Stereoselective Synthesis of Seven-Membered Carbocycles from 2-Amino-1,3-butadienes and Vinyl Chromium Fischer-Type Carbenes

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Abstract: Seven-membered ring carbocycles are prepared by reaction of easily avaliable 2-amino-1,3-butadienes with vinyl Fischer carbenes. Hydrolysis of the cycloadduct initially formed gives rise to cyclohepta-1,3-diones with total regio- and stereoselectivity in a one-pot process. When 2-aminobutadienes bearing a prolinol derivative as a chiral auxiliary are used, the corresponding cyclic diketones are obtained with very high enantiomeric excesses. The absolute configuration of the stereogenic centers generated was determined with the aid of ROESY and CD measurements.

Introduction

The preparation of functionalized seven-membered carbocycles, in a stereoselective manner, has been an area of considerable interest because the cycloheptane moiety is present in a variety of natural products.[1] The most general stereoselective approaches have been through expansion of six-membered rings,[2] annulation reactions of dienes and allyl cations[3] or nucleophilic vinylcarbenes,[4] annulations of heterocyclic betains and alkenes,[5] intramolecular cyclizations of unsaturated carbonylic compounds promoted by metal complexes,[1a,6] transition metal catalyzed [5 + 2] cycloadditions of vinylcyclopropanes and alkynes,[7] and the Cope rearrangement of *cis*-divinylcyclopropanes.[8] Conceptually, the latter reaction should lead to cycloheptadienes with high stereoselectivities and predictable stereochemistry, since they are formed in a concerted process through a boat transition state.

The preparation of *cis*-divinylcyclopropanes can be achieved by the cyclopropanation reaction of vinylcarbenes and 1,3-dienes, but in many cases, the cyclopropanes thus prepared are accompanied by other side products arising from the rearrangement of vinylcarbenes.[9] To minimize these competing processes, more stable carbenes have been used. Thus, rhodium-catalyzed decomposition of diazoalkanes in the presence of 1,3-dienes gives rise to cycloheptadienes.[10]

On the other hand, isolable Fischer-type carbene complexes have been widely used in the cyclopropanation of olefins and dienes,[11] but the reaction of Fischer vinylcarbenes and 1,3-dienes usually leads to [4 + 2] cycloadducts.[12] In fact, there are few reports of cycloheptadiene preparations by the [4 + 3] cycloaddition of these systems.[12b,13]

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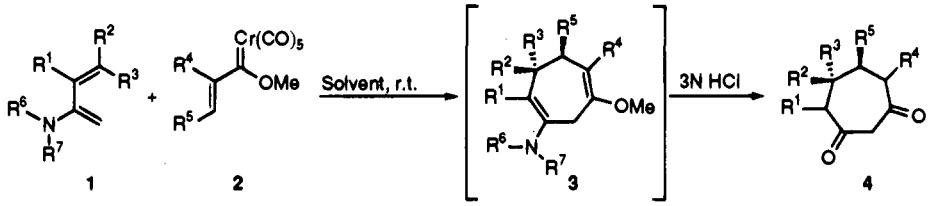
Scheme 1



Diene 1	R^1	R^2	R^3	R^6	R^7
a	CH_3	CH_2OCH_3	H	CH_3	Ph
b	CH_3	CH_2OBn	H	CH_3	Ph
c	$(CH_2)_4$		H	CH_3	Ph
d	CH_3	H	CH_2OCH_3	CH_3	Ph
e	CH_3	CH_2OCH_3	H	$(CH_2)_2$-O-$(CH_2)_2$	

Complex 2	R^4	R^5
a	H	2-Fu
b	H	Ph
c	H	*m*-$(CH_3)_3SiO$-Ph
d	$(CH_2)_4$	

Recently, we have been engaged in the study of the behavior and synthetic applications of 2-amino-1,3-dienes. The initial results of their reactions with Fischer carbene complexes have shown that these dienes can act either as dienophiles toward tungsten vinylcarbene complexes[12j-k] or as activated enamines in cyclopropanation reactions when chromium derivatives are used.[13c-d]

As an extension of our earlier work, we set out to investigate the scope and generality of the tandem cyclopropanation–Cope rearrangement reaction between 2-amino-1,3-butadienes and Fischer vinylcarbene complexes. In this paper, we report the stereospecific preparation of cycloheptenone and cycloheptadione derivatives.[14] The unexpected rearrangement of some of these products to γ-lactone derivatives and the stereochemical implications of the chiral pyrrolidine substituent in the asymmetric [4 + 3] cycloadditions with chiral 2-aminodienes are also described.

Results and Discussion

2-Amino-1,3-butadienes **1** (Scheme 1) react with Fischer methoxyvinylcarbene complexes **2** (molar ratio 1:1) leading to 1-amino-6-methoxycycloheptadienes **3** in a totally stereospecific manner. The stereochemistry of the resulting cycloadducts is dependent on the nature of the substitution in the C-4 position of the diene. Thus, when the diene has *E* configuration in the C-3–C-4 double bond (R^3 = H), only cycloheptadienes with *cis* relative stereochemistry in positions 3 and 4 are formed. On the other hand, the *Z* diene **1d** (R^2 = H) affords only the *trans* isomer of the cycloadduct.

The structure of the postulated adducts **3** were inferred from the ^1H and ^{13}C analysis of the crude reaction mixture that contains **3** as well as variable amounts of the [4 + 2] cycloadducts.[15] Stereochemical assignment was not possible from this analysis, and attempted purification of **3** led to partially hydrolyzed enamines and/or cycloheptadienes with a rearranged unsaturated structure. Due to this, the stereochemistry of compounds **3** was ascertained from their hydrolysis derivatives **4** (Table 1).

Table 1. 1,3-Cycloheptadiones **4** Prepared

compd	*t* (h)	solvent	diene	carbene	yield (%)
4a	24	CH_3CN	**1a**	**2a**	82
4a	24	CH_3CN	**1e**	**2a**	58
4b	24	CH_3CN	**1a**	**2b**	71
4c	3	THF	**1a**	**2d**	39
4d	48	THF	**1e**	**2c**	37
4e	48	CH_3CN	**1b**	**2a**	78
4f	48	CH_3CN	**1b**	**2b**	76
4g	48	CH_3CN	**1d**	**2a**	62
4h	3	CH_3CN	**1c**	**2a**	81
4i	48	THF	**1c**	**2d**	35

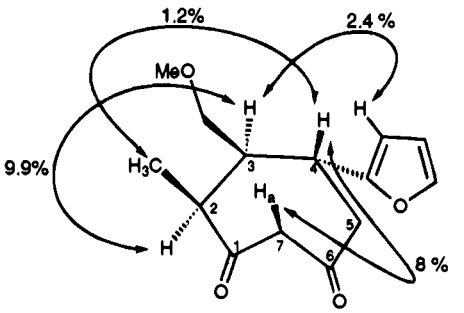


Figure 1. Some selected NOEs for **4g**.

Hydrolysis of **3** was accomplished by treatment of their solutions in THF with 3 N aqueous HCl at room temperature for 3 h. Under these conditions, only one of the possible epimers in the α ketone centers was obtained. Longer reaction times or higher temperatures led to mixtures of epimers.

The relative configurations of the asymmetric centers of cycloheptadiones **4a,h** were assigned by single-crystal X-ray analysis.[16] The structures of the other cycloheptadiones were deduced by the comparison of their ^1H and ^{13}C NMR spectra with those of compounds **4a,h** as well as some additional NOE experiments. As an example, the *trans* relative configuration of carbons 3 and 4 in the cycloheptadione **4g** was deduced from comparison of the ^1H and ^{13}C spectra of the crude reaction mixtures obtained from dienes **1a,g** and by NOE experiments (stationary phase) performed using **4g** as a model (Figure 1). Thus, saturation of the hydrogen H_4 produces positive NOEs in H_{7a} and the methyl hydrogens, which points to the *syn* configuration of these groups. Moreover, when the signal of H_2 is saturated, a positive NOE is observed for H_3 and no effect is observed in H_4, indicating a *cis* relationship between $-CH_3$ and $-CH_2OCH_3$.

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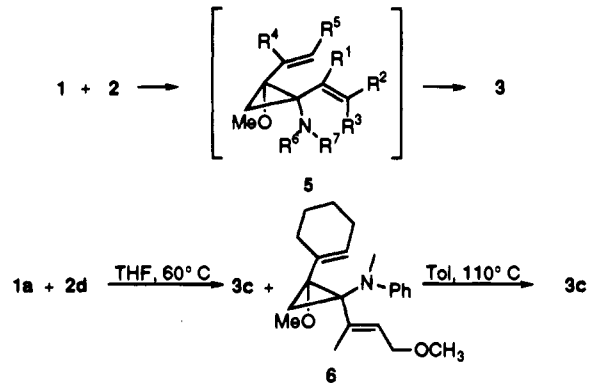
(14) For a preliminery communication, see ref 12c,d.

