Stereoselective Photochemical Synthesis and Structure Elucidation of 1-Methyl-Substituted Tricyclo[6.2.0.0^{2,6}]decanes and Tricyclo[7.2.0.0^{2,7}]undecanes

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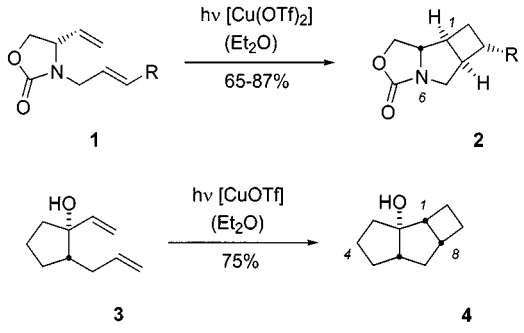
The *trans*- and *cis*-substituted 2-allyl-1-(2-propenyl)cyclopentanes **5a** (47% yield) and **5b** (33% yield) as well as the *trans*- and *cis*-substituted 2-allyl-1-(2-propenyl)cyclohexanes **6a** (48% yield) and **6b** (64% yield) were synthesized from the corresponding 1-acetyl-1-cycloalkenes. Their intramolecular, Cu-catalyzed [2+2] photocycloaddition reaction was studied in ether as the solvent. The reaction proceeded with excellent facial diastereoselectivity. The *trans*-cycloalkanes **5a** and **6a** exclusively yielded the *trans-anti-cis* products **11a** (80%) and **12a** (80%), whereas the *cis*-cycloalkanes **5b** and **6b** yielded the *cis-syn-cis* products **11b** (77%) and **12b** (88%). The structures of the products **11a** and **12a** were elucidated by NMR spectroscopy. The configuration assignments of compounds **11b** and **12b** were confirmed by independent syntheses of these compounds. Stereoselective hydrogenation of the unsaturated tricycloalkenes **13** and **14** gave access to the tricycloalkanes **11b** (69%) and **12b** (79%).

The intramolecular Cu-catalyzed [2+2] photocycloaddition of 1,ω-dienes is a powerful method for the construction of bicyclic compounds.[1] The facial diastereoselectivity of the reaction can be controlled by a stereogenic center within the carbon chain[2] or by chiral auxiliaries.[3] Attempts to induce significant enantiofacial differentiation by chiral catalysis have encountered only limited success.[3] Recent applications of the intramolecular Cu-catalyzed [2+2] photocycloaddition have centered on the synthesis of multiply substituted, naturally occurring cyclopentanes and cyclobutanes.[4] These are formed from the primary photoadducts through subsequent ring-opening or rearrangement reactions.[5]

We became interested in the preparative use of the [2+2] photocycloaddition in connection with our studies on the stereoselective synthesis of biologically active 3-azabicyclo[3.2.0]heptanes from amino acid derived diallylamines.[6] In this context it turned out that *N*-allyl-4-ethenyloxazolidinones **1** react with perfect facial diastereoselectivity to afford the corresponding heterocyclic tricyclo[6.2.0.0^{2,6}]decanes **2** (Scheme 1; Tf = trifluoromethanesulfonate). The stable Cu(OTf)$_2$ proved to be a suitable precursor for the catalytically active Cu^{I}.[2e][6b]

The only other tricyclic products that have previously been synthesized by means of Cu-catalyzed photocycloaddition reactions are 2-hydroxytricyclo[6.2.0.0^{2,6}]decanes (e.g., **4**), which are formed from the corresponding dienes (e.g., **3**; Scheme 1).[2c] In the latter case, the high facial diastereoselectivity was attributed to the known binding affinity of Cu^{I} to hydroxy groups.[2a] The coordination of the two olefinic double bonds to the metal ion forces the carbon−carbon bond formation at the vinylic carbon atom to occur from its (*Si*) face. Analogous stereochemical results were obtained in the synthesis of 2-hydroxytricyclo[7.2.0.0^{2,7}]undecanes and higher homologues.[2c]



Scheme 1. Previous syntheses of hetero- and carbocyclic tricyclo[6.2.0.0^{2,6}]decanes by Cu-catalyzed [2+2] photocycloadditions

To account for the high facial diastereoselectivity in the oxazolidinone photocycloaddition (**1** → **2**, Scheme 1) it was assumed that a preferred conformation **1-I** exists, in which the hydrogen atom H-4 and the vinylic hydrogen atom are oriented perfectly *anti*-periplanar to each other.[6b] The metal ion coordinates to the (*Re*) face of the ethenyl group and the photocycloaddition transforms the conformation **1-I** into the depicted configuration of compound **2**, in which the hydrogen atoms at C-1 and C-2 are located *trans*.

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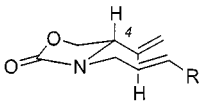
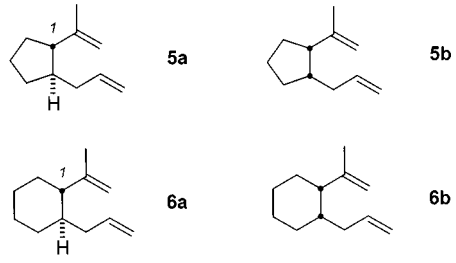


1-I

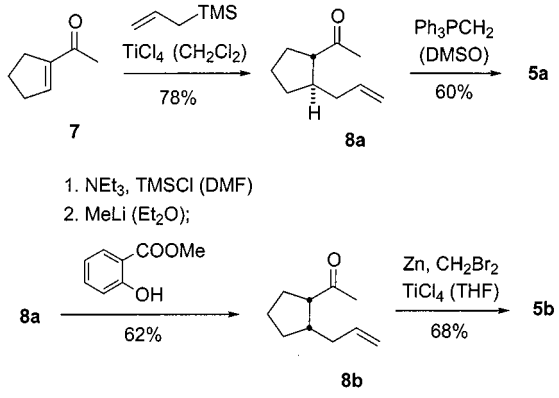
From this argument one would expect that other five- and six-membered rings bearing vicinal vinyl and allyl groups should stereoselectively yield the corresponding tricyclic products upon [2+2] photocycloaddition. In this study we looked into photocycloaddition reactions of the cyclopentanes **5** and the cyclohexanes **6**, which display this substitution pattern. Unlike the hydroxy-substituted substrates such as **3**, these cycloalkanes lack sites for additional Cu^I coordination, and so any diastereoselection should consequently derive from conformational preferences of the cyclic 1,6-dienes. The tricyclo[6.2.0.0^{2,6}]decane and tricyclo[7.2.0.0^{2,7}]undecane skeletons[7] of the potential products were considered to be of synthetic interest due to their occurrence in natural products and we made an effort to prove their relative configurations unambiguously and to assign all carbon and hydrogen atoms. For a number of reasons, we selected the 1-(2-propenyl)-substituted substrates instead of their 1-ethenyl counterparts as starting materials. Firstly, several naturally occurring tricyclo[6.2.0.0^{2,6}]decanes have a methyl group located at C-1.[8] Secondly, we hoped that the structure elucidation of the product would be facilitated by the distinctive methyl substituent. Finally, the *syn*-periplanar arrangement of a methyl group and a hydrogen atom was expected to be strongly disfavored, and this might limit the conformational freedom around the alkenyl−cycloalkyl bond.



According to the argument given above, the stereogenic centers at C-1 in the substrates should be solely responsible for the facial discrimination. This hypothesis was tested by the use of both substrate diastereoisomers: **5a/5b** and **6a/6b**. As it turned out, the *trans* isomers **5a** and **6a** did indeed conform with our expectations and delivered tricyclic products with *trans* orientations of the methyl group at C-1 and the hydrogen atom at C-2. The *cis* isomers **5b** and **6b**, however, formed products in which the new central five-membered ring was fused to the other rings in a concave *cis-syn-cis* fashion; that is, the methyl group at C-1 and the hydrogen atom at C-2 were *cis*-oriented. Details of the study are provided below.

