromatography, a mixture of two inseparable regioisomeric cycloadducts **20a** and **21a** was obtained (0.56 g, quant.).

(1*R*,3*R*,4*S*)-8-Phenylmenthyl (4*R,5*S**)-4,5-Dihydro-1,3,4-triphenyl-1*H*-pyrazole-5-carboxylate (20a) and (1*R*,3*R*,4*S*)-8-Phenylmenthyl (4*R**,5*S**)-4,5-Dihydro-1,3,5-triphenyl-1*H*-pyrazole-4-carboxylate (21a):** Fluorescent syrup; yield quant. (**20a/21a:** 38:62). – R_f = 0.26 (hexane/AcOEt = 20:1). – FT-IR (neat, cm^{-1}): 1726, 1599, 1503, 1495. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.88–6.92 (m, 80 H), 5.81 (d, 1 H, *J* = 5.4 Hz, maj. regio.-maj. diast.), 5.41 (d, 1 H, *J* = 4.9 Hz, maj. regio.-min. diast.), 5.00 (d, 1 H, *J* = 3.8 Hz, min. regio.-maj. diast.), 5.02–4.84 (m, 4 H), 4.63 (d, 1 H, *J* = 4.0 Hz, min. regio.-min. diast.), 4.37 (d, 1 H, *J* = 3.8 Hz, min. regio.-maj. diast.), 4.20 (d, 1 H, *J* = 4.0 Hz, min. regio.-min. diast.), 3.86 (d, 1 H, *J* = 4.9 Hz, maj. regio.-min. diast.), 3.71 (d, 1 H, *J* = 5.4 Hz, maj. regio.-maj. diast.), 2.42–0.48 (m, 68 H). – MS (EI, 70 eV): *m/z* (%): 556 [M^+] (46), 510 (20), 342 (58), 327 (80), 297 [$M^+ - CO_2R^*$] (100).

Reduction of Cycloadducts 20a and 20a + 21a: $LiAlH_4$ (1.95 mL, 1.0 M in THF) was added to a solution of cycloadduct **20a** or to the mixture of cycloadducts **20a** and **21a** (0.83 g, 1.5 mmol) in THF (20 mL) at 0 °C and the reaction was stirred at room temperature for 12 h. After it was checked by TLC that the starting material had disappeared, the reaction was carefully hydrolyzed by sequential addition of H_2O (2 mL), 3 N NaOH (2 mL) and H_2O (6 mL). The resulting suspension was filtered through celite and the filtrate was dried with anhydrous Na_2SO_4. Finally, the solvent was evaporated under vacuum and the residue was purified by flash chromatography over silica gel with hexane/AcOEt = 20:1, 9:1, and 5:1 as sequential eluents to yield alcohol **23** (0.44 g, 89%) or the regioisomeric mixture of **23** and **24** (0.47 g, 95%), as fluorescent syrups. The chiral auxiliary employed in the cycloaddition process, (–)-8-phenylmenthol, was almost quantitatively recovered with high purity during the chromatographic purification.

(4*R*,5*S*)-4,5-Dihydro-5-hydroxymethyl-1,3,4-triphenyl-1*H*-pyrazole (23): Fluorescent syrup; yield 89%. – R_f = 0.37 (hexane/AcOEt = 5:1). – FT-IR (neat, cm^{-1}): 3500–3300 (OH), 1597, 1493. – ^1H

NMR ($CDCl_3$, 200 MHz): δ = 7.79–7.74 (m, 2 H), 7.47–7.25 (m, 12 H), 6.98–6.90 (m, 1 H), 4.73 (d, 1 H, *J* = 4.0 Hz), 4.29 (ddd, 1 H, *J* = 5.2, 4.0 and 3.4 Hz), 3.86 (m, 2 H), 2.45 (br s, 1 H, OH). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 150.1 (s), 144.3 (s), 140.6 (s), 131.7 (s), 129.2 (d), 129.0 (d), 128.2 (d), 128.1 (d), 127.3 (d), 127.2 (d), 126.3 (d), 119.3 (d), 113.2 (d), 71.1 (d), 61.5 (t), 54.5 (d). – MS (EI, 70 eV): *m/z* (%): 328 [M^+] (80), 297 [$C_{21}H_{17}N_2$] (100). – HRMS for $C_{22}H_{20}N_2O$: calcd. 328.1576; found 328.1573. – $C_{22}H_{20}N_2O$: C 80.46, H 6.14, N 8.53; found: C 80.58, H 6.22, N 8.42.

Mixture of Regioisomers. (4*R,5*S**)-4,5-Dihydro-5-hydroxymethyl-1,3,4-triphenyl-1*H*-pyrazole (23) and (4*R**,5*S**)-4,5-Dihydro-4-hydroxymethyl-1,3,5-triphenyl-1*H*-pyrazole (24):** Fluorescent syrup; yield 95% (**23/24**: 38:62). – R_f = 0.37 (hexane/AcOEt = 5:1). – FT-IR (neat, cm^{-1}): 3500–3300 (OH), 1597, 1503, 1495. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.79–7.73 (m, 4 H), 7.42–7.13 (m, 24 H), 6.97–6.81 (m, 2 H), 5.41 (d, 1 H, *J* = 3.4 Hz, maj.), 4.73 (d, 1 H, *J* = 4.0 Hz, min.), 4.29 (ddd, 1 H, *J* = 5.2, 4.0 and 3.4 Hz, min.), 4.00–3.68 (m, 4 H + 1 H, maj.); 2.20–2.00 (br s, 2 H, OH). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 150.2 (s, min.), 145.8 (s, maj.), 144.4 (s, min.), 143.7 (s, maj.), 141.1 (s, maj.), 140.7 (s, min.), 131.9 (s, maj.), 131.7 (s, min.), 129.2 (d), 129.1 (d), 129.0 (d), 128.9 (d), 128.6 (d), 128.4 (d), 128.3 (d), 127.4 (d), 127.2 (d), 126.3 (d), 125.8 (d), 125.6 (d), 119.4 (d, min.), 118.9 (d, maj.), 113.3 (d, min.), 112.9 (d, maj.), 71.1 (d, min.), 67.2 (d, maj.), 62.2 (t, maj.), 61.7 (t, min.), 58.6 (d, maj.), 54.6 (d, min.). – MS (EI, 70 eV): *m/z* (%): 328 [M^+], (39), 297 [$C_{21}H_{17}N_2$] (100).

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