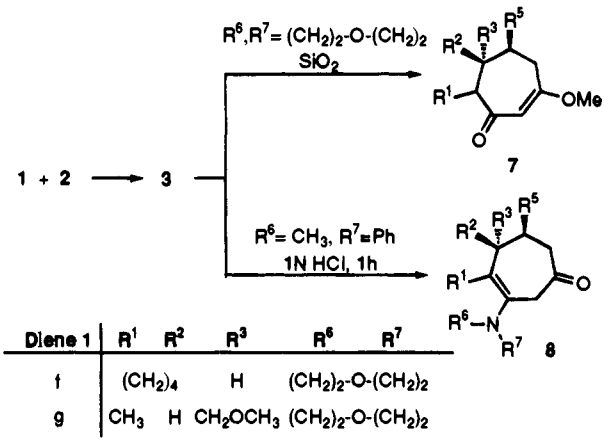
(15) Chemical species derived from [4 + 2] cycloaddition are minor compounds and are easily removed during the workup procedure.

(16) For **4a**, see ref 12c. For **4b**, see: Martín, F. Ph.D. Thesis, Universidad de Oviedo, 1994.

Scheme 2



Scheme 3



Diene 1	R^1	R^2	R^3	R^6	R^7
f	$(CH_2)_4$		H	$(CH_2)_2$-O-$(CH_2)_2$	
g	CH_3	H	CH_2OCH_3	$(CH_2)_2$-O-$(CH_2)_2$	

The formation of seven-membered carbocycles **3** can be understood in terms of carbene ligand transfer from **2** to the enamine carbon−carbon double bond of **1**, giving rise to cyclopropane derivatives **5** (Scheme 2). Further Cope rearrangement of these *cis*-divinylcyclopropanes occurs under the reaction conditions to yield **3**.[17] The cyclopropanation reaction appears to be totally *cis*-selective at room temperature, since no *trans*-divinylcyclopropane derivatives were detected with exception of the reaction between **1a** and **2d**. In this case, the reaction does not take place under the standard conditions (THF or CH_3CN, room temperature) but upon heating at 60 °C (THF, 3 h). After hydrolytic workup, cycloheptadione **4c** could be isolated in 26% yield as well as 17% of the *trans*-divinylcyclopropane **6**. Compound **6** was transformed into **4c** in 76% yield, after hydrolysis, by heating at 110 °C in toluene overnight.

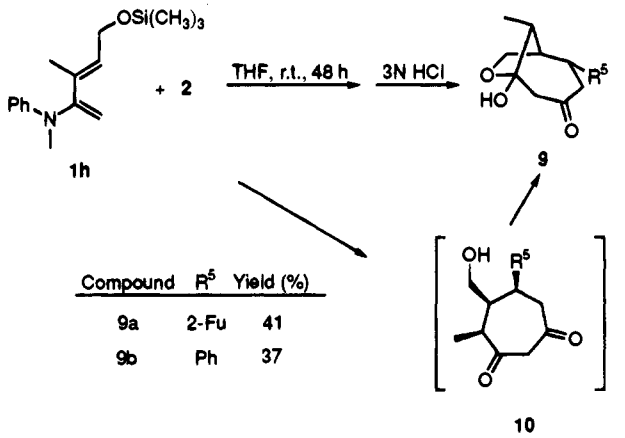
The different nature of the two carbonyl protecting groups in the cycloheptadienes **3** allowed us to perform selective deprotection of both ketones (Scheme 3). Thus, elution of morpholine-containing cycloheptadienes on silica gel yielded methoxycycloheptenones **7** in 35−51% overall yield (Table 2). On the other hand, aminocycloheptenones **8** can be obtained from dienes **1**, derived from *N*-methylaniline, in 35−48% overall yield by treating the crude reaction mixture with aqueous 1 N HCl for 1 h (Table 2). The structures of **7** and **8** were inferred from their ^1H and ^{13}C NMR spectra. These results were confirmed by total hydrolysis of **7** and **8** in 3 N HCl (see Scheme 1) which yielded the respective cycloheptadiones **4**.

By the use of diene **1h** in which the R^2 group is $CH_2OSi(CH_3)_3$ (Scheme 4), the reaction takes place to afford the cycloheptadiene derivative, but after hydrolysis, the hemiacetal **9** was obtained instead of the expected cycloheptadione **10**. The structure of **9** was deduced from NMR analysis.

Table 2. Methoxycycloheptenones **7** and Aminocycloheptenones **8** Prepared

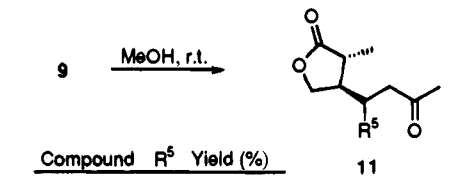
compd	diene	carbene	yield (%)
7a	**1e**	**2a**	51
7b	**1e**	**2b**	42
7c	**1f**	**2a**	43
7d	**1g**	**2a**	35
8a	**1a**	**2a**	38
8b	**1c**	**2a**	45
8c	**1d**	**2a**	42

Scheme 4



Compound	R^5	Yield (%)
9a	2-Fu	41
9b	Ph	37

Scheme 5



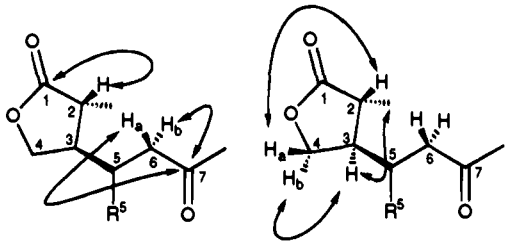
Compound	R^5	Yield (%)
11a	2-Fu	85
11b	Ph	81

Hemiacetals **9** are stable in their solid state but, in methanolic solution, decompose slowly to γ-lactones **11** (Scheme 5). The structure and stereochemistry of **11b** were assigned from the ^1H and ^{13}C NMR analysis as well as the $^1H-^{13}C$ correlation and NOESY experiments (Figure 2). Thus, the selection of the γ-lactone between the two possible structures of γ- and δ-lactones was inferred from the three-bond $^1H-^{13}C$ correlation between H_2 and C_1 as well as the correlation of H_{6a} and H_{6b} with C_7. The *trans* arrangement of the methyl group was deduced from the positive NOEs between $H_{4b}-H_3$, H_3-CH_3, and $H_{4a}-H_2$. The structure and relative configuration of **11a** were deduced from comparison of its ^1H and ^{13}C spectra with those of **11b**.

In view of the high stereoselection found in the formation of the seven-membered carbocycles, we next turned our attention to the enantioselective preparation of these compounds. We have previously reported the [4 + 2] and [4 + 3] cycloaddition reactions of dienes bearing a chiral amino group in C-2 position.[12f,g,13d,18] Thus, dienes **12** react with complexes **2**, giving rise to cycloheptadienes **13** along with minor amounts

(17) It is known that *cis*-divinylcyclopropanes undergo Cope rearrangement below room temperature, and they are not usually isolated. (a) Brown, J. M.; Golding, T.; Stofko, J. *J. Chem. Soc., Chem. Commun.* **1973**, 319. (b) Wender, P.; Filosa, M. P. *J. Org. Chem.* **1976**, *41*, 3490.

(18) There are other reports of the use of chiral 2-amino-1,3-butadienes in asymmetric synthesis: (a) Enders, D.; Meyer, O.; Raabe, G. *Synthesis* **1992**, 1242. (b) Enders, D.; Meyer, O.; Raabe, G.; Runsink, J. *Synthesis* **1994**, 67. (c) Schlessinger, R. H.; Pettus, T. R. R. *J. Org. Chem.* **1994**, *59*, 3246.



(a) (b)

Figure 2. Some selected crosspeaks for **11a** in (a) $^1H-^{13}C$ correlation and (b) NOESY experiments.