1. Stereoselective Preparation of the Substrates 5 and 6

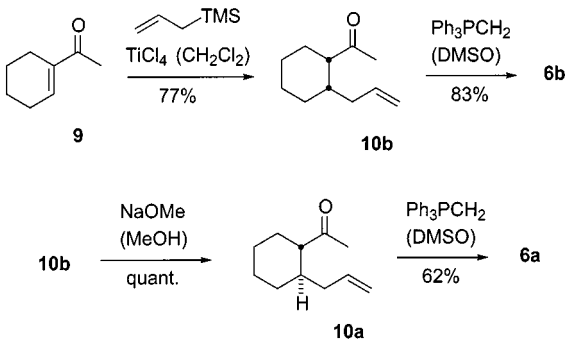
Compounds **5a** and **5b** were available from 1-acetyl-1-cyclopentene (**7**),[9] as outlined in Scheme 2 (TMS = trimethylsilyl). A Sakurai reaction yielded the thermodynamically preferred *trans*-substituted cyclopentane **8a** as the major product (*trans*/*cis* = 80:20).[10] A Wittig reaction with ketone **8a** proceeded smoothly in DMSO as the solvent, with compound **5a** being obtained as the major product (*trans*/*cis* = 92:8). Apparently, the basic conditions of the Wittig reaction allow for further equilibration in favor of the more stable product. The *cis*-ketone **8b** was obtained in significant diastereomeric excess by use of the method of Krause et al;[11] the higher substituted lithium enolate of ketones **8**, which was in turn available from the corresponding silyl enol ether (82% yield), was stereoselectively protonated by methyl salicylate (77% yield), a proton source superior to other esters of salicylic acid. By this means, ketone **8b** was prepared in a stereoselective fashion, although it was still contaminated with ketone **8a** (*cis*/*trans* = 80:20). The Wittig reaction proved unsuited for the conversion of ketone **8b** into alkene **5b**, as it resulted in a rapid epimerization in favor of the *trans* compound **8a**. The Lombardo reagent[12] finally turned out to be the methylenation reagent of choice, as it interfered only slightly with the stereochemical integrity of the cyclopentane. The *cis* product **5b** was obtained as the major diastereoisomer (*cis*/*trans* = 76:24).



Scheme 2. Preparation of the *trans*- and *cis*-substituted 2-allyl-1-(2-propenyl)cyclopentanes **5a** and **5b**

In the case of the six-membered 1-acetyl-1-cyclohexene (**9**),[9a] the Sakurai reaction yielded the kinetically favored *cis*-cyclohexane **10b** (*cis*/*trans* = 90:10), which did not epimerize as readily as its five-membered analogue (Scheme 3). The subsequent methylenation proceeded smoothly and gave the desired *cis*-substituted product **6b** after chromatographic purification (*cis*/*trans* = 96:4). An equilibration of compound **10b** into the thermodynamically favored acetylcyclohexane **10a** was achieved by base treatment (*trans*/*cis* = 92:8). Interestingly, the Wittig reaction used to convert ketone **10a** into the diene **6a** proceeded with a decrease

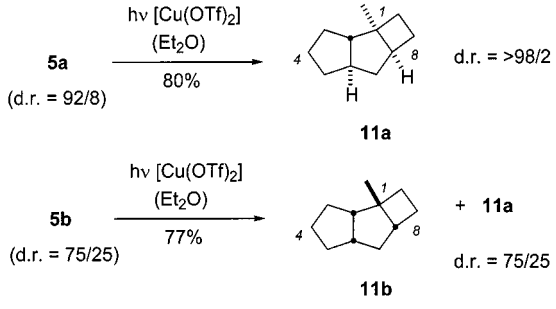
in the *trans*/*cis* ratio (*trans*/*cis* = 80:20). Possible reasons for this result were not sought experimentally. It is conceivable that the acetyl group in the *cis* diastereoisomer **10b** is more readily accessible by the nucleophile and that the higher rate of its methylenation causes the observed stereochemical drift.



Scheme 3. Preparation of the *trans*- and *cis*-substituted 2-allyl-1-(2-propenyl)cyclohexanes **6a** and **6b**

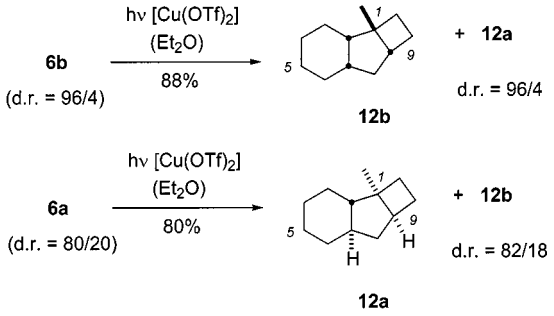
2. [2+2] Photocycloaddition and Proof of the Relative Configuration

All four desired compounds − **5a**, **5b**, **6a**, and **6b** − were prepared in sufficient stereochemical purity by the reactions presented above. The subsequent photocycloaddition reactions were conducted in anhydrous diethyl ether as the solvent with a short-wave irradiation source (Rayonet RPR-2537 Å) and with $Cu(OTf)_2$ or CuOTf as the catalyst (8 mol %). In the five-membered ring series, both photocycloaddition reactions proceeded smoothly. Compound **5a** exclusively yielded a single product, **11a**. Compound **5b**, which was not fully diastereomerically pure (*cis*/*trans* = **5b**/**5a** = 75:25, vide supra), yielded two diastereomeric products. The minor diastereoisomer turned out to be the hydrocarbon **11a**; the major diastereoisomer **11b** (**11b**/**11a** = 75:25) was apparently formed by the stereoselective [2+2] photocycloaddition of compound **5b** (Scheme 4).



Scheme 4. Diastereoselective [2+2] photocycloaddition reactions of the *trans*- and *cis*-substituted 2-allyl-1-(2-propenyl)cyclopentanes **5a** and **5b**

The cyclohexanes **6** behaved similarly to the corresponding cyclopentanes **5** in the course of their [2+2] photocycloadditions (Scheme 5). The diastereomeric ratios of the starting materials corresponded to the diastereomeric ratios of the products. The *cis*-substituted cyclohexane **6b**, obtained in high diastereomeric purity (*dr* = 96:4) from 1-acetyl-1-cyclohexene (Scheme 3), gave a main product **12b**, with compound **12a** as a minor impurity (*dr* = 96:4). The more impure starting material *trans*-cyclohexane **6a**, which contained significant amounts of **6b** (*dr* = 80:20), gave two products in a ratio of 82:18. The minor product was identified as tricycloundecane **12b** (vide infra), the major product − derived exclusively from *trans*-cyclohexane **6a** − was identified as compound **12a**.

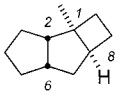


Scheme 5. Diastereoselective [2+2] photocycloaddition reactions of the *trans*- and *cis*-substituted 2-allyl-1-(2-propenyl)cyclohexanes **6a** and **6b**

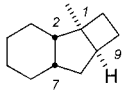
In order to prove the relative configurations of the tricyclic hydrocarbons **11** and **12**, all carbon and hydrogen atoms in the product were assigned by conventional one- and two-dimensional NMR techniques (DEPT, HMQC, HMBC, ^{1}H-^{1}H COSY). Typically, the easily identifiable (DEPT) methyl group was taken as the starting point of the assignment in the tricyclo[6.2.0.0^{2,6}]decane series. The quaternary carbon atom C-1 was also easily detectable by DEPT experiments. Direct ^{1}H-^{13}C correlations ($^1J_{CH}$) were assigned by HMQC. HMBC ($^2J_{CH}$, $^3J_{CH}$) revealed that two (at C-2 or C-8) out of three methine protons were located in the position γ to the methyl carbon atom. The third methine proton, which showed no HMBC correlation to the methyl carbon atom, had to be the methine proton at C-6. In addition, the only two methylene protons that exhibited an HMBC correlation to the methyl carbon atom had to be located at C-10. A similar HMBC analysis starting from the assigned carbon atom C-10 revealed the chemical shifts of the methylene protons at C-9. All further assignments (C-3, C-4, C-5, C-7, C-8) could be deduced from trivial ^{1}H-^{1}H COSY correlations. In an analogous fashion, peak assignment was performed for the tricyclo[7.2.0.0^{2,7}]undecanes **12**.

As essentially no data on configuration assignments of tricyclo[6.2.0.0^{2,6}]decanes or tricyclo[7.2.0.0^{2,7}]undecanes were available, we studied the obtained photocycloaddition products carefully by ^{1}H NOESY experiments. In particular, we hoped to ascertain the relevant substitution pattern on the central five-membered ring by this means. We were aware, however, that the photocycloaddition products of the

cis compounds **5b** and **6b** would be difficult to study. The possible diastereoisomers **11b′** and **12b′** would show essentially no ^{1}H NOE contacts, thanks to the *trans* arrangement of hydrogen atoms or methyl groups at C-1/C-2 and C-6/C-8 (**11b′**) and at C-1/C-2 and C-7/C-9 (**12b′**).

