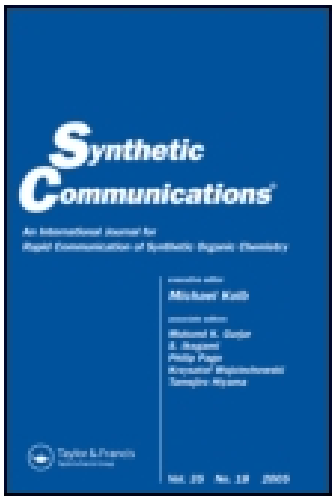

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SYNTHESIS OF DIASTEREOMERICALLY ENRICHED CYCLIC HOMOALLYLIC ALCOHOLS USING MOLYBDENUM π-ALLYL COMPLEXES

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ABSTRACT

Condensation of CpMo(NO)(π-allyl)I complexes bearing a tethered aldehyde gave cyclic homoallylic alcohols with a varying degree of diastereoselectivity. Cyclohexyl and tetrahydronaphthyl derivatives were prepared in moderate to good yields. The diastereoselectivity is highly dependent on the substituents on the ring.

Key Words: π-Allyl complexes; Homoallylic alcohols; Molybdenum; Carbocyclization

INTRODUCTION

Homoallylic alcohols are important intermediates required for natural product synthesis.[1–4] Therefore, stereocontrolled syntheses of these compounds are of consequence. Faller obtained homoallylic alcohols with regio-

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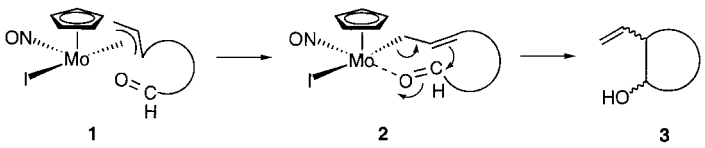
and diastereocontrol by condensation of monosubstituted η^3-allylmolybdenum complexes and aldehydes.[5–7] An enantioselective version of this reaction was carried out by using enantiomerically pure CpMo(NO)(π-allyl)X (X=halogen) complexes.[8,9] Liu performed inter- and intramolecular reactions of π-allyl complexes with aldehydes to obtain the homoallylic alcohol moiety in an array of products.[10–21] Organomolybdenum complexes bearing a π-allyl ligand tethered to a chelating heteroatom were converted to homoallylic alcohols containing an amine or sulfide with high regio- and diastereoselectivity upon reaction with an aldehyde.[22,23] In this work, we investigated the influence of different ring-substituents on the diastereoselectivity of the resulting cyclic homoallylic alcohols. New cyclohexyl and tetrahydronaphthyl derivatives were prepared and characterized.

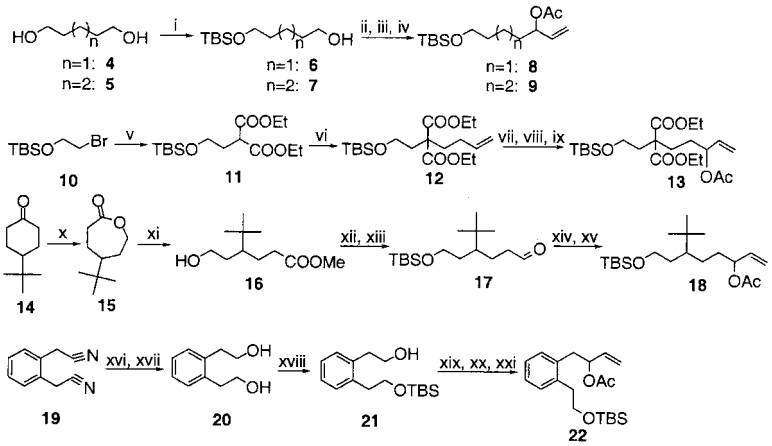
RESULTS AND DISCUSSION

CpMo(NO)(π-allyl)I complexes **1** bearing an aldehyde are unstable and give cyclization products **3** via intermediate **2**, formed by a π to σ allyl shift (Scheme 1). Due to the coordination of the aldehyde to the metal, a preferred conformation of a cyclic intermediate **2** leads to diastereomerically enriched homoallylic alcohols **3**.