Scheme 6

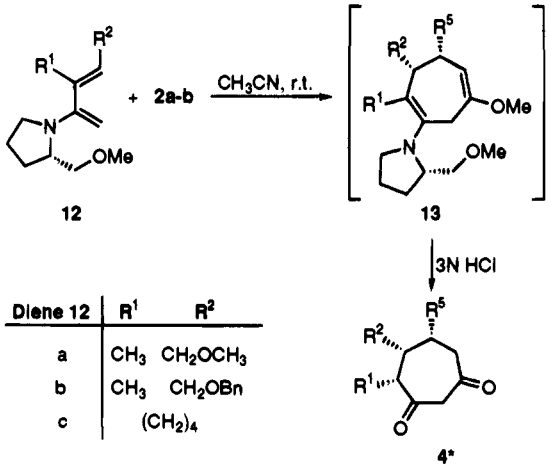
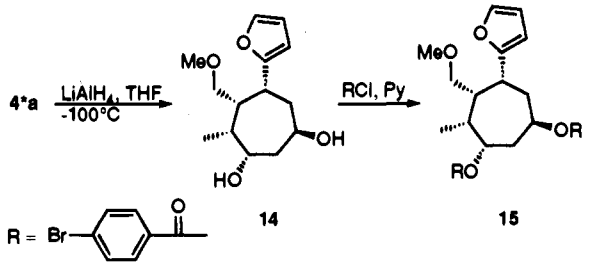


Table 3. Cycloheptadiones **4*** Prepared

compd	diene	carbene	yield (%)	ee (%)
4*a	**12a**	**2a**	45	86
4*e	**12b**	**2a**	52	81
4*f	**12b**	**2b**	55	72
4*h	**12c**	**2a**	40	55

Scheme 7



of the [4 + 2] cycloadducts (Scheme 6). Hydrolysis of the cycloadducts **13** in 3 N HCl gives rise to the same cycloheptadiones **4*** obtained from dienes containing morpholine or *N*-methylaniline, but optically active (Table 3).

The enantiomeric excesses of compounds **4*** were determined by ^1H NMR experiments with the $Eu(hfc)_3$ shift reagent (**4*e,f**) or by HPLC analysis performed with a Chiracell-ODH column (UV−vis array detector) (**4*a,h**).

The absolute configurations of the chiral centers in these compounds were deduced from those of **15** (Scheme 7), obtained by CD analysis. Compound **15** was prepared by reaction of **4*a** with $LiAlH_4$ at −100 °C to yield the diol **14** as a mixture of diastereoisomers. The major isomer was separated by flash column chromatography (silica gel, hexane−ethyl acetate (1:6)) and isolated in 71% yield. Further acylation of **14** with *p*-bromobenzoyl chloride in pyridine yielded **15** in 79% yield.

The relative configurations of the two hydroxyl groups as

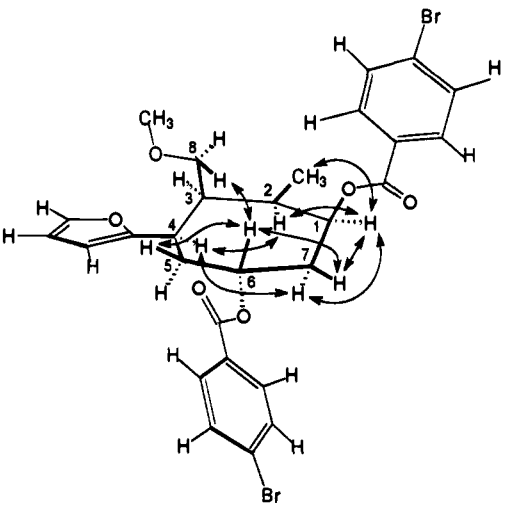


Figure 3. ROESY experiments for **15**.

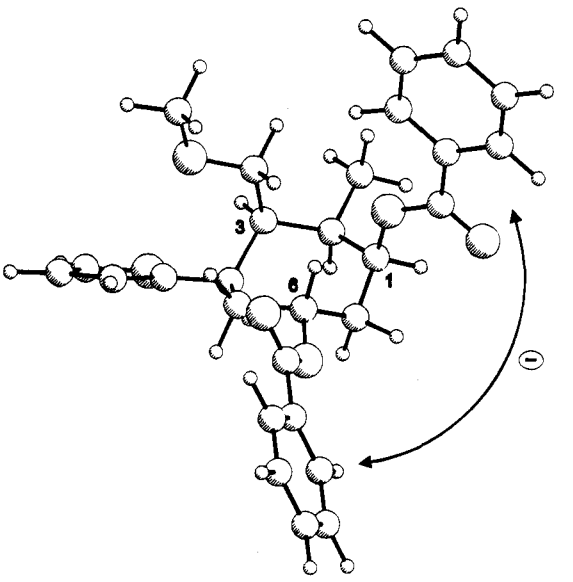


Figure 4. Most stable conformation for **15**.

well as the most stable conformation for compound **14** were determined from NMR spectroscopic data and molecular mechanics calculations. A ROESY experiment (C_6D_6) carried out on this compound and its di-*p*-bromobenzoate derivative **15** showed the same NOEs (Figure 3) for both compounds, except for that between H_6 and H_8 missing in the diol compound. Other NOEs in agreement with Figure 3 were observed together with a NOE between H_1 and H_3 which confirmed the relative configuration of the hydroxyl group at the 1 position and indicated the existence of a conformational equilibrium in solution. Thus, the relative configuration of the two hydroxyl groups proved to be as shown in Figure 3.

In order to confirm the conformation derived from ROESY experiments, MMX molecular mechanics calculations of the seven-membered-ring compounds **14** and **15** were carried out.[19] This study revealed several energy minima conformers, but only the most stable one found for **15**, the twist chair conformation shown in Figure 4, is in excellent agreement with the coupling constants and NOEs observed for this compound, the dihedral angle O6−C6−C1−O1 being −101°.[20]

(19) The MMX force field was used to perform the molecular mechanics calculations. PCMODEL-PI (V. 4.0), Serena Software, P.O. Box 3076, Bloomington, IN, 47402-3076.

(20) The dihedral angle O6−C6−C1−O1 obtained for the rest of the energy minima conformers was also negative.

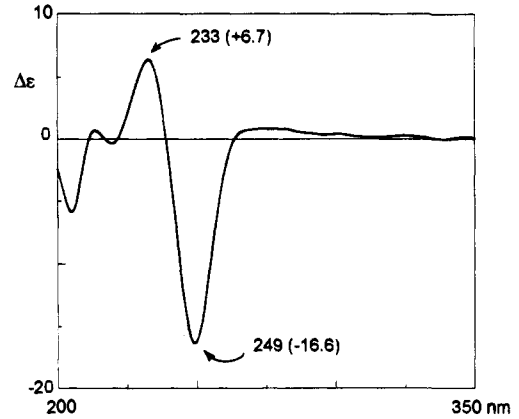


Figure 5, CD spectrum for **15**.

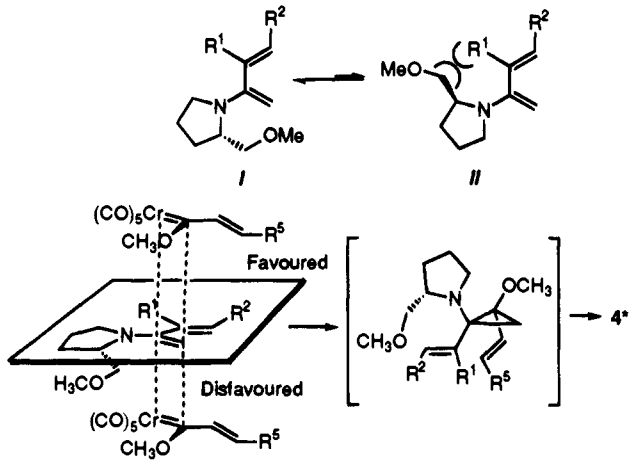


Figure 6, Approximation model for the cyclopropanation reaction.

The absolute stereochemistry of compound **15** was determined by applying the dibenzoate chirality method, an extension of the more general circular dichroic exciton chirality method which has proved to be an excellent tool for the determination of absolute configurations.[21] Its UV spectrum (CH_3CN) exhibited the intense intramolecular charge transfer (^1L_a) band of the benzoate chromophores at 243 nm (ϵ 38 200), the electric transition moments of which are polarized along the long axis of the chromophores.[21,22] The CD spectrum (Figure 5)[23] exhibited split Cotton effects of the exciton coupling type and was unaffected by the furan chromophore absorbing around 200 nm. The observed negative first Cotton effect at 249 nm ($\Delta\epsilon$ −16.6) and the positive second Cotton effect at 233 nm ($\Delta\epsilon$ +6.7) led to the conclusion that the exciton chirality between transition moments of the two benzoate chromophores is negative and left-handed. This unambiguously leads to the absolute configuration shown for compound **15**.