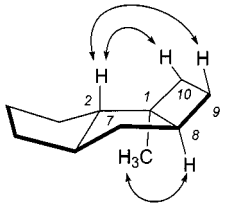


11b'

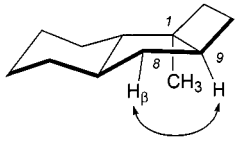


12b'

The problem was further complicated by the fact that the products derived from **5b** and **6b** displayed only a few distinct ^{1}H NMR signals, with many overlapping signals in the aliphatic region (δ = 1.0−2.5), due to resonance at almost identical frequencies. The initial experiments facilitated clear stereochemical assignments for the photocycloaddition product **11a**. No conclusive data, however, were obtained for compounds **12a**, **11b/11b′**, and **12b/12b′**. The assignment of compound **11a** on the basis of its major ^{1}H NOE contacts was straightforward (Figure 1). There were unambiguous contacts between the protons of the methyl group and proton H-8 and, more importantly, between proton H-2 and the methylene protons of the cyclobutane ring (H-9 and H-10). The relative configuration of compound **12a** was deduced from the apparent analogy to compound **11a**, which is reflected by close similarities in their ^{1}H NMR spectra. As an example, the ^{1}H NMR spectroscopic data of compound **12a** for the two protons at C-8 [δ = 1.05 (pseudo dt, 1 H, J = 5.1 Hz, J = 11.6 Hz), 1.99 (ddd, 1 H, J = 6.5 Hz, J = 8.3 Hz, J = 11.8 Hz)] were almost identical to the data obtained for the protons at C-7 of compound **11a** [δ = 1.07 (pseudo dt, 1 H, J = 5.1 Hz, J = 11.8 Hz), 1.99 (ddd, 1 H, J = 6.7 Hz, J = 8.2 Hz, J = 11.9 Hz)]. From inspection of molecular models and the observed coupling constants, it appeared sensible to assign the protons at lower field to H-7$_\beta$ (for **11a**) and H-8$_\beta$ (for **12a**) and the protons at higher field to H-7$_\alpha$ (for **11a**) and H-8$_\alpha$ (for **12a**). The NOESY contact between the proton signal at δ = 1.99 (H-8$_\beta$) and that of proton H-9 recorded for compound **12a** was fully in line with this assignment (Figure 1).



11a

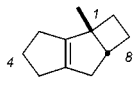


12a

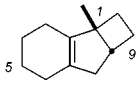
Figure 1. Major ^{1}H NOE signals recorded for compounds **11a** and **12a**

A weak ^{1}H NOE contact was observed for the protons of the methyl group and the proton H-7 in compound **12b/12b′**. This result was significant because it suggested a *cis-syn-cis* arrangement as in **12b**, but ruled out a *cis-anti-cis* arrangement as in **12b′**. In intensity, the signal was similar to the contact between the methyl group and proton H-9, which are located in a vicinal *cis* fashion. Despite this evidence, we looked for additional proof of the assignment in particular, as the result conflicted with our initial idea about the face selectivity (vide supra).

Chemical proof of the assignment was potentially available from independent syntheses of these products. Earlier work had shown that electrophilic or nucleophilic attack (hydrogenation, hydride reduction, epoxidation) at the double bond of unsaturated bi- and tricyclic compounds related to **13** and **14** occurs from the concave face.[13] In our case, the hydrogenation of compounds **13** and **14** should consequently directly deliver the *cis-syn-cis* compounds **11b** and **12b**.

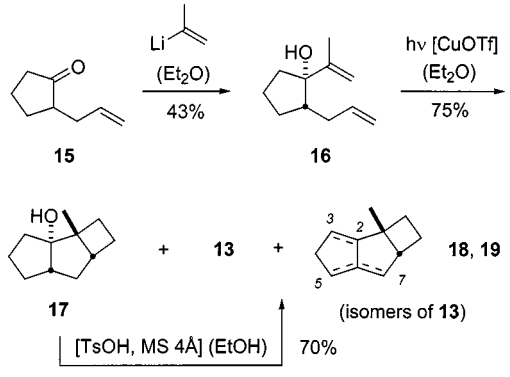


13



14

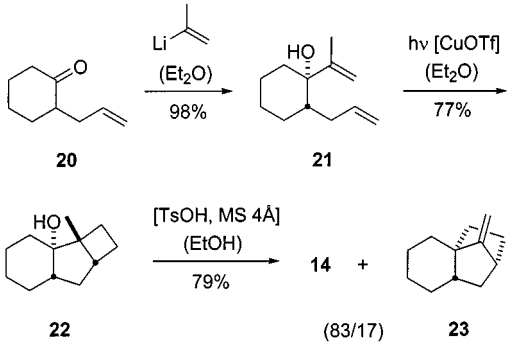
The attempted synthesis of compound **13** commenced with the allylated cyclopentanone **15**[14] (Scheme 6). Carbonyl addition of 2-propenyllithium gave the tertiary alcohol **16**. The subsequent photocycloaddition yielded not only the direct photocycloaddition product **17**, but also the three elimination products **13**, **18**, and **19**. The elimination could not be fully suppressed, even if the less Lewis acidic CuOTf was employed instead of Cu(OTf)$_2$ as the photocatalyst. The alcohol **17** and the elimination products were typically formed in a ratio of 34:66. The alkene **13** was inseparable from its double bond isomers **18** and **19**. The relative ratio of the olefins **13**, **18**, and **19** determined by ^{13}C NMR spectroscopy and GC was 55:30:15. Elimination of the separated alcohol **17** under controlled conditions (TsOH = *p*-toluenesulfonic acid) yielded a ratio of alkenes more strongly in favor of the tetrasubstituted olefin **13** (ratio: 80:14:6). The structures of the olefins **18** and **19** were not elucidated, but they undoubtedly represent isomers of **13**. As potential locations for their double bonds, the positions C-2/C-3, C-5/C-6, or C-6/C-7 are likely.



Scheme 6. Preparation of the unsaturated tricyclo[6.2.0.0^{2,6}]-decene **13**

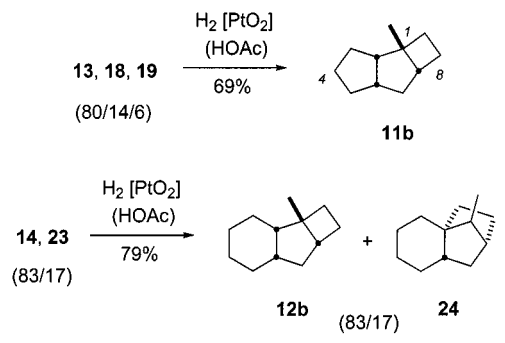
The synthesis of olefin **14** was performed in close analogy to the synthesis of olefin **13**, starting with the commercially

available cyclohexanone **20** (Scheme 7). Both the carbonyl addition and the Cu^{I}-catalyzed photocycloaddition proceeded smoothly and in high yields. Contrary to our findings in the five-membered ring case, there was no severe hydro-hydroxy elimination to the desired alkene **14** in the photocycloaddition step. Besides the alcohol **22**, which was isolated in 77% yield, an inseparable pair of alkenes was isolated in 19% yield and in a ratio of 70:30. These were identified as the rearranged[2c] 1,1-disubstituted alkene **23** and the desired alkene **14**. The alkene **14** was eventually prepared by an acid-catalyzed elimination reaction from the alcohol **22**. It was accompanied by minor amounts of alkene **23** (ratio: 83:17).



Scheme 7. Preparation of the unsaturated tricyclo[7.2.0.0^{2,7}]undecene **14**

The hydrogenation experiments were conducted under atmospheric hydrogen pressure with Adams catalyst (PtO_2) in glacial acetic acid (Scheme 8). The alkene mixture **13**, **18**, and **19** obtained from the elimination of alcohol **17** yielded a single product. According to its NMR spectra, the substance was fully identical with the photocycloaddition product obtained from 1,6-diene **5b** (Scheme 4). The alkene mixture obtained from alcohol **22** gave two products, the minor one of which was alkane **24**, the hydrogenation product of alkene **23**. The major product was derived from alkene **14** and proved identical to the photocycloaddition product previously obtained from substrate **6b** (Scheme 5). The results unequivocally established the structure assignment originally tentatively based on the ^{1}H NOESY data of compounds **11b** and **12b**.