For the preparation of the pre-cyclization complexes, a variety of allylic acetates **8**, **9**, **13**, **18** and **22** (Scheme 2) were prepared. Monoprotection[24] of diols **4** and **5** afforded the alcohols **6** and **7**, which were oxidized[25,26] to the corresponding aldehydes (Scheme 2). Subsequent treatment with vinylmagnesium bromide[27] and acetylation gave the substituted allylic acetates **8** and **9**. Alkylation of diethyl malonate with bromide **10** furnished the monosubstituted malonate derivative **11**.[28] A second alkylation with 4-bromo-1-butene resulted in the formation of alkene **12**, which was oxidized to the corresponding aldehyde using ozonolysis. A Grignard reaction followed by acetylation gave allylic acetate **13**. Analog **18** was synthesized from 4-*tert*-butylcyclohexanone, **14**. A Baeyer-Villiger oxidation[29] led to the formation of lactone **15**, which was then hydrolyzed[30]



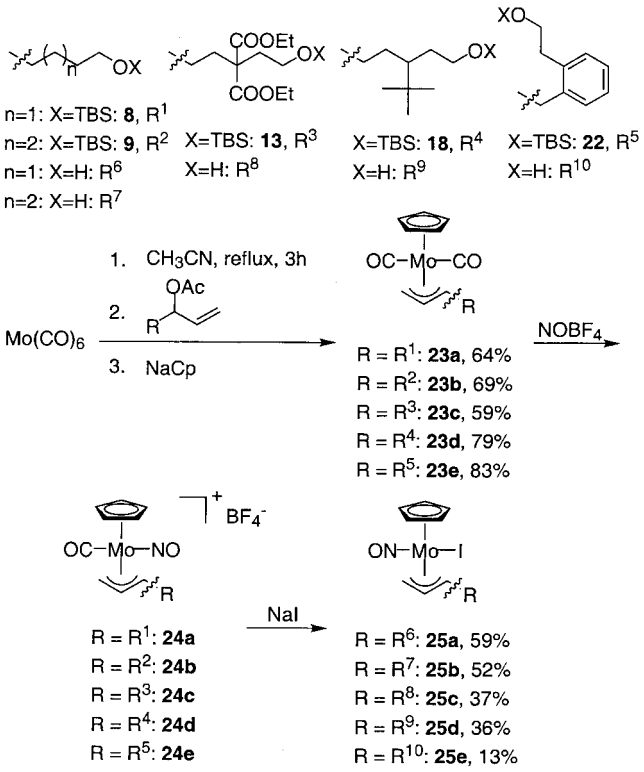
Scheme 1. Formation of cyclic homoallylic alcohols **3** from CpMo(NO)(π-allyl)I complexes **1**.