The stereochemical results of the asymmetric tandem cyclopropanation−Cope rearrangement reaction of Fischer vinylcarbenes and 2-amino-1,3-butadienes allow us to depict a model of approximation of the diene and carbene complex. The two favored conformers that dienes **12** can adopt in solution and secure the coplanarity of the nitrogen substituents and the enaminic double bond of the diene are depicted in Figure 6 as **I** and **II**. These two conformers can coexist, but probably, **I** is the one of low energy because the disfavorable steric interaction between R^1 and the methoxymethyl group attached at the pyrrolidine skeleton is minimized. In this situation, attack on the upside face of the diene (as depicted in Figure 6) is favored over that on the downside face, and therefore, the stereoisomer **16** of the *cis*-divinylcyclopropane would be formed preferentially. Evolution of **16** and further hydrolysis yield cycloheptadiones **4*** with the correct relative and absolute configurations of their chiral centers.

In conclusion, we describe in this paper a simple and versatile single-pot method of synthesis of seven-membered-ring carbocycles. The process takes place with total regio- and stereoselectivity and very high enantiomeric excesses when chiral aminodienes are employed. The aminodiene can be prepared in a very simple way from commercially available starting materials. Moreover, the chiral auxiliary is removed under very mild conditions. The application of this methodology in the synthesis of polycyclic systems is currently under study in our department.

Experimental Section

Materials. All reactions were run under N_2 atmosphere. THF, CH_3CN, hexane, and pyridine were dried and distilled upon standard procedures before use. Solvents used in the extractions were distilled prior to use. All other reagents were of the best comercial grade available. Column chromatography was carried out on silica gel 60 (230−400 mesh). All melting points are uncorrected. NMR spectra were recorded at 300 or 200 MHz for ^1H and 75 or 50.3 MHz for ^{13}C in $CDCl_3$, with tetramethylsilane as an internal standard, and chemical shift values are given in δ (ppm). Mass spectra were obtained by EI (70 ev). IR spectra are given in cm^{-1}.

Fischer carbene complexes[24] and 2-amino-1,3-butadienes[25] were prepared according to the methods described in the literature.

General Procedure for the Synthesis of 1,3-Cycloheptadiones 4. To a solution of a Fischer carbene complex **2** (1 mmol) in 8 mL of the dry solvent at room temperature was added 1 mmol of 2-aminodiene **1** (**12**). The reaction mixture was stirred at room temperature for the time indicated and concentrated at reduced pressure (10^{-2} Torr). The crude was dissolved in dry hexane, filtered through a pad of Celite, and cooled at −20 °C overnight to induce precipitation/crystallization of $Cr(CO)_6$ or $Cr(CO)_5(CH_3CN)$ complexes. The clear solution was decanted and concentrated at reduced pressure (water aspirator). The residue was dissolved in 10 mL of THF and 10 mL of aqueous 3 N HCl was added. The mixture was stirred for 3 h and extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (20 mL), dried over Na_2SO_4 and evaporated. The crude was chromatographed in silica gel using a mixture of hexane and ethyl acetate (3:1) unless other wise indicated.

***cis*-4-(2-Furyl)-3-(methoxymethyl)-2-methyl-1,6-cycloheptadione (4a).** Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]-chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with (*E*)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)-*N*-methylaniline (**1a**) (1 mmol, 0.22 g) in CH_3CN for 24 h to yield 0.21 g (82%): R_f = 0.26; recrystallized from methanol (white prisms), mp 101−102 °C; ^1H NMR δ 1.18 (d, 3H, J = 6.7 Hz), 2.4−2.5 (m, 1H), 2.75−2.90 (m, 2H), 3.09 (s, 3H), 3.15 (d, d, 1H, J = 15.5, 13.5 Hz), 3.33 (d, d, 1H, J = 10.1, 1.9 Hz), 3.40 (d, d, 1H, J = 10.1, 3.7 Hz), 3.61 (d, 1H, J = 13.0 Hz), 3.78 (m, 1H), 3.85(d, 1H, J = 13.0 Hz), 6.09 (d, 1H, J = 3.3 Hz), 6.32 (d, d, 1H, J = 3.3, 1.8 Hz), 7.35 (d, 1H, J = 1.8 Hz) ppm; ^{13}C NMR δ 14.3 (CH_3), 39.6 (CH), 43.5 (CH_2), 45.7 (CH), 50.1 (CH), 57.9 (CH_3), 60.6 (CH_2), 67.6 (CH_2), 105.4 (CH), 110.1 (CH), 141.5 (CH), 155.9 (C), 201.1 (C), 202.4 (C) ppm; IR (KBr) 1702, 1715 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.02; H, 7.12. For **4*a**, $[\alpha]^{20}_D$ −24 (CH_2Cl_2, c 3.9 × 10^{-3} g cm^{-3}, ee 90%).

(21) Harada, N.; Nakanishi, K. *J. Am. Chem. Soc.* **1969**, *91*, 3989.
(22) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy-Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983.
(23) The NMR spectrum of compound **14** recorded in CD_3CN showed multiplicities and coupling constants similar to those observed in C_6D_6 and $CDCl_3$.
(24) (a) Wulff, W. D.; Bauta, W. E.; Kaesler, R. A.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642. (b) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.
(25) Barluenga, J.; Aznar, F.; Valdés, C.; Cabal, M. P. *J. Org. Chem.* **1991**, *56*, 6166.

***cis*-3-(Methoxymethyl)-2-methyl-4-phenyl-1,6-cycloheptadione (4b)**, Pentacarbonyl[1-methoxy-*trans*-3-phenyl-2-propenylidene]chromium(0) (**2b**) (1 mmol, 0.34) was treated with (*E*)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)-*N*-methylaniline (**1a**) (1 mmol, 0.22 g) in CH_3CN for 24 h to yield 0.18 g (71%): $R_f = 0.30$; ^1H NMR δ 1.15 (d, 3H, $J = 6.7$ Hz), 1.96 (m, 1H), 2.64 (d, d, 1H, $J = 10.1, 1.0$ Hz), 2.88 (q, d, 1H, $J = 6.7, 3.0$ Hz), 3,16 (s, 3H), 3.30 (d, d, 1H, $J = 10.1, 3.2$ Hz), 3.39 (d, d, 1H, $J = 10.1, 2.3$ Hz), 3.60 (d, d, 1H, $J = 14.8, 1.0$ Hz), 3.61−3.74 (m, 2H), 3.79 (d, 1H, $J = 14.8$ Hz), 7.22−7.40 (m, 5H) ppm; ^{13}C NMR δ 14.9 (CH_3), 45.8 (CH_2), 47.4 (CH), 49.9 (CH), 50.4 (CH), 58.2 (CH_3) 60.1 (CH_2), 67.3 (CH_2), 126.8 (CH), 127.1 (CH), 128.5 (CH), 143,1 (C), 202.7 (C), 206.2 (C) ppm; IR (neat) 1679, 1716 cm^{-1}. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.99; H, 7.64.

1,2-*cis*-2-(Methoxymethyl)-3-methyl-4,6-bicyclo[5.4.0]-undecadione (4c), Pentacarbonyl[methoxy-(1-cyclohexenyl)methylidene]-chromium(0) (**2d**) (1 mmol, 0.32 g) was treated with (*E*)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)-*N*-methylaniline (**1a**) (1 mmol, 0.22 g) in THF at 60 °C for 3 h to yield 0.06 g (26%): $R_f = 0.20$; ^1H NMR δ 0.83 (q, d, 1H, $J = 12.9, 3.4$ Hz), 1.09 (d, 3H, $J = 6.9$ Hz), 1.13−1.37 (m, 2H), 1.41−1.49 (m, 2H), 1.56−1.79 (m, 2H), 2.09−2.21 (m, 2H), 2.78−2.92 (m, 2H), 2.98 (q, 1H, $J = 7.3$ Hz), 3.37−3.43 (m + s, 5H), 3.49 (d,d 1H, $J = 9.0, 7.3$ Hz), 4,34 (d, 1H, $J = 9.5$ Hz) ppm; ^{13}C NMR δ 10.7 (CH_3), 21.7 (CH_2), 26.2 (CH_2), 26.6 (CH_2), 27.1 (CH_2), 40.6 (CH), 42.0 (CH), 47.1 (CH), 54.5 (CH_3), 58.7 (CH), 60.4 (CH_2), 73.6 (CH_2), 201.0 (C), 203.4 (C) ppm. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.70; H, 9.25. Also obtained was 0.06 g of **6** (17%): $R_f = 0.54$; ^1H NMR δ 1.30 (d, 1H, $J = 7$ Hz), 1.51−1.69 (m, 5H), 1.74 (s, 3H), 1.93−2.12 (m, 4H), 2.96 (s, 3H), 3.11 (s, 3H), 3.25 (s, 3H), 4.1 (d, 2H, $J = 6.4$ Hz), 5.57 (t, 1H, $J = 6.4$ Hz), 5.65 (s broad, 1H), 6.63−6.73 (m, 3H), 7.14−7.24 (m, 2H) ppm; ^{13}C NMR δ 14.9 (CH_3), 45.6 (CH_2), 46.9 (CH), 49.7 (CH), 50.6 (CH_3), 58.1 (CH), 60.2 (CH_2), 67.3 (CH_2), 113.9 (CH), 114.3 (CH), 119.0 (CH), 129.7 (CH), 144.9 (C), 156.2 (C), 203.1 (C), 206.6 (C) ppm; IR (neat) 1502, 1599 cm^{-1}. Anal. Calcd for $C_{22}H_{31}NO_2$: C, 77.38; H, 9.15; N, 4.10. Found: C, 77.29; H, 9.09; N, 4.06.