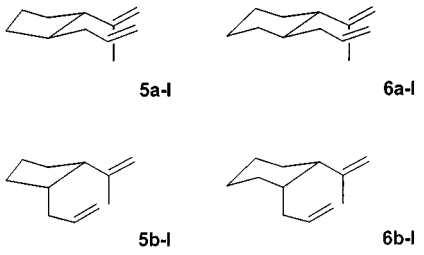


Scheme 8. Independent syntheses of compounds **11b** and **12b** by hydrogenation of the alkenes **13** and **14**

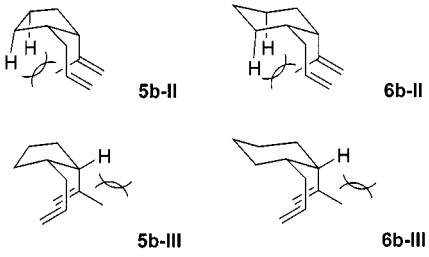
3. Discussion and Conclusion

A remarkable result of the study is the perfect facial diastereoselectivity observed in the photocycloaddition reactions of all four substrates **5a**, **5b**, **6a**, and **6b**. For the *trans*-substituted bridged 1,6-dienes **5a** and **6a**, the outcomes of the reactions can be interpreted straightforwardly by conformations **5a-I** and **6a-I**. The Cu^{I} ion can be viewed as residing between the two double bonds and facilitating the photocycloaddition, as previously postulated for related cases.[1] Both substituents at the ring can adopt strain-minimized equatorial or pseudo-equatorial positions.

The situation for the *cis*-substrates **5b** and **6b** is clearly different. Conformations **5b-I** and **6b-I**, with equatorially oriented 2-propenyl groups and axial allyl groups, are not suited for intramolecular photocycloaddition reactions. The reactive double bonds are too far apart from each other and the four centers that form the cyclobutane cannot be perfectly aligned. The π-systems are parallel to each other but they are substantially shifted relative to the corresponding reaction centers.



In order to achieve a perfect alignment for cyclobutane formation, conformations **5b-II**, **5b-III**, **6b-II**, and **6b-III** have to be populated. The allyl group resides in an equatorial and the 2-propenyl group in an axial position. In **5b-II** and **6b-II**, the methyl group suffers from severe strain due to disfavored interactions with the hydrogen atoms of the five- or six-membered ring. The strain is less substantial in the conformations **5b-III** and **6b-III**, which are accessible through rotation around the cycloalkyl−2-propenyl single bonds and in which the methylidene group points towards the ring. We consider these conformations responsible for the observed facial diastereoselectivity.



Clear differences from the oxazolidinones **1** that we had previously studied (Scheme 1) are obvious from this analysis. Most importantly, the allyl group at the nitrogen atom is not fixed in a dihedral angle of 60 ° relative to the alkenyl group. The dihedral angle is smaller and consequently al-

lows a better alignment of the double bonds in conformation **1-I** than in **5b-I** and **6b-I**. In addition, the alkenyl group used in the oxazolidinone series was not a 2-propenyl moiety but an ethenyl group. This aspect is of minor importance for oxazolidinones, as the alkenyl group in compounds of type **1** will not adopt an axial position. The size differences between methyl and methylidene and between hydrogen and methylidene are not relevant for the facial diastereoselectivity. It should, however, be relevant for substituted cyclohexanes and cyclopentanes. Since we might expect the configuration assignment of the photocycloaddition products from 2-allyl-1-ethenylcyclopentanes and 2-allyl-1-ethenylcyclohexanes to be even more complex than assignment in the 1-(2-propenyl) series, we have not looked into their photocycloaddition reactions.[15]

In summary, it has been shown that Cu-catalyzed [2+2] photocycloadditions of 2-allyl-1-(2-propenyl)-substituted cycloalkanes proceed with high facial diastereoselectivities. The *trans*-substituted substrates yield the *trans-anti-cis* products, whereas the *cis*-substituted substrates yield the *cis-syn-cis* products. The configurations of the products were established by NMR spectroscopy and by independent synthesis. Applications of the photocycloaddition methodology to the synthesis of naturally occurring 1-methyl-substituted tricyclo[6.2.0.0^{2,6}]decanes and tricyclo[7.2.0.0^{2,7}]undecanes are plausible, and are currently being pursued in our laboratories.

Experimental Section

General: All reactions involving water-sensitive compounds were carried out in flame-dried glassware with magnetic stirring under argon. Common solvents [*tert*-butyl methyl ether (TBME), pentane (P), ethyl acetate (EA), diethyl ether, and dichloromethane] were distilled prior to use. Anhydrous CH_2Cl_2 was distilled from CaH_2, anhydrous Et_2O and tetrahydrofuran (THF) from K/Na immediately prior to use. *N*,*N*-Dimethyl formamide (DMF, Fluka puriss. abs.), dimethyl sulfoxide (DMSO, Fluka puriss. abs.), zinc powder (Fluka, p.a., ≥ 99%), 2-allylcyclohexanone (Aldrich, 97%), and all other reagents were used as received. IR: Nicolet 510M FT-IR or Perkin−Elmer 1600 FT-IR. MS: Varian CH7 (EI). HRMS: Finnigan MAT 95S or MAT 8200. GC-MS: Agilent 6890 (GC system), Agilent 5973 (Mass selective detector). Elementary analysis: Varian Elementar vario EL. ^{1}H and ^{13}C NMR:[16] Bruker ARX 200, AC 250, AC 300, AMX 400, and AMX 500. Chemical shifts are reported relative to tetramethylsilane as internal reference. Interchangeable assignments are marked with an asterisk (*). The multiplicities of the ^{13}C NMR signals were determined by APT or DEPT experiments. TLC: Merck glass sheets 0.25 mm silica gel 60 F_{254}. Detection by coloration with potassium permanganate solution (1% in H_2O). Flash chromatography:[17] Merck 60 silica gel (230−400 mesh) (ca. 50 g for 1 g of material to be separated), eluent given in brackets.

***trans*-2-Allyl-1-(2-propenyl)cyclopentane (5a)**

Typical Procedure A: Methyltriphenylphosphonium iodide (888 mg, 2.20 mmol) was dissolved in 5 mL of DMSO and a solution of *n*-butyllithium in *n*-hexane (2.20 mmol, 1.28 mL of a 1.7 M solution) was added at room temperature. The mixture was stirred at room temperature for an additional 2 h. Subsequently, *trans*-1-acetyl-2-allyl-cyclohexane[10] (**8a**, 258 mg, 1.69 mmol) was added dropwise by syringe. After 12 h, the reaction mixture was quenched with water (10 mL) and extracted with pentane (3 × 10 mL). The organic layers were washed with water (10 mL) and brine (10 mL), and dried with $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was purified by flash chromatography (P). Compound **5a** (150 mg, 60%) was obtained as a colorless liquid (*trans*/*cis* = 92:8). R_f = 0.67 (P). IR (film): $\tilde{\nu}$ = 3075 cm^{-1} (m, CH), 2955 (s, CH), 2870 (w, CH), 1640 (m, C=C), 1455 (m, CH), 1375 (w, CH), 1250 (m), 910 (m, CH), 890 (m, CH). ^{1}H NMR (500 MHz): δ = 1.25−1.30 (m, 1 H, C*H*H), 1.50−1.56 (m, 1 H, CH*H*), 1.63 (pseudo quint, *J* = 7.3 Hz, 2 H, $CH_2CH_2CH_2$), 1.71 (s, 3 H, CH_3), 1.75−1.90 (m, 4 H, C*H*CH_2CH=CH_2, C*H*HCH=CH_2, CH_2), 2.11 [pseudo q, *J* = 9.0 Hz, 1 H, C*H*C(Me)=CH_2], 2.25−2.30 (m, 1 H, CH*H*CH=CH_2), 4.75 [s, br, 2 H, C(Me)=C*H*$_2$], 4.97 (d, *J* = 10.0 Hz, 1 H, *cis*-CH=C*H*H), 5.02 (d, *J* = 17.1 Hz, *trans*-CH=CH*H*), 5.79−5.88 (m, 1 H, C*H*=CH_2). ^{13}C NMR (125 MHz): δ = 19.4 (q, CH_3), 23.8 (t, $CH_2CH_2CH_2$), 31.5 (t, CH_2), 31.6 (t, CH_2), 38.6 (t, *C*H_2CH=CH_2), 42.8 (d, *C*HCH_2CH=CH_2), 53.7 [d, *C*HC(Me)=CH_2], 110.2 [t, CHC(Me)=*C*H_2], 114.9 (t, CH=*C*H_2), 138.0 (d, *C*H=CH_2), 147.6 [s, *C*(Me)=CH_2]. MS (70 eV): *m*/*z* (%) = 150 (< 1) [M$^+$], 135 (12) [(M − CH_3)$^+$], 108 (100) [(M − C_3H_6)$^+$], 93 (43) [$C_7H_9^+$], 81 (27), 73 (37), 67 (31) [$C_5H_7^+$], 55 (27) [$C_4H_7^+$], 41 (36) [$C_3H_5^+$]. HRMS: calcd. for $C_{11}H_{18}$ 150.1409; found 150.1394.