Scheme 2. *Reagents and conditions*: (i) NaH (1eq.), THF, reflux, 1 h, then TBSCl, rt, 0.5 h, $n=1$: 68%, $n=2$: 58%; (ii) Swern ox., $n=1$: 84%, $n=2$: 80%; (iii) vinylmagnesium bromide (1.5 eq.), THF, $-78^{\circ}C$ to rt, 1.5 h, $n=1$: 57%, $n=2$: 60%; (iv) Ac_2O, pyridine, DMAP, CH_2Cl_2, 5 h, $n=1$: 90%, $n=2$: 97%; (v) sodium diethylmalonate (1 eq.), THF, reflux, 24 h, 73%; (vi) NaH (1.5 eq.), DMF, 15 min., rt, then 4-bromo-1-butene (1.3 eq.), reflux, 4 h, 88%; (vii) O_3, CH_2Cl_2, $-78^{\circ}C$, then Me_2S (5 eq.), NEt_3 (2 eq.), rt, 24 h, 61%; (viii) vinylmagnesium bromide (1.2 eq.), Et_2O, $-78^{\circ}C$ to rt, 25 min., 54%; (ix) Ac_2O, pyridine, DMAP, CH_2Cl_2, 5 h, 90%; (x) *m*-CPBA (2 eq.), CH_2Cl_2, $0^{\circ}C$ to rt, 8 h, 98%; (xi) MeOH/conc. H_2SO_4 (40/1 = v/v), rt, 24 h, 97%; (xii) TBSCl, imidazole, DMF, rt, 24 h, 78%; (xiii) DIBAL-H (1.0 M in toluene), pentane/Et_2O (9/1 = v/v), $-78^{\circ}C$, 1 h, 97%; (xiv) vinylmagnesium bromide (1.3 eq.), THF, $-78^{\circ}C$ to rt, 1.5 h, 65%; (xv) Ac_2O, pyridine, DMAP, CH_2Cl_2, 5 h, 94%; (xvi) EtOH/conc. H_2SO_4 (2.3/1 = v/v), reflux, 7 h, 84%; (xvii) $LiAlH_4$, Et_2O, reflux, 1 h, 92%; (xviii) NaH (1 eq.), THF, rt, 1 h, then TBSCl, reflux, 1 h, 79%; (xix) Swern ox., 63%; (xx) vinylmagnesium bromide (1.3 eq.), THF, $-78^{\circ}C$ to rt, 1.5 h, 58%; (xxi) Ac_2O, pyridine, DMAP, CH_2Cl_2, 5 h, 61%.

yielding hydroxy ester **16**. After a Swern oxidation to the aldehyde, a reaction sequence as outlined above produced allylic acetate **18**. To synthesize allylic acetate **22**, dinitrile **19** was converted to the corresponding diester, then reduced to diol **20**.[31] Monoprotection afforded alcohol **21** which was then oxidized to the corresponding aldehyde. Treatment with vinylmagnesium bromide followed by acetylation gave allylic acetate **22**.

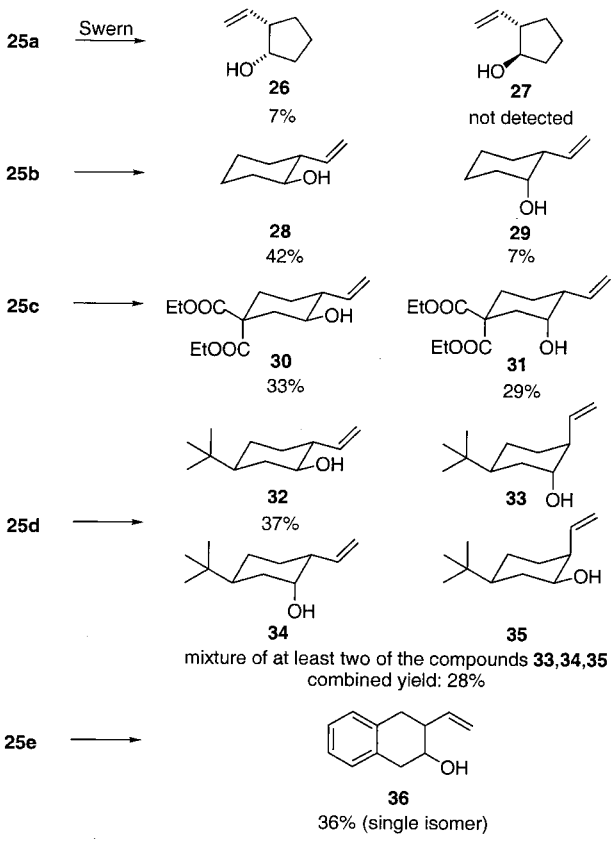
The requisite aldehyde complexes were prepared in situ from the related compounds **25a–e** bearing an alcohol instead of an aldehyde (Scheme 3). Thus, the allylic acetates **8**, **9**, **13**, **18** and **22** were heated with $Mo(CO)_3(CH_3CN)_3$, generated in situ by thermolysis of $Mo(CO)_6$ in acetonitrile. Oxidative addition produces orange (π-allyl)$Mo^{II}(CO)_2(CH_3$-



Scheme 3. Synthesis of the CpMo(NO)(π-allyl)I complexes **25a–e**.