***cis*-4-(3-Hydroxyphenyl)-3-(methoxymethyl)-2-methyl-1,6-cycloheptadione (4d)**, Pentacarbonyl[3-(3-(trimethylsiloxy)phenyl)-1-methoxy-*trans*-2-propenylidene]chromium(0) (**2c**) (1 mmol, 0.40 g) was treated with (*E*)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)morpholine (**1e**) (1 mmol, 0.20 g) in THF for 48 h to yield 0.10 g (37%): $R_f = 0.54$ (hexane−ethyl acetate, 1:2); recrystallized from dichloromethane (yellow prisms), mp 165−167 °C; ^1H NMR δ 1.09 (d, 3H, $J = 7.0$ Hz), 1.92 (m, 1H), 2.57 (d, 1H, $J = 9.2$ Hz), 2.78 (q, d, 1H, $J = 7.0, 3.2$ Hz), 3.09 (s, 3H), 3.19 (d, d, 1H, $J = 10.2$ Hz, 3.2 Hz), 3.36 (d, 1H, $J = 10.2, 2.2$ Hz), 3.46−3.59 (m, 3H), 3.72 (d, 1H, $J = 14.6$ Hz), 4.94 (s broad, 1H), 6.66 (m, 2H), 6.74 (d, 1H, $J = 7.9$ Hz), 7.12 (d, 1H, $J = 7.9$ Hz) ppm; ^{13}C NMR δ 14.9 (CH_3), 45.6 (CH_2), 46.9 (CH), 49.7 (CH), 50.6 (CH_3), 58.1 (CH), 60.2 (CH_2), 67.3 (CH_2), 113.9 (CH), 114.3 (CH), 119.0 (CH), 129.7 (CH), 144.9 (C), 156.2 (C), 203.1 (C), 206.6 (C) ppm; IR (KBr) 1682, 1718, 3338 cm^{-1}. Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.69; H, 7.25.

***cis*-3-((Benzyloxy)methyl)-4-(2-furyl)-2-methyl-1,6-cycloheptadione (4e)**, Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]-chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with (*E*)-*N*-(4-(benzyloxy)-2-methyl-1-methylene-2-butenyl)-*N*-methylaniline (**1b**) (1 mmol, 0.29 g) in CH_3CN for 48 h to yield 0.25 g (78%): $R_f = 0.33$; recrystallized from dichloromethane (white prisms), mp 119−120 °C; ^1H NMR δ 1.07 (d, 3H, $J = 6.8$ Hz), 2.30−2.40 (m, 1H), 2.62−2.88 (m, 2H), 3.11 (d, 1H, $J = 13.3$ Hz), 3.23 (d, d, 1H, $J = 10.2, 1.3$ Hz), 3.35 (d, d, 1H, $J = 10.2, 3.5$ Hz), 3.50 (d, 1H, $J = 13.4$ Hz), 3.61−3.72 (m, 1H), 3.68 (d, 1H, $J = 13.4$ Hz), 4.18 (s, 2H), 5.95 (d, 1H, $J = 3.2$ Hz), 6.22 (d, d, 1H, $J = 3.2, 1.8$ Hz), 7.11−7.31 (m, 6H) ppm; ^{13}C NMR δ 14.3 (CH_3), 39.7 (CH), 43.7 (CH_2), 45.7 (CH), 49.9 (CH), 60.5 (CH_2), 64.9 (CH_2), 73.0 (CH_2), 105.4 (CH), 110.0 (CH), 127.6 (CH), 127.9 (CH), 128.1 (CH), 136.9 (C), 141.4 (CH), 155.7 (C), 201.3 (C), 202.9 (C) ppm. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.66; H, 6.83. For **4*e**, $[\alpha]^{20}_D$ −4 (CH_2Cl_2, c 5.0 × 10^{-3} g cm^{-3}, ee 81%).

***cis*-3-((Benzyloxy)methyl)-2-methyl-4-phenyl-1,6-cycloheptadione (4f)**, Pentacarbonyl[1-methoxy-*trans*-3-phenyl-2-propenylidene]-chromium(0) (**2b**) (1 mmol, 0.34 g) was treated with (*E*)-*N*-(4-(benzyloxy)-2-methyl-1-methylene-2-butenyl)-*N*-methylaniline (**1b**) (1 mmol, 0.29 g) in CH_3CN for 48 h to yield 0.25 g (76%): $R_f = 0.30$; ^1H NMR δ 1.16 (d, 3H, $J = 6.7$ Hz), 1.93−2.05 (m, 1H), 2.53−2.65 (m, 1H), 2.87 (q, d, 1H, $J = 6.7, 2.9$ Hz), 3.28−3.48 (m, 2H), 3.51 (d, 1H, $J = 10.5$ Hz), 3.70−3.74 (m, 2H), 3.78 (d, 1H, $J = 10.5$ Hz), 4.24 (d, 1H, $J = 11.4$ Hz), 4.26 (d, 1H, $J = 11.4$ Hz), 7.20−7.50 (m, 10H) ppm; ^{13}C NMR δ 15.0 (CH_3), 45.9 (CH_2), 47.4 (CH), 49.8 (CH), 50.2 (CH), 60.0 (CH_2), 64.8 (CH_2), 73.3 (CH_2), 126.7 (CH), 127.0 (CH), 127.7 (CH), 128.1 (CH), 128.2 (CH), 128.4 (CH), 137.0 (C), 142.8 (C), 202.9 (C), 206.6 (C) ppm; IR (KBr) 1691, 1709 cm^{-1}. Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.45; H, 7.15. For **4*f**, $[\alpha]^{20}_D$ +22 (CH_2Cl_2, c 5.0 × 10^{-3} g cm^{-3}, ee 72%).

4-*trans*-4-(2-Furyl)-3-(methoxymethyl)-2-methyl-1,6-cycloheptadione (4g), Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]-chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with (*Z*)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)-*N*-methylaniline (**1d**) (1 mmol, 0.22 g) in CH_3CN for 48 h to yield 0.16 g (62%): $R_f = 0.33$; ^1H NMR δ 1.16 (d, 3H, $J = 6.7$ Hz), 2.46 (d, q, 1H, $J = 13.4, 6.7$ Hz), 2.76−3.02 (m, 3H), 3.22 (s, 3H), 3.32−3.42 (m, 2H), 3.45 (d, 1H, $J = 16.5$ Hz), 3.66 (t, d, 1H, $J = 8.6, 5.1$ Hz), 3.83 (d, 1H, $J = 16.5$ Hz), 6.18 (d, 1H, $J = 3.2$ Hz), 6.33 (d, d, 1H, $J = 3.2, 1.9$ Hz), 7.38 (d, 1H, $J = 1.9$ Hz) ppm; ^{13}C NMR δ 13.0 (CH_3), 35.6 (CH), 44.7 (CH_2), 44.8 (CH), 45.6 (CH), 58.8 (CH_3), 59.0 (CH_2), 69.9 (CH_2), 106.1 (CH), 110.1 (CH), 141.6 (CH), 155.6 (C), 203.9 (C), 204.6 (C) ppm. Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.24; H, 7.20.