***cis*-1-Acetyl-2-allyl-cyclopentane (8b):** A solution of *trans*-1-acetyl-2-allylcyclopentane[10] (**8a**, 4.46 g, 29.3 mmol) in 4 mL of DMF was added dropwise to a refluxing solution of triethylamine (5.90 g, 8.10 mL, 58.4 mmol) and chlorotrimethylsilane (6.61 g, 7.70 mL, 60.9 mmol) in 40 mL of DMF. The mixture was refluxed for 15 h, allowed to cool to ambient temperature, and subsequently partitioned between pentane (200 mL) and cold aqueous $NaHCO_3$ (100 mL). The organic layer was washed with brine (50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. Further purification of the residue was carried out by flash chromatography (P/Et_2O = 95:5). The product [1-(2-allylcyclopentylidene)ethoxy]trimethylsilane (4.13 g, 63%) was isolated as a yellow oil as a mixture of diastereoisomers. In addition, the starting material **8a** (1.04 g, 23%) was recovered. R_f = 0.73 (P/Et_2O = 95:5). ^{1}H NMR (200 MHz): δ = 0.14−0.20 [m, 9 H, Si(CH_3)$_3$], 1.40−2.70 (m, 12 H, aliph. H), 4.88−5.05 (m, 2 H, CH=C*H*$_2$), 5.65−5.90 (m, 1 H, C*H*=CH_2). MS (70 eV): *m*/*z* (%) = 224 (23) [M$^+$], 209 (< 1) [(M − CH_3)$^+$], 184 (15) [(M − C_3H_4)$^+$], 183 (86) [(M − C_3H_5)$^+$], 181 (2) [(M − $SiMe_3$)$^+$], 147 (10), 75 (31) [$C_2H_7OSi^+$], 73 (100) [Me_3Si^+]. Methyllithium in Et_2O (20.3 mmol, 13.5 mL of a 1.5 M solution) was added dropwise to a solution of [1-(2-allylcyclopentylidene)ethoxy]trimethylsilane (4.00 g, 17.8 mmol) in 50 mL of anhydrous Et_2O. The resulting mixture was stirred for 1 h at room temperature. A solution of methyl salicylate (9.15 mL, 10.8 g, 7.13 mmol) in 70 mL of Et_2O was cooled to −78 °C. The lithium enolate was added dropwise to this solution by syringe. The mixture was allowed to warm to room temperature. Acetic acid (4.10 mL, 4.31 g, 71.7 mmol) was added to the suspension. The mixture was filtered through a Celite pad. The filtrate was washed with aqueous KOH (10%, 3 × 100 mL), water (100 mL), and brine (100 mL), and dried with $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was purified by kugelrohr distillation (b.p. 65 °C/3 mbar). Compound **8b** (2.08 g, 77%) was obtained as a colorless liquid (*cis*/*trans* = 80:20). R_f = 0.43 (P/Et_2O = 80:20). IR (film): $\tilde{\nu}$ = 3075 cm^{-1} (m, CH), 2960 (s, CH), 2870 (w, CH), 1710 (s, C=O), 1640 (w, C=C), 1440 (m, CH), 1355 (m, CH), 1250 (m), 910 (m). ^{1}H NMR (200 MHz): δ = 1.40−2.30 (m, 10 H, aliph. H),

2.11 (s, 3 H, CH_3), 4.90−5.02 (m, 2 H, CH=CH_2), 5.58−5.83 (m, 1 H, CH=CH_2). ^{13}C NMR (50 MHz): δ = 22.9 (t, CH_2), 26.6 (t, CH_2), 30.7 (t, CH_2), 31.1 (q, CH_3), 34.7 (t, CH_2), 42.5 (d, CHCH_2), 55.2 (d, CHCOMe), 115.6 (t, CH=CH_2), 137.4 (d, CH=CH_2), 211.0 (s, CO). MS (70 eV): *m/z* (%) = 152 (2) [M^+], 137 (3) [(M − CH_3)$^+$], 109 (39) [(M − $COCH_3$)$^+$], 94 (26) [$C_7H_{10}^+$], 71 (32), 67 (52) [$C_5H_7^+$], 55 (11) [$C_4H_7^+$], 43 (100) [$COCH_3^+$]. $C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 78.80, H 10.65.

***cis*-2-Allyl-1-(2-propenyl)cyclopentane (5b):** A mixture of zinc powder (1.00 g, 15.3 mmol) and dibromomethane (0.35 mL, 763 mg, 4.06 mmol) in 9 mL of anhydrous THF was cooled to −40 °C. Titanium tetrachloride (0.40 mL, 0.69 g, 3.65 mmol) was added dropwise to the stirred mixture over 15 min. The mixture was stirred at 5 °C for 3 d. The dark gray slurry was then cooled to 0 °C and diluted with 2 mL of CH_2Cl_2. A solution of *cis*-1-acetyl-2-allylcyclopentane (529 mg, 3.22 mmol) (**8b**) in 2 mL of dichloromethane was added to the stirred mixture, which was stirred at room temperature for 8 h. After dilution with pentane (10 mL), a solution of Na_2CO_3 (5 g) in water (3 mL) was added cautiously. The organic layer was separated and the aqueous layer was extracted with pentane (3 × 10 mL). The combined organic solutions were dried with 3.5 g of Na_2SO_4 and 0.7 g of Na_2CO_3, filtered and concentrated. Further purification of the residue was carried out by flash chromatography (P). Compound **5b** (353 mg, 68%) was obtained as a colorless liquid (*cis*/*trans* = 76:24). R_f = 0.67 (P). IR (film): $\tilde{\nu}$ = 3075 cm^{-1} (w, CH), 2955 (s, CH), 2870 (w, CH), 1640 (s, C=C), 1440 (m, CH), 995 (w), 910 (m, CH), 890 (m, CH). ^{1}H NMR (300 MHz): δ = 0.88−0.95 (m, 2 H, CH_2), 1.08−1.15 (m, 2 H, CH_2), 1.20−2.40 (m, 6 H, aliph. H), 1.68 (s, 3 H, CH_3), 4.60−4.75 [m, 2 H, C(Me)=CH_2], 4.82−4.95 (m, 2 H, CH=CH_2), 5.60−5.80 (m, 1 H, CH=CH_2). ^{13}C NMR (75 MHz): δ = 22.4 (q, CH_3), 23.5 (t, CH_2), 27.3 (t, CH_2), 29.7 (t, CH_2), 34.0 (t, CH_2), 40.6 (d, CHCH_2), 50.7 [d, CHC(Me)=CH_2], 110.2 [t, CHC(Me)=CH_2], 114.9(t, CH=CH_2), 138.6 (d, CH=CH_2), 146.2 [s, C(Me)=CH_2]. MS (70 eV): *m/z* (%) = 150 (2) [M^+], 135 (23) [(M − CH_3)$^+$], 109 (25) [(M − C_3H_5)$^+$], 108 (23) [(M − C_3H_6)$^+$], 107 (27) [(M − C_3H_7)$^+$], 93 (40) [$C_7H_9^+$], 81 (34), 79 (55), 67 (100) [$C_5H_7^+$], 55 (43) [$C_4H_7^+$], 41 (69) [$C_3H_5^+$]. HRMS: calcd. for $C_{11}H_{18}$ 150.1409; found 150.1401.

***trans*-2-Allyl-1-(2-propenyl)cyclohexane (6a):** The reaction was carried out as described in Typical Procedure A, with *trans*-1-acetyl-2-allyl-cyclohexane[10] (**10a**, 410 mg, 2.46 mmol), methyltriphenylphosphonium iodide (1.26 g, 3.12 mmol), and *n*-butyllithium in *n*-hexane (3.12 mmol, 1.80 mL of a 1.7 M solution). Compound **6a** (251 mg, 62%) was obtained as a colorless liquid (*trans*/*cis* = 80:20). R_f = 0.83 (P/TBME = 90:10). IR (film): $\tilde{\nu}$ = 3075 cm^{-1} (w, CH), 2925 (s, CH), 2855 (m, CH), 1640 (m, C=C), 1445 (s, CH), 1375 (w, CH), 910 (m, CH), 890 (m, CH). ^{1}H NMR (200 MHz): δ = 0.87−2.98 (m, 12 H, aliph. H), 1.66 (s, 3 H, CH_3), 4.73 [br s, 2 H, C(Me)=CH_2], 4.93−4.98 (m, 2 H, CH=CH_2), 5.65−5.87 (m, 1 H, CH=CH_2). ^{13}C NMR (50 MHz): δ = 18.9 (q, CH_3), 26.6 (t, CH_2), 26.6 (t, CH_2), 31.7 (t, CH_2), 32.8 (t, CH_2), 38.6 (t, CH$_2$CH=CH_2), 39.2 (d, CHCH$_2$CH=CH_2), 51.9 [d, CHC(Me)=CH_2], 110.9 [t, C(Me)=CH_2], 115.5 (t, CH=CH_2), 137.6 (d, CH=CH_2), 149.1 [s, C(Me)=CH_2]. MS (70 eV): *m/z* (%) = 164 (3) [M^+], 149 (22) [(M − CH_3)$^+$], 135 (14) [(M − H − C_2H_4)$^+$], 121 (56) [(M − C_3H_7)$^+$], 110 (22), 95 (23), 93 (34), 81 (80) [$C_6H_9^+$], 79 (41), 67 (100) [$C_5H_7^+$], 55 (59) [$C_4H_7^+$], 41 (62) [$C_3H_5^+$]. HRMS: calcd. for $C_{12}H_{20}$ 164.1565; found 164.1561.