$CN)_2$(OAc) complexes, which were then treated with NaCp to give the air-sensitive dicarbonyl complexes **23a–e** as yellow oils. Addition of $NOBF_4$ in acetonitrile resulted in replacement of one of the carbonyl ligands by a nitrosyl group giving cationic complexes **24a–e**, which were used directly in the next step without further purification. Then, an excess of NaI was added to solutions of **24a–e** in acetone, which caused TBS cleavage and replacement of a CO with iodide. After column chromatography, the complexes **25a–e** were obtained as orange-red oils, that appeared to be a mixture of isomers in solution.[32] The compounds may be handled in air, but decompose when stored at room temperature for longer periods of time.

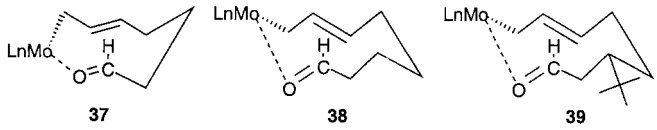
The hydroxyl groups in complexes **25a–e** were oxidized to aldehydes using a Swern oxidation at low temperature. After quenching with triethylamine, the reaction mixture was warmed slowly to room temperature.



Scheme 4. Cyclic homoallylic alcohols obtained from complexes **25a–e** after Swern oxidation and decomplexation.

Before reaching room temperature, the initially orange-red solution turned dark brown. After additional stirring at room temperature, the cyclic homoallylic alcohols were isolated and purified by column chromatography. Scheme 4 shows the cyclization products obtained from the complexes **25a–e**.

The formation of the 2-vinylcyclopentanol from compound **25a** proceeds via the favored 9-membered boat–chair-like transition state **37** shown in Scheme 5, which leads to the *cis*-isomer **26**.[10] Indeed, only **26** could be isolated and detected by ^{1}H-NMR spectroscopy. However, due to the low yield of 7% (average), the formation of small amounts of the *trans*-isomer **27** cannot be ruled out. To form a six-membered ring, complex **25b** was



Scheme 5. Proposed transition states that lead to diastereomerically enriched cyclic homoallylic alcohols.

synthesized. The yield of cyclization products increased to 49% and the *trans*-isomer **28** of 2-vinylcyclohexanol was favored over the *cis*-isomer **29** in a ratio of 6 : 1. The chair–chair-like transition state **38** is evidently preferred and leads primarily to the *trans*-isomer **28**.[10] To investigate the influence of tether substituents on the diastereoselectivity and the yield of the reaction, complexes **25c–e** were prepared. It was expected that two ester groups on the cyclohexyl system would facilitate the cyclization so complex **25c** was studied. While the yield increased to 62%, almost all diastereoselectivity was lost and isomers **30** and **31** were isolated as a 1:1 mixture of diastereomers. A *tert*-butyl group on the tether could theoretically provide the four isomers **32–35**. The major product from the reaction of **25d** was identified as the *trans*-isomer **32**, presumably formed through transition state **39**. At least two of the other isomers were isolated as a mixture and not further characterized. The combined yield of cyclization products from complex **25d** was 65%.

A Swern oxidation of complex **25e** with subsequent condensation leads exclusively to a single isomer of **36** in 36% yield. The relative configuration could not be determined unequivocally since the ^{1}H NOE spectra were inconclusive.

In summary, it was shown that the diastereoselectivity in the resulting cyclic homoallylic alcohols **3** is highly dependent on the tether substituents on the ring. The unsubstituted cyclopentyl derivative was obtained in poor yield, probably caused by the volatility of the compound, whereas the new cyclohexyl and tetrahydronaphthyl derivatives were isolated in moderate to good yields.