***cis*-6-(2-Furyl)-2,4-bicyclo[5.4.0]undecadione (4h)**, Pentacarbonyl-[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with *N*-[1-(1-cyclohexenyl)ethenyl]-*N*-methylaniline (**1c**) (1 mmol, 0.21 g) in CH_3CN for 3 h to yield 0.20 g (81%): $R_f =$ 0.38; recrystallized from hot hexane (white needles), mp 126−127 °C; ^1H NMR δ 0.89 (q, d, 1H, $J = 12.9, 3.4$ Hz), 1.18 (q, t, 1H, $J = 12.5, 4.3$ Hz), 1.36 (t, t, 1H, $J = 12.9, 4.7$ Hz), 1.47−1.64 (m, 4H), 1.68−1.78 (m, 1H), 2.20−2.30 (m, 1H), 2.46-2.55 (m, 1H), 2.75 (d, d, 1H, $J = 18.1, 12.0$ Hz), 2.86 (d, d, 1H, $J = 18.1, 4.7$ Hz), 3.06−3.14 (m, 1H), 3.48 (d, 1H, $J = 10.3$ Hz), 3.94 (d, d, 1H, $J = 12.0, 4.7$ Hz), 4.37 (d, 1H, $J = 10.3$ Hz), 6.06 (d, 1H, $J = 3.0$ Hz), 6.34 (d, d, 1H, $J = 3.0, 1.7$ Hz), 7.38 (d, 1H, $J = 1.7$ Hz) ppm; ^{13}C NMR δ 21.6 (CH_2), 23.5 (CH_2), 26.1 (CH_2), 27.5 (CH_2), 38.5 (CH), 41.9 (CH_2), 42.7 (CH), 54.2 (CH), 61.9 (CH_2), 105.2 (CH), 110.1 (CH), 141.5 (CH), 156.0 (C), 200.7 (C), 201.1 (C) ppm. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.97; H, 7.34. For **4*h**, $[\alpha]^{20}_D$ −53 (CH_2Cl_2, c 6.15 × 10^{-3} g cm^{-3}, ee 55%).

***meso*-4,6-Tricyclo[5.4.0.0^{4,3}]pentadecadione (4i)**, Pentacarbonyl-[methoxy-(1-cyclohexenyl)methylidene]chromium(0) (**2d**) (1 mmol, 0.32 g) was treated with *N*-[1-(1-cyclohexenyl)ethenyl]-*N*-methylaniline (**1c**) (1 mmol, 0.21 g) in THF for 48 h to yield 0.08 g (35%): $R_f =$ 0.47; recrystallized from hot hexane (white needles), mp 94−95 °C; ^1H NMR δ 1.16−1.43 (m, 6H), 1.47−1.69 (m, 6H), 1.70−1.91 (m, 4H), 2.33−2.49 (m, 2H), 2.61−2.72 (m, 2H), 3.34 (d, 1H, $J = 10.8$ Hz), 4.18 (d, 1H, $J = 10.8$ Hz) ppm; ^{13}C NMR δ 22.8 (CH_2 × 2), 24.8 (CH_2 × 2), 26.2 (CH_2 × 2), 31.5 (CH_2 × 2), 42.4 (CH × 2), 53.0 (CH × 2), 60.7 (CH_2), 203.4 (C × 2) ppm. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.69; H, 9.50.

General Procedure for the Synthesis of Methoxycycloheptenones 7. The same procedure as that for compounds **4** was used, except for the hydrolysis method. After elimination of the metal complexes, the crude reaction mixture was chromatographed in silica gel (hexane−ethyl acetate, 3:1).

***cis*-4-(2-Furyl)-6-methoxy-3-(methoxymethyl)-2-methyl-6-cyclohepten-1-one (7a)**, Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with (*E*)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)morpholine (**1e**) (1 mmol, 0.20 g) in CH_3CN for 24 h to yield 0.13 g (51%): $R_f = 0.33$; ^1H NMR δ 1.18 (d, 3H, $J = 7.0$ Hz), 2.52−2.59 (m, 1H), 2.79 (d, d, 1H, $J =$ 17.5, 4.3 Hz), 2.83 (q, d, 1H, $J = 7.0, 3.8$ Hz), 2.97 (d, d, 1H, $J =$ 17.5, 10.7 Hz), 3.15 (s, 3H), 3.32 (d, d, 1H, $J = 9.9, 4.3$ Hz), 3.39 (d, d, 1H, $J = 9.9, 5.6$ Hz), 3.52−3.61 (m, 1H), 3.62 (s, 1H), 5.51(s, 1H), 6.09 (d, 1H, $J = 3.3$ Hz), 6.33 (d, d, 1H, $J = 3.3, 1.9$ Hz), 7.36 (d, 1H, $J = 1.9$ Hz) ppm; ^{13}C NMR δ 15.4 (CH_3), 34.9 (CH_2), 38.9 (CH), 43.6 (CH), 49.2 (CH), 55.2 (CH_3), 58.4 (CH_3), 69.6 (CH_2), 104.9 (CH), 105.7

(CH), 109.9 (CH), 140.8 (CH), 156.8 (C), 169.5 (C), 201.2 (C) ppm. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.00; H, 7.67.

***cis*-6-Methoxy-3-(methoxymethyl)-2-methyl-4-phenyl-6-cyclohepten-1-one (7b)**, Pentacarbonyl[1-methoxy-*trans*-3-phenyl-2-propenylidene]chromium(0) (**2b**) (1 mmol, 0.34 g) was treated with (*E*)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)morpholine (**1e**) (1 mmol, 0.20 g) in CH_3CN for 24 h to yield 0.12 g (42%): R_f = 0.31; recrystallized from dichloromethane (white prisms), mp 115−116 °C; ^{1}H NMR δ 1.26 (d, 3H, J = 6.7 Hz), 2.22−2.32 (m, 1H), 2.71 (d, d, d, 1H, J = 17.0, 3.5, 0.7 Hz), 2.93 (q, d, 1H, J = 6.7, 3.5 Hz), 3.07 (s, 3H), 3.24 (d, d, d, 1H, J = 17.0, 11.4, 1.0 Hz), 3.35 (d, 1H, J = 0.6 Hz), 3.37 (s, 1H), 3.51−3.62 (d, t, 1H, J = 11.4, 3.5 Hz), 3.64 (s, 3H), 5.50 (s, 1H), 7.17−7.39 (m, 5H) ppm; ^{13}C NMR δ 15.9 (CH_3), 36.2 (CH_2), 45.4 (CH), 47.2 (CH), 50.2 (CH), 55.2 (CH_3), 58.4 (CH_3), 68.9 (CH_2), 105.6 (CH), 126.3 (CH), 127.2 (CH), 128.2 (CH), 144.5 (C), 171.1 (C), 201.8 (C) ppm. Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.25; H, 8.06.

***cis*-6-(2-Furyl)-4-methoxy-3-bicyclo[5.4.0]undecen-2-one (7c)**, Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with 1-(1-cyclohexenyl)-ethenylmorpholine (**1f**) (1 mmol, 0.19 g) in CH_3CN for 24 h to yield 0.11 g (43%): R_f = 0.46; ^{1}H NMR δ 1.02−1.40 (m, 4H), 1.41−1.58 (m, 2H), 1.64−1.71 (m, 1H), 2.18−2.28 (m, 1H), 2.46−2.54 (m, 1H), 2.63 (d, d, 1H, J = 18.0, 3.9 Hz), 2.79 (d, d, 1H, J = 18.0, 12.0 Hz), 3.30 (d, d, 1H, J = 12.5, 3.9 Hz), 3.57 (s, 3H), 5.53 (s, 1H), 5.98 (d, 1H, J = 3.4 Hz), 6.22 (d, d, 1H, J = 3.4, 2.1 Hz),7.29 (d, 1H, J = 2.1 Hz) ppm; ^{13}C NMR δ 22.9 (CH_2), 23.5 (CH_2), 26.3 (CH_2), 30.2 (CH_2), 34.1 (CH_2), 39.4 (CH), 41.1 (CH), 53.0 (CH_3), 55.3 (CH_3), 104.3 (CH), 107.4 (CH), 109.1 (CH), 141.0 (CH), 157.6 (C), 170.3 (C), 200.9 (C) ppm. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.99; H, 7.70.