***cis*-2-Allyl-1-(2-propenyl)cyclohexane (6b):** The reaction was carried out as described in Typical Procedure A, with *cis*-1-acetyl-2-allyl-cyclohexane[10] (**10b**, 2.00 g, 12.0 mmol), methyltriphenylphosphonium iodide (6.32 g, 15.6 mmol), and *n*-butyllithium in *n*-hexane (15.6 mmol, 9.10 mL of a 1.7 M solution). Compound **6b** (1.63 g, 83%) was obtained as a colorless liquid (*cis*/*trans* = 96:4). R_f = 0.83 (P/TBME = 90:10). IR (film): $\tilde{\nu}$ = 3075 cm^{-1} (w, CH), 2925 (s, CH), 2855 (m, CH), 1640 (m, C=C), 1450 (s, CH), 1375 (w, CH), 910 (m, CH), 890 (m, CH). ^{1}H NMR (500 MHz): δ = 1.38−1.48 (m, 4 H, CH_2, CHH, CHH), 1.55−1.58 (m, 1 H, CHH), 1.76 (s, 3 H, CH_3), 1.80−1.86 (m, 3 H, CH_2, CHH), 2.07 [d, *J* = 11.9 Hz, 1 H, CHC(Me)=CH_2], 4.58−4.62 [m, 1 H, C(Me)=CHH], 4.83−4.87 [m, 1 H, C(Me)=CHH], 4.94−5.00 (m, 2 H, CH=CH_2), 5.69−5.77 (m, 1 H, CH=CH_2). ^{13}C NMR (125 MHz): δ = 20.3 (t, CH_2), 22.5 (q, CH_3), 25.2 (t, CH_2), 26.5 (t, CH_2), 28.6 (t, CH_2), 30.0 (t, CH_2CH=CH_2), 35.0 (d, CHCH$_2$CH=CH_2), 47.2 [d, CHC(Me)=CH_2], 109.6 [t, C(Me)=CH_2], 115.0 (t, CH=CH_2), 138.8 (d, CH=CH_2), 148.5 [s, C(Me)=CH_2]. MS (70 eV): *m/z* (%) = 164 (21) [M^+], 149 (25) [(M − CH_3)$^+$], 123 (11) [(M − C_3H_5)$^+$], 121 (81) [(M − C_3H_7)$^+$], 110 (28), 95 (38), 93 (35), 81 (80) [$C_6H_9^+$], 79 (57), 67 (100) [$C_5H_7^+$], 55 (61) [$C_4H_7^+$], 41 (69) [$C_3H_5^+$]. HRMS: calcd. for $C_{12}H_{20}$ 164.1565; found 164.1560.

***trans-anti-cis*-1-Methyltricyclo[6.2.0.0^{2,6}]decane (11a)**

Typical Procedure B: A 15-mL quartz tube was charged with *trans*-2-allyl-1-(2-propenyl)cyclopentane (**5a**, 99.0 mg, 0.66 mmol) in anhydrous Et_2O (5 mL). After addition of cupric trifluoromethanesulfonate [Cu(OTf)$_2$] (20.0 mg, 0.06 mmol), the tube was sealed under argon with a rubber septum and the mixture was shaken until the Cu(OTf)$_2$ was mostly dissolved. The resulting solution was irradiated (light source: Rayonet RPR-2537 Å) for 12 h. The reaction mixture was diluted with Et_2O (10 mL) and washed with a mixture of ice (7 g) and concentrated aqueous NH_3 (7 g). The organic layer was separated, dried with Na_2SO_4, and filtered. The solvent was removed in vacuo and the residue was purified by flash chromatography (P). Compound **11a** (79.0 mg, 80%) was obtained as a colorless liquid (**11a**/**11b** = 98:2). R_f = 0.79 (P). IR (film): $\tilde{\nu}$ = 2950 cm^{-1} (s, CH), 2860 (s, CH), 2720 (w), 1740 (w), 1710 (w), 1455 (s, CH), 1375 (m, CH), 1255 (m), 1170 (w), 1085 (m), 1030 (m), 905 (w), 840 (m), 810 (w), 730 (m, CH). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.03 (s, 3 H, CH_3), 1.07 (pseudo dt, *J* = 5.1 Hz, *J* = 11.8 Hz, 1 H, H-7$_\beta$), 1.10−1.28 (m, 1 H, H-5), 1.13−1.20 (m, 1 H, H-3), 1.46−1.52 (m, 1 H, H-3), 1.63−1.69 (m, 1 H, H-5), 1.72−1.78 (m, 1 H, H-9), 1.75−1.95 (m, 2 H, H-6, H-10), 1.96 (ddd, *J* = 6.7 Hz, *J* = 8.2 Hz, *J* = 11.9 Hz, 1 H, H-7$_\beta$), 2.02−2.20 (m, 2 H, H-4), 2.05−2.15 (m, 1 H, H-2), 2.28 (pseudo ddt, *J* = 4.0 Hz, *J* = 9.0 Hz, *J* = 11.4 Hz, 1 H, H-9), 2.61−2.67 (m, 1 H, H-8). ^{13}C NMR (125 MHz, C_6D_6): δ = 21.2 (t, C-3), 22.2 (q, CH_3), 25.6 (t, C-9), 26.5 (t, C-5), 30.0 (t, C-4), 31.3 (t, C-10), 36.6 (t, C-7), 41.7 (s, C-1), 53.0 (d, C-8), 54.2 (d, C-6), 62.5 (d, C-2). MS (70 eV): *m/z* (%) = 150 (6) [M^+], 135 (71) [(M − CH_3)$^+$], 122 (58) [(M − C_2H_4)$^+$], 109 (30) [(M − C_3H_5)$^+$], 108 (57) [(M − C_3H_6)$^+$], 107 (52) [(M − C_3H_7)$^+$], 95 (42), 93 (96), 81 (53), 79 (61), 67 (100) [$C_5H_7^+$], 55 (34) [$C_4H_7^+$], 41 (58) [$C_3H_5^+$]. HRMS: calcd. for $C_{11}H_{18}$ 150.1401; found 150.1399.

***cis-syn-cis*-1-Methyltricyclo[6.2.0.0^{2,6}]decane (11b):** The reaction was carried out according to Typical Procedure B, with *cis*-2-allyl-1-(2-propenyl)cyclopentane (**5b**, 236 mg, 1.57 mmol) and [Cu(OTf)$_2$] (46.0 mg, 0.12 mmol). Compound **11b** (181 mg, 77%) was obtained as a colorless liquid (**11b**/**11a** = 75:25). R_f = 0.78 (P). IR (film): $\tilde{\nu}$ = 2950 cm^{-1} (s, CH), 2865 (s, CH), 1455 (m, CH), 1375 (w, CH), 1260 (w), 1095 (w), 910 (m), 740 (m, CH). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.20 (s, 3 H, CH_3), 1.39−1.43 (m, 1 H, H-3), 1.43−1.52 (m, 1 H, H-7), 1.48−1.55 (m, 3 H, H-9*, H-10*, H-4), 1.60−1.70 (m, 1 H, H-5), 1.63−1.71 (m, 1 H, H-4), 1.80−1.85 (m, 1 H, H-5), 2.08−2.19 (m, 2 H, H-2, H-3), 2.10−2.25

(m, 4 H, H-7, H-8, H-9*, H-10*), 2.59−2.68 (m, 1 H, H-6). ^{13}C NMR (125 MHz, C_6D_6): δ = 22.4 (t, C-3), 27.5 (t, C-9), 27.6 (t, C-10), 28.0 (t, C-5), 28.1 (q, CH_3), 33.4 (t, C-4), 40.5 (t, C-7), 47.8 (d, C-8), 49.2 (d, C-6), 50.8 (s, C-1), 56.0 (d, C-2). MS (70 eV): *m*/*z* (%) = 150 (< 1) [M^+], 149 (1) [[M − H]$^+$], 135 (49) [(M − CH_3)$^+$], 121 (24) [(M − H−C_2H_4)$^+$], 108 (100) [(M − C_3H_6)$^+$], 93 (61), 73 (96), 57 (52), 43 (45) [$C_3H_7^+$], 41 (44) [$C_3H_5^+$]. HRMS: calcd. for $C_{11}H_{18}$ 150.1401; found 150.1407.