EXPERIMENTAL

Typical Procedure for the Synthesis of the Complexes $CpMo(CO)_2(\pi$-allyl) 23a–e

Freshly sublimed $Mo(CO)_6$ (1.11 g, 4.20 mmol) was refluxed in anhydrous CH_3CN (35 mL) for 3 h under an argon atmosphere. Allylic acetate **18**

(1.50 g, 4.21 mmol, neat) was then added to the boiling yellow solution via syringe. After refluxing for 12 h, the dark orange solution was cooled to 0°C, followed by the dropwise addition of a 2 M solution of NaCp in THF (2.52 mL, 5.04 mmol). The resulting mixture was stirred for 1.5 h at rt. Removal of the solvent in vacuo gave a dark brown semi-solid, which was then treated with ether and filtered through a glass filter funnel under an inert atmosphere. The filtrate was concentrated in vacuo and the resulting brown oil was purified by column chromatography under nitrogen (SiO_2, degassed Et_2O : hexanes = 1 : 6), which gave complex **23d** as a yellow, air-sensitive oil in 79% yield.

Typical Procedure for the Synthesis of the Complexes CpMo(NO)(π-allyl)I 25a–e

Complex **23d** (1.59 g, 3.09 mmol) was dissolved in 20 mL of dry CH_3CN under nitrogen. To the cooled solution (0°C) was added $NOBF_4$ (397 mg, 3.40 mmol) in one portion and the mixture was stirred for 5 min after the CO evolution had ceased. After removal of the solvent at 0°C, the residue consisting of **24d** was dissolved in degassed, anhydrous acetone (20 mL). NaI (1.16 g, 7.74 mmol) was added at −25°C, the mixture was stirred for 15 min and then slowly warmed up to 0°C, where it was stirred for a further 30 min under nitrogen. After removal of the solvent in vacuo, the red-brown residue was treated with CH_2Cl_2 and filtered through a short plug of SiO_2 with ether. The solvent was removed at rt followed by purification of the crude product by column chromatography (SiO_2, degassed Et_2O). The resulting complex **25d** was obtained as a red oil in 36% yield.

Typical Procedure for the Synthesis of the Cyclization Products 30–32 and 36

To a cold (−78°C) solution of oxalyl chloride (128 mg, 88.0 μL, 1.01 mmol) in CH_2Cl_2 (8 mL) was added slowly DMSO (144 mg, 131 μL, 1.84 mmol). After 5 min, complex **25d** (420 mg, 0.84 mmol) in CH_2Cl_2 (14 mL) was added dropwise. After 1 h at −78°C under nitrogen, the reaction was quenched with triethylamine (424 mg, 584 μL, 4.19 mmol), stirred for 5 min, then warmed slowly to rt. After 2.5 h, the dark brown mixture was filtered through a plug of silica gel and washed with ether. The solvent was removed and the crude material was purified by column chromatography (SiO_2, Et_2O : hexanes = 1 : 1) to yield 37% of **32** and 28% as a mixture of at least two of the isomers **33–35**).

Characterization of the Cyclization Products 30–32 and 36

The compounds **26–29** are described elsewhere.[33,34] The conformations of the products were determined by ^{1}H NOE spectroscopy, the peaks assigned by homonuclear decoupling.

30: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.65 (ddd, $J = 17.4$, 10.2, 8.5 Hz, 1H), 5.16 (td, $J = 0.9$, 17.4 Hz, 1H), 5.13 (td, $J = 0.9$, 10.2 Hz, 1H), 4.22–4.13 (m, 4H), 3.46 (ddd, $J = 10.2$, 10.2, 4.0 Hz, 1H), 2.63 (ddd, $J = 13.0$, 4.0, 2.3 Hz, 1H), 2.32 (dddd, $J = 13.6$, 3.2, 2.8, 2.3 Hz, 1H), 1.94 (s, 1H), 1.93 (obscured dddd, $J = 12.5$, 10.2, 8.5, 3.4 Hz, 1H), 1.75 (obscured dddd, $J = 13.8$, 3.8, 3.4, 2.8 Hz, 1H), 1.68 (m, 1H), 1.65 (dd, $J = 13.0$, 10.2 Hz, 1H), 1.36 (dddd, $J = 13.8$, 13.4, 12.5, 3.2 Hz, 1H), 1.25 (t, $J = 7.0$ Hz, 3H), 1.22 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 170.9, 139.7, 117.4, 69.4, 61.5, 61.3, 55.4, 49.8, 37.7, 29.9, 26.9, 13.9, 13.8. Anal. calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 62.42; H, 8.36.