4-*trans*-4-(2-Furyl)-6-methoxy-3-(methoxymethyl)-2-methyl-6-cyclohepten-1-one (7d), Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with (*Z*)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)morpholine (**1g**) (1 mmol, 0.20 g) in CH_3CN for 48 h to yield 0.09 g (35%): R_f = 0.17; recrystallized from hexane−dichloromethane (white prisms), mp 103−104 °C; ^{1}H NMR δ 1.15 (d, 3H, J = 6.9 Hz), 2.22 (d, q, 1H, J = 7.7, 4.7 Hz), 2.59 (d, t, 1H, J = 15.9, 2.0 Hz), 2.92−3.21 (m, 3H), 3.12 (s, 3H), 3.23 (d, 1H, J = 4.7 Hz), 3.55 (s, 3H), 5.40 (s, 1H), 6.00 (d, 1H, J = 3.0 Hz), 6.22 (d, d, 1H, J = 3.0, 1.7 Hz), 7.26 (d, 1H, J = 1.7 Hz) ppm; ^{13}C NMR δ 14.2 (CH_3), 37.3 (CH_2), 38.4 (CH), 44.0 (CH), 55.7 (CH_3), 58.7 (CH_3), 71.3 (CH_2), 106.0 (CH), 107.3 (CH), 109.9 (CH), 141.3 (CH), 157.4 (C), 174.8 (C), 200.6 (C) ppm. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.01; H, 7.66.

General Procedure for the Synthesis of Aminocycloheptenones 8. The same procedure as that for compounds **4** was used, except for the hydrolysis method. After elimination of the metal complexes, the crude reaction mixture was dissolved in 10 mL of THF and 10 mL of aqueous 1 N HCl was added. The mixture was stirred for 1 h, then 10 mL of 3 N NaOH was added and the mixture was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and evaporated. The crude was chromatographed in silica gel using a mixture of hexane and ethyl acetate (3:1).

***cis*-4-(2-Furyl)-3-(methoxymethyl)-2-methyl-1-(*N*-methyl-*N*-phenylamino)-1-cyclohepten-6-one (8a)**, Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with (*E*)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)-*N*-methylaniline (**1a**) (1 mmol, 0.22 g) in CH_3CN for 24 h to yield 0.13 g (38%): R_f = 0.63; ^{1}H NMR δ 1.48 (s, 3H), 2.69−2.86 (m, 2H), 2.97 (s, 3H), 3.12−3.23 (m, 2H), 3.34 (s, 3H), 3.37−3.51 (m, 2H), 3.66−3.76 (m, 2H), 6,13 (d, 1H, J = 3.4 Hz), 6.32 (d,d, 1H J = 3.4, 1.9 Hz), 6.64−6.73 (m, 3H), 7.19−7.27 (m, 2H), 7.36 (d, 1H, J = 1.9 Hz) ppm; ^{13}C NMR δ 14.6 (CH_3), 36.7 (CH), 38.5 (CH), 43.7 (CH_3), 45.5 (CH_2), 46.1 (CH_2), 58.5 (CH_3), 71.9 (CH_2), 106.6 (CH), 110.0 (CH), 112.6 (CH), 117.0 (CH), 128.9 (CH), 134.6 (CH), 134.7 (C), 141.3 (C), 146.6 (C), 154.3 (C), 207.2 (C) ppm. Anal. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.20; H, 7.44; N, 4.10.

***cis*-6-(2-Furyl)-2-(*N*-methyl-*N*-phenylamino)-1-bicyclo[5.4.0]-undecen-4-one (8b)**, Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with *N*-[1-(1-cyclohexenyl)ethenyl]-*N*-methylaniline (**1c**) (1 mmol, 0.21 g) in CH_3CN for 3 h to yield 0.15 g (45%): R_f = 0.42; ^{1}H NMR δ 0.72−0.86 (m, 1H), 1.02−1.41 (m-4H), 1.47−1.75 (m, 4H), 2.41−2.87 (m, 3H), 2.92 (s, 3H), 3.89−4.08 (m, 2H), 6.01 (d, 1H, J = 3.5 Hz), 6.26 (d,d, 1H, J = 3.5, 1.9 Hz), 6.57−6.70 (m, 3H), 7.13−7.21 (m, 2H), 7.31 (d, J =1.9 Hz, 1H) ppm; ^{13}C NMR δ 26.4 (CH_2), 27.6 (CH_2), 28.0 (CH_2), 31.8 (CH_2), 35.9 (CH_3), 36.6 (CH), 42.8 (CH_2), 44.6 (CH_2), 45.3 (CH), 105.9 (CH), 110.1 (CH), 112.7 (CH), 117.0 (CH), 127.5 (C), 129.1 (CH), 141.3 (CH), 141.8 (C), 155.7 (C), 206.5 (C) ppm. Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.99; H, 7.54; N, 4.15.

***trans*-4-(2-Furyl)-3-(methoxymethyl)-2-methyl-1-(*N*-methyl-*N*-phenylamino)-1-cyclohepten-6-one (8c)**, Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with (*Z*)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)-*N*-methylaniline (**1d**) (1 mmol, 0.22 g) in CH_3CN for 48 h to yield 0.14 g (42%): R_f = 0.26; ^{1}H NMR δ 1.78 (s, 3H), 2.75 (d, d, 1H, J = 16.5, 3.8 Hz), 2.87−3.00 (m, 5H), 3.07 (d, d, 1H, J = 16.5, 8.9 Hz), 3.45 (s, 3H), 3.51−3.64 (m, 2H), 3.70 (d, d, 1H, J = 8.9, 3.8 Hz), 3.76 (d, d, 1H, J = 8.9, 3.8 Hz), 6.17 (d, 1H, J = 3.2 Hz), 6.37 (d, 1H, J = 3.2, 1.9 Hz), 6.63−6.80 (m, 3H), 7.18−7.31 (m, 2H), 7.39 (d, 1H, J = 1.9 Hz) ppm; ^{13}C NMR δ 19.1 (CH_3), 35.0 (CH), 36.3 (CH_3), 44.1 (CH_2), 45.7 (CH_2), 48.5 (CH), 55.8 (CH_3), 71.8 (CH_2), 105.3 (CH), 109.9 (CH), 112.4 (CH), 116.9 (CH), 129.0 (CH), 133.4 (C), 133.5 (C), 141.2 (CH), 148.5 (C), 156.6 (C), 108.2 (C) ppm. Anal. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.60; H, 7.38; N, 4.12.

1-Hydroxy-5-(*endo*-2-furyl)-9-(*exo*-methyl)-8-oxa-3-bicyclo[4.2.1]-nonanone (9a), The reaction was performed as described in the General Procedure for **4**. Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]chromium(0) (**2a**) (1 mmol, 0.33 g) was treated with (*E*)-*N*-(2-methyl-1-methylene-4-(trimethylsiloxy)-2-butenyl)-*N*-methylaniline (**1h**) (1 mmol, 0.28 g) in CH_3CN for 48 h to yield 0.10 g (41%): R_f = 0.25; ^{1}H NMR δ 1.19 (d, 3H, J = 7.3 Hz), 2.13 (q, 1H, J = 7.3 Hz), 2.54 (d, 1H, J = 4.7 Hz), 2.66 (d, 1H, J = 6.7 Hz), 2.79 (d, 1H, J = 15.7 Hz), 2.72−2.85 (s broad, 1H), 2.98 (d,d, 1H, J = 15.7, 1.3 Hz), 3.17 (d, 1H, J = 1.3 Hz), 3.19 (d, 1H, J = 6.7 Hz), 3.97 (d, 1H, J = 9.2 Hz), 4.19 (d,d, 1H, J = 9.2, 4.7 Hz), 6.01 (d, 1H, J = 3.18 Hz), 6.24 (d,d, 1H, J = 3.18, 1.9 Hz), 7.32 (d, 1H, J = 1.9 Hz) ppm; ^{13}C NMR δ 14.6 (CH_3), 40.6 (CH), 42.5 (CH_2), 45.7 (CH), 49.2 (CH), 57.1 (CH_2), 67.0 (CH_2), 104.2 (C), 104.9 (CH), 109.8 (CH), 141.2 (CH), 155.9 (C), 208.9 (C) ppm. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.91; H, 6.85.

1-Hydroxy-9-(*exo*-methyl)-8-oxa-5-(*endo*-2-phenyl)-3-bicyclo-[4.2.1]nonanone (9b), The reaction was performed as described in the General Procedure for **4**. Pentacarbonyl[1-methoxy-*trans*-3-phenyl-2-propenylidene]chromium(0) (**2b**) (1 mmol, 0.34 g) was treated with (*E*)-*N*-(2-methyl-1-methylene-4-(trimethylsiloxy)-2-butenyl)-*N*-methylaniline (**1h**) (1 mmol, 0.28 g) in CH_3CN for 24 h to yield 0.09 g (37%): R_f = 0.30; ^{1}H NMR δ 1.20 (d, 3H, J = 7.2 Hz), 2.23 (q, 1H, J = 7.2 Hz), 2.28−2.33 (m, 1H), 2.57 (d, d, 1H, J = 10.5, 2.8 Hz), 2.83 (d, 1H, J = 15.4 Hz), 2.85 (s broad, 1H), 3.05 (d, d, 1H, J = 15.4, 1.3 Hz), 3.13−3.22 (m, 1H), 3.46 (d, d, 1H, J = 13.5, 10.5 Hz), 4.05 (t, 1H, J = 10.5 Hz), 7.16−7.42 (m, 5H) ppm; ^{13}C NMR δ 14.6 (CH_3), 45.3 (CH_2), 46.3 (CH), 46.5 (CH), 52.9 (CH), 57.3 (CH_2), 66.2 (CH_2), 104.7 (C), 126.5 (CH), 126.7 (CH), 129.3 (CH), 143.1 (C), 210.3 (C) ppm. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.31; H, 7.40.