***trans-anti-cis*-1-Methyltricyclo[7.2.0.0^{2,7}]undecane (12a):** The reaction was carried out as described in Typical Procedure B, with *trans*-2-allyl-1-(2-propenyl)cyclohexane (**6a**, 138 mg, 0.84 mmol) and [Cu(OTf)$_2$] (26.7 mg, 0.07 mmol). Compound **12a** (109 mg, 80%) was obtained as a colorless liquid (**12a**/**12b** = 82:18). R_f = 0.80 (P). IR (film): $\tilde{\nu}$ = 2920 cm^{-1} (s, CH), 2855 (s, CH), 2720 (w), 2660 (w), 1450 (s, CH), 1370 (m, CH), 1290 (w), 1250 (w), 1220 (w), 940 (w), 910 (w), 840 (m), 745 (w, CH). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.95 (s, 3 H, CH_3), 1.05 (pseudo dt, *J* = 5.1 Hz, *J* = 11.6 Hz, 1 H, H-8$_\beta$), 1.10−1.18 (m, 1 H, H-4), 1.15−1.20 (m, 1 H, H-6), 1.20−1.30 (m, 2 H, H-5, H-7), 1.03−1.10 (m, 1 H, H-3), 1.37 (pseudo dt, *J* = 3.3 Hz, *J* = 11.7 Hz, 1 H, H-2), 1.54−1.63 (m, 1 H, H-10), 1.70−1.80 (m, 2 H, H-3, H-5), 1.78−1.83 (m, 2 H, H-11), 1.80−1.85 (m, 1 H, H-6), 1.95−2.00 (m, 1 H, H-4), 1.99 (ddd, *J* = 6.5 Hz, *J* = 8.3 Hz, *J* = 11.8 Hz, 1 H, H-8$_\alpha$), 2.10−2.14 (m, 1 H, H-9), 2.20−2.28 (m, 1 H, H-10). ^{13}C NMR (62.5 MHz, C_6D_6): δ = 22.6 (q, CH_3), 25.3 (t, C-10), 26.6 (t, C-6), 27.0 (t, C-3), 27.0 (t, C-5), 31.1 (t, C-11), 33.0 (t, C-4), 41.1 (t, C-8), 44.3 (d, C-9), 46.5 (d, C-7), 47.0 (s, C-1), 55.2 (d, C-2). MS (70 eV): *m*/*z* (%) = 164 (10) [M^+], 149 (37) [(M − CH_3)$^+$], 135 (45) [(M − H−C_2H_4)$^+$], 121 (95) [(M − C_3H_7)$^+$], 107 (21) [$C_8H_{11}^+$], 94 (43), 81 (29) [$C_6H_9^+$], 67 (100) [$C_5H_7^+$], 57 (38), 43 (42) [$C_3H_7^+$], 41 (21) [$C_3H_5^+$]. HRMS: calcd. for $C_{12}H_{20}$ 164.1565; found 164.1568.

***cis-syn-cis*-1-Methyltricyclo[7.2.0.0^{2,7}]undecane (12b):** The reaction was carried out as described in Typical Procedure B, with *cis*-2-allyl-1-(2-propenyl)cyclohexane (**6b**, 246 mg, 1.50 mmol) and [Cu(OTf)$_2$] (45.0 mg, 0.12 mmol). Compound **12b** (218 mg, 88%) was obtained as a colorless liquid (**12b**/**12a** = 96:4). R_f = 0.79 (P). IR (film): $\tilde{\nu}$ = 2845 cm^{-1} (s, CH), 2720 (w), 1450 (s, CH), 1370 (m, CH), 1245 (m), 840 (m). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.15 (s, 3 H, CH_3), 1.25−1.34 (m, 1 H, H-4), 1.45−1.50 (m, 1 H, H-2), 1.43−1.55 (m, 1 H, H-10), 1.47−1.60 (m, 1 H, H-3), 1.48−1.55 (m, 2 H, H-5), 1.60−1.62 (m, 1 H, H-3), 1.61−1.69 (m, 1 H, H-6), 1.64 (pseudo dt, *J* = 5.7 Hz, *J* = 11.7 Hz, 1 H, H-8), 1.64−1.68 (m, 1 H, H-11), 1.70−1.80 (m, 1 H, H-4), 1.73−1.79 (m, 1 H, H-6), 1.81−1.88 (m, 1 H, H-8), 2.05−2.10 (m, 1 H, H-7), 2.21 (pseudo dt, *J* = 5.1 Hz, *J* = 11.7 Hz, 1 H, H-11), 2.20−2.27 (m, 1 H, H-9), 2.21−2.30 (m, 1 H, H-10). ^{13}C NMR (62.5 MHz, C_6D_6): δ = 22.2 (t, C-3), 24.7 (t, C-10), 25.6 (t, C-5), 26.0 (t, C-11), 26.2 (t, C-4), 27.6 (t, C-6), 29.7 (q, CH_3), 37.8 (t, C-8), 40.8 (d, C-7), 45.0 (d, C-9), 48.3 (d, C-2), 49.0 (s, C-1). MS (70 eV): *m*/*z* (%) = 164 (17) [M^+], 149 (84) [(M − CH_3)$^+$], 136 (26) [(M − C_2H_4)$^+$], 121 (90) [(M − C_3H_7)$^+$], 110 (39), 94 (67), 93 (61) [$C_5H_{11}^+$], 81 (78) [$C_6H_9^+$], 79 (89), 67 (73) [$C_5H_7^+$], 55 (54) [$C_4H_7^+$], 43 (29) [$C_3H_7^+$], 41 (74) [$C_3H_5^+$]. HRMS: calcd. for $C_{12}H_{20}$ 164.1565; found 164.1560.

***trans*-2-Allyl-1-(2-propenyl)cyclopentanol (16)**

Typical Procedure C: 2-Bromo-1-propene (1.95 mL, 2.70 g, 22.3 mmol) was dissolved in diethyl ether (100 mL) and a solution of *tert*-butyllithium in *n*-pentane (46.9 mmol, 31.3 mL of a 1.5 M solution) was added at −78 °C. The mixture was stirred at that temperature for 15 min. 2-Allylcyclopentanone (**15**, 2.13 g, 17.2 mmol) was then added dropwise. After 4 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (50 mL) and extracted with Et_2O (3 × 100 mL). The solvent was removed in vacuo and the residue was purified by flash chromatography over a short column (P/EA = 95:5). Compound **16** (1.22 g, 43%) was obtained as a colorless liquid. R_f = 0.43 (P/EE = 95:5). IR (film): $\tilde{\nu}$ = 3485 cm^{-1} (s, OH), 3075 (w, CH), 2965 (s, CH), 2870 (m, CH), 1640 (s, C=C), 1450 (m, CH), 910 (s), 735 (w). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.48−1.65 (m, 3 H, aliph. H), 1.73 (s, 3 H, CH_3), 1.77−1.98 (m, 5 H, aliph. H), 2.08−2.16 (m, 1 H, C*H*HCH=CH_2), 4.87−5.07 (m, 4 H, =CH_2), 5.75−5.85 (m, 1 H, C*H*=CH_2). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 19.6 (q, CH_3), 21.5 (t, CH_2), 29.3 (t, CH_2), 32.8 (t, CH_2), 39.1 (t, CH_2), 45.9 (d, *C*HCH$_2$CH=CH_2), 84.8 (s, COH), 110.4 (t, =CH_2), 115.0 (t, CH=*C*H$_2$), 138.0 (d, *C*H=CH_2), 148.5 [s, *C*(Me)=CH_2]. MS (70 eV): *m*/*z* (%) = 166 (< 1) [M^+], 165 (< 1) [(M − H)$^+$], 151 (23) [(M − CH_3)$^+$], 137 (10), 133 (27), 123 (37) [$C_8H_{11}O^+$], 111 (40), 109 (35) [$C_7H_9O^+$], 107 (25) [$C_8H_{11}^+$], 97 (77), 84 (58), 79 (48), 69 (100), 55 (52) [$C_4H_7^+$]. HRMS: calcd. for $C_{11}H_{18}O$ 166.1358; found 166.1355.

***trans*-2-Allyl-1-(2-propenyl)cyclohexanol (21):** The reaction was carried out as described in Typical Procedure C, with 2-bromo-1-propene (2.05 mL, 2.84 g, 23.5 mmol), *tert*-butyllithium in *n*-pentane (49.3 mmol, 32.9 mL of a 1.5 M solution), and 2-allylcyclohexanone (**20**, 2.72 mL, 2.50 g, 18.1 mmol). Compound **21** (3.18 g, 98%) was obtained as a colorless liquid. R_f = 0.38 (P/EE = 95:5). IR (film): $\tilde{\nu}$ = 3490 cm^{-1} (s, OH), 3075 (w, CH), 2930 (s, CH), 2855 (s, CH), 1640 (s, C=C), 1375 (w, OH), 1140 (m, CO), 975 (m), 905 (s). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10−1.80 [m, 11 H, CH_2, C*H*HCH=CH_2, C(OH)C*H*], 1.71 (s, 3 H, CH_3), 2.00−2.12 (m, 1 H, CH*H*CH=CH_2), 4.81−4.84 (m, 1 H, =C*H*H), 4.90 (br. s, 1 H, CH=C*H*H), 4.92−4.97 (m, 1 H, CH=CH*H*), 5.04−5.06 (m, 1 H, =CH*H*), 5.65−5.82 (m, 1 H, C*H*=CH_2). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 19.5 (q, CH_3), 21.5 (t, CH_2), 25.9 (t, CH_2), 26.4 (t, CH_2), 34.5 (t, *C*H$_2$CH=CH_2), 37.5 (t, CH_2), 47.2 (d, *C*HCH$_2$CH=CH_2), 76.9 (s, COH), 109.9 (t, =CH_2), 115.6 (t, CH=*C*H$_2$), 137.8 (d, *C*H=CH_2), 150.9 [s, *C*(Me)=CH_2]. MS (70 eV): *m*/*z* (%) = 180 (8) [M^+], 165 (22) [(M − CH_3)$^+$], 162 (11) [(M − H_2O)$^+$], 147 (23), 137 (31) [(M − C_3H_7)$^+$], 123 (34) [$C_8H_{11}O^+$], 109 (49), 97 (100), 69 (98), 55 (45) [$C_4H_7^+$]. HRMS: calcd. for $C_{12}H_{20}O$ 180.1514; found 180.1507.

***trans-anti-cis*-2-Hydroxy-1-methyltricyclo[6.2.0.0^{2,6}]decane (17):** The reaction was carried out as described in Typical Procedure B, with *trans*-2-allyl-1-(2-propenyl)cyclopentanol (**16**, 700 mg, 4.21 mmol) and copper(I) trifluoromethanesulfonate toluene complex (2:1) [(CuOTf)$_2$·C_7H_8] (88.0 mg, 0.17 mmol). Compound **17** (172 mg, 25%) was obtained as a colorless liquid. In addition, 218 mg (50%) of the dehydration compounds **13**, **18**, and **19** were isolated. R_f = 0.46 (P/EE = 95:5). IR (film): $\tilde{\nu}$ = 3615 cm^{-1} (m, OH), 3500 (br. s, OH), 2945 (s, CH), 2885 (s, CH), 1450 (m, CH), 1375 (m, CH), 1265 (m, OH), 995 (m), 910 (s), 735 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (s, 3 H, CH_3), 1.22−1.32 (m, 1 H, H-7), 1.32−1.38 (m, 1 H, H-3), 1.45−1.55 (m, 3 H, H-3, H-5), 1.62−1.70 (m, 2 H, H-9, H-10), 1.78 (ddd, *J* = 6.9 Hz, *J* = 8.4 Hz, *J* = 11.8 Hz, 1 H, H-7), 1.95−2.04 (m, 1 H, H-6), 2.05−2.20 (m, 2 H, H-9, H-4), 2.22−2.32 (m, 2 H, H-4), H-10), 2.59−2.68 (m, 1 H, H-8). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 22.0 (t, C-5), 25.3 (q, CH_3), 25.5 (t, C-9), 25.8 (t, C-10), 28.1 (t, C-4), 29.2 (t, C-3), 32.0 (t, C-7), 45.2 (s, C-2), 51.8 (d, C-8), 55.7 (d, C-6), 94.0 (s, C-1). MS (70 eV): *m*/*z* (%) = 166 (< 1) [M^+], 165 (< 1) [(M − H)$^+$], 151 (38) [(M − CH_3)$^+$], 133 (35) [(M − H_2O−CH_3)$^+$], 123 (50) [$C_8H_{11}O^+$], 111 (100), 97 (85), 84 (100), 79 (57), 69 (65), 55 (52) [(C_4H_7)$^+$]. HRMS: calcd. for $C_{11}H_{18}O$ 166.1358; found 166.1356.

***trans-anti-cis*-2-Hydroxy-1-methyltricyclo[7.2.0.0^{2,7}]undecane (22):** The reaction was carried out as described in Typical Procedure B, with *trans*-2-allyl-1-(2-propenyl)cyclohexanol (**21**, 1.90 g, 10.5 mmol) and [(CuOTf)$_2$·C$_7$H$_8$] (240 mg, 0.46 mmol). Compound **22** (1.47 g, 77%) was obtained as a colorless liquid. R_f = 0.46 (P/EE = 95:5). IR (film): $\tilde{\nu}$ = 3620 cm^{-1} (w, OH), 3515 (s, OH), 2935 (s, CH), 2860 (s, CH), 1455 (m, CH), 1375 (m, OH), 1250 (m), 1130 (w, CO), 1045 (w), 960 (m). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.97 (s, 3 H, CH$_3$), 1.05−1.72 (m, 13 H, aliph. H), 1.78−1.86 (m, 1 H, H-8), 2.05−2.18 (m, 3 H, H-9, H-10, C*H*H). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 21.4 (t, CH$_2$), 25.0 (t, CH$_2$), 25.1 (q, CH$_3$), 25.2 (t, C-10), 25.6 (t, CH$_2$), 26.0 (t, CH$_2$), 32.6 (t, CH$_2$), 37.1 (t, C-8), 43.4 (d, C-9), 47.4 (d, C-7), 50.7 (s, C-2), 80.1 (s, C-1). MS (70 eV): *m*/*z* (%) = 180 (38) [M$^+$], 165 (28) [(M − CH$_3$)$^+$], 162 (23) [(M − H$_2$O)$^+$], 147 (32), 137 (52) [(M − C$_3$H$_7$)$^+$], 123 (43) [C$_8$H$_{11}$O$^+$], 109 (73), 98 (100) [C$_6$H$_{10}$O$^+$], 79 (57), 69 (58), 55 (47) [C$_4$H$_7^+$]. HRMS: calcd. for C$_{12}$H$_{20}$O 180.1514; found 180.1511. A 70:30 mixture (318 mg, 19%) of 11-methylidenetricyclo-[6.2.1.0^{1,8}]undecane (**23**) and 1-methyltricyclo[7.2.0.0^{2,7}]undec-2(7)-ene (**14**) was obtained as a side product. The analytical data for compound **23** are given below. R_f = 0.96 (P). IR (film): $\tilde{\nu}$ = 2960 (s, CH), 2860 (s, CH), 1685 (m, C=C), 1455 (m, CH), 880 (s). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.78−2.40 (m, 16 H, aliph. H), 4.43 (s, 1 H, =C*H*H), 4.49 (s, 1 H, =CH*H*). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 22.4 (t, CH$_2$), 25.6 (t, CH$_2$), 26.6 (t, CH$_2$), 26.8 (t, CH$_2$), 29.4 (t, CH$_2$), 30.8 (t, CH$_2$), 34.7 (t, CH$_2$), 41.0 (d, CH), 43.5 (d, CH), 45.4 (s, C-1), 92.6 (t, =CH$_2$), 163.7 (s, *C*=CH$_2$). MS (70 eV): *m*/*z* (%) = 162 (52) [M$^+$], 147 (10), 133 (100) [(M − H−C$_2$H$_4$)$^+$], 119 (62), 105 (50), 91 (80), 79 (38), 67 (10), 53 (5). HRMS: calcd. for C$_{12}$H$_{18}$ 162.1409; found 162.1407.

1-Methyltricyclo[6.2.0.0^{1,6}]dec-2(6)-ene (13)

Typical Procedure D: 2-Hydroxy-1-methyltricyclo[6.2.0.0^{2,6}]decane (**22**, 96.0 mg, 0.60 mmol) was dissolved in 10 mL of ethanol. A catalytic amount of *p*-toluenesulfonic acid monohydrate (18.0 mg, 0.10 mmol) and