31: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.91 (ddd, $J = 17.4$, 10.6, 6.6 Hz, 1H), 5.14 (td, $J = 1.5$, 10.6 Hz, 1H), 5.11 (td, $J = 1.5$, 17.4 Hz, 1H), 4.22–4.13 (m, 4H), 3.96 (very br s, 1H), 2.47 (dd, $J = 14.2$, 4.0 Hz, 1H), 2.34 (br ddd, $J = 13.6$, 4.7, 3.6 Hz, 1H), 2.22 (br dddd, $J = 14.5$, 6.6, 4.0, 3.8 Hz, 1H), 2.09 (dd, $J = 13.2$, 3.0 Hz, 1H), 2.01 (br s, 1H), 1.89 (dddd, $J = 14.5$, 11.3, 11.3, 3.6 Hz, 1H), 1.71 (ddd, $J = 13.6$, 11.3, 4.0, 1H), 1.56 (dddd, $J = 13.6$, 4.7, 4.0, 4.0 Hz, 1H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.22 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 172.1, 139.1, 116.3, 67.8, 61.4, 61.3, 52.4, 44.4, 36.2, 29.6, 21.8, 13.9, 13.8. Anal. calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 62.21; H, 8.20.

32: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.68 (ddd, $J = 17.6$, 10.3, 8.8 Hz, 1H), 5.17 (td, $J = 1.5$, 17.6 Hz, 1H), 5.13 (td, $J = 1.5$, 10.3 Hz, 1H), 3.26 (ddd, $J = 9.8$, 9.8, 4.4 Hz, 1H), 2.09 (dddd, $J = 12.2$, 4.4, 2.5, 2.5 Hz, 1H), 1.89 (s, 1H), 1.82 (obscured dddd, $J = 12.2$, 3.4, 3.4, 2.5 Hz, 1H), 1.83 (obscured dddd, $J = 12.2$, 9.8, 8.8, 3.4 Hz, 1H), 1.72 (ddddd, $J = 12.2$, 2.9, 2.9, 2.5, 2.5 Hz, 1H), 1.18 (dddd, $J = 12.2$, 12.2, 12.2, 2.9 Hz, 1H), 1.12 (dddd, $J = 12.2$, 12.2, 2.9, 2.5 Hz, 1H), 1.02 (partly obscured ddd, $J = 12.2$, 12.2, 9.8 Hz, 1H), 1.01 (partly obscured dddd, $J = 12.2$, 12.2, 2.9, 2.5 Hz, 1H), 0.87 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.8, 116.8, 73.3, 51.1, 46.5, 35.0, 32.3, 30.8, 27.5, 26.0. Anal. calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.87; H, 12.23.

36: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05–6.98 (m, 4H), 5.96 (ddd, $J = 17.2$, 10.4, 7.2 Hz, 1H), 5.09 (td, $J = 1.5$, 17.2 Hz, 1H), 5.05 (td, $J = 1.5$, 10.4 Hz, 1H), 4.09 (ddd, $J = 5.0$, 4.7, 2.7 Hz, 1H), 2.97 (dd, $J = 17.2$, 4.7 Hz, 1H), 2.90 (dd, $J = 16.3$, 9.1 Hz, 1H), 2.79 (dd, $J = 17.2$, 5.4 Hz, 1H), 2.76 (dd, $J = 17.2$, 5.4 Hz, 1H), 2.56–2.52 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.1, 138.6, 134.7, 133.2, 129.5, 128.9, 126.0, 116.5, 68.4, 42.6,

36.5, 30.1. Anal. calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.63; H, 8.20.

ACKNOWLEDGMENTS

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32. An equilibrium of *endo* and *exo* isomers was detected in $CDCl_3$ for **25a–e** as well as for **23a–e**. It should be noted that the presence of a mixture of isomers should not have an influence on the diastereoselectivity of the homoallylic alcohols obtained from the cyclization reaction. This is explained by the reaction pathway outlined in Scheme 1 involving a π-σ-π interconversion mechanism.
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