3(*S)-[1(*S**)-(2-Furyl)-3-oxobutyl]-2(*R**)-methyl-4-butanolide (11a)**, **9a** (1 mmol, 0.24 g) was dissolved in 10 mL of methanol and stirred until the TLC showed the absence of the starting material (ca. 48 h). The solvent was evaporated at reduced pressure and the residue chromatographed in silica gel using hexane−ethyl acetate (3:2) to yield 0.20 g (85%): R_f = 0.19; ^{1}H NMR δ 0.82 (d, 3H, J = 7.0 Hz), 1.97 (s, 3H), 2.12−2.46 (m, 2H), 2.54 (d, d, 1H, J = 16.8, 5.1 Hz), 2.89 (d, d, 1H, J = 16.8, 8.9 Hz), 3.24−3.39 (m, 1H), 3.85 (t, 1H, J = 8.9 Hz), 4.29 (t, 1H, J = 8.9 Hz), 6.04 (s, 1H), 6.21 (s, 1H), 7.26 (s, 1H) ppm; ^{13}C NMR δ 14.2 (CH_3), 30.0 (CH_3), 35.8 (CH), 38.2 (CH), 44.5 (CH_2), 46.4 (CH), 69.1 (CH_2), 106.7 (CH), 110.0 (CH), 141.4 (CH), 153.5

(C), 179.0 (C), 205.6 (C) ppm; IR (neat) 1716, 1772 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.84; H, 6.79.

3(*S)-2(*R**)-Methyl-[3-oxo-1(*R**)-phenylbutyl]-4-butanolide (11b).** The reaction was performed with **9b** as described for **11a**. **9b** (1 mmol, 0.25 g) yielded 0.20 g (81%): $R_f = 0.24$; ^1H NMR δ 0.72 (d, 3H, J = 7.0 Hz), 2.05 (s, 3H), 2.26 (d, q, 1H, J = 10.1, 7.0 Hz), 2.45 (m, 1H), 2.69 (d, d, 1H, J = 16.7, 4.5 Hz), 2.98 (d, d, 1H, J = 16.7, 9.4 Hz), 3.25 (t, d, 1H, J = 9.4, 4.5 Hz), 3.98 (t, 1H, J = 9.1 Hz), 4.44 (d, d, 1H, J = 9.1, 7.7 Hz), 7.1−7.4 (m, 5H) ppm; ^{13}C NMR δ 15.0 (CH_3), 30.7 (CH_3), 39.2 (CH), 44.1 (CH), 47.2 (CH_2), 48.5 (CH), 69.7 (CH_2), 127.4 (CH), 127.7 (CH), 128.9 (CH), 140.9 (C), 179.4 (C), 206.1 (C) ppm. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.01; H, 7.35.

(1R,3S,4R,5S,6R)-6-(2-Furyl)-5-(methoxymethyl)-4-methyl-1,3-cycloheptanediol (14). To a solution of **4*a** (1 mmol, 0.25 g) in 20 mL of dried THF cooled at −100 °C was added dropwise 2 equiv of $LiAlH_4$ 0.2 M in THF. The reaction mixture was stirred at −100 °C for 2 h and then warmed to room temperature for an additional 3 h. The solution was hydrolyzed with 3 N aqueous NaOH, the organic layer separated, and the aqueous layer extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, and evaporated. The resulting oil was chromatographed in hexane−ethyl acetate (1:6) to yield 0.18 g 71%: $R_f = 0.18$; ^1H NMR δ 1.13 (d, 3H, J = 7.0 Hz), 1.93−1.96 (m, 1H), 2.01−2.14 (m, 2H), 2.21 (d, d, d, 1H, J = 14.0, 7.2, 2.7 Hz), 2.29−2.31 (m, 1H), 2.46 (t, d, 1H, J = 12.6, 6.6 Hz), 2.90 (s, 3H), 3.18 (d, d, 1H, J = 10.1, 4.5 Hz), 3.28 (d, d, 1H, J = 10.1, 4.0 Hz), 3.30−3.33 (m, 1H), 3.90−3.92 (m, 1H), 4.47 (d, d, t, 1H, J = 9.6, 6.6, 2.7 Hz), 6.01 (d, 1H, J = 3.2 Hz), 6.16 (d, d, 1H, J = 3.2, 1.9 Hz), 7.15 (d, 1H, J = 1.9 Hz) ppm; ^{13}C NMR δ 17.2 (CH_3), 37.0 (CH_2), 38.0 (CH), 42.5 (CH_2), 43.4 (CH), 46.2 (CH), 58.6 (CH_3), 65.1 (CH), 67.8 (CH_2), 70.6 (CH), 105.0 (CH), 109.9 (CH), 140.7 (CH), 158.5 (C) ppm; $[\alpha]^{20}_{456}$ −5 (CH_2Cl_2, 6.4 × 10^{-3} g cm^{-3}, ee 90%). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.40; H, 8.69.

(1R,3S,4R,5S,6R)-1,3-Bis((p-bromobenzoyl)oxy)-6-(2-furyl)-5-(methoxymethyl)-4-methylcycloheptane (15). To a solution of **13** (0.25 mmol, 0.06 g) in 2 mL of dried pyridine was added a small crystal of 4-(*N*,*N*-dimethylamino)pyridine and 2.2 equiv of *p*-bromobenzoyl chloride. The formed suspension is stirred at room temperature for 13 h, then the solvent was evaporated and the reaction crude dissolved in 5 mL of diethyl ether and washed with aqueous 1 N HCl (3 × 5 mL), saturated aqueous $NaHCO_3$ (2 × 5 mL), and brine. The organic layer was dried with Na_2SO_4 and evaporated. The crude was then chromatographed in silica gel using hexane−ethyl acetate (3:1) to yield 0.12 g (79%): $R_f = 0.18$; ^1H NMR δ 1.15 (d, 3H, J = 7.3 Hz), 2.31−2.55 (m, 6H), 3.24 (s, 3H), 3.40 (d, t, 1H, J = 11.0, 4.7 Hz), 3.49 (d, d, 1H, J = 9.7, 5.4 Hz), 3.62 (d, d, 1H, J = 9.7, 7.2 Hz), 5.49−5.52 (m, 1H), 5.59−5.65 (m, 1H), 6.08 (d, 1H, J = 3.2 Hz), 6.31 (d, d, 1H, J = 3.2, 1.9 Hz), 7.34 (d, 1H, J = 1.9 Hz), 7.57 (d, 2H, J = 8.5 Hz), 7.60 (d, 2H, J = 8.5 Hz), 7.87 (d, 2H, J = 8.5 Hz), 7.92 (d, 2H, J = 8.5 Hz) ppm; ^{13}C NMR δ 14.8 (CH_3), 34.0 (CH_2), 35.3 (CH_2), 37.3 (CH), 40.7 (CH), 44.6 (CH), 58.5 (CH_3), 69.4 (CH), 72.0 (CH_2), 74.8 (CH), 105.6 (CH), 110.1 (CH), 128.0 (C), 128.1 (C), 129.0 (C), 129.2 (C), 131.0 (CH), 131.7 (CH), 131.8 (CH), 132.3 (CH), 140.8 (CH), 156.9 (C), 164.9 (C), 165.1 (C) ppm $[\alpha]^{20}_D$ −30 (CH_2Cl_2, 2.9 × 10^{-3} g cm^{-3}, ee 90%). Anal. Calcd for $C_{28}H_{28}O_6Br_2$: C, 54.21; H, 4.55. Found: C, 54.00; H, 4.58. UV (CH_3CN): λ_{max} 243 nm (ϵ 38 200). CD (CH_3CN): λ_{ext} ($\Delta\epsilon$) 275 (+1.0), 249 (−16.6), 239 (0.0), 233 (+6.7) nm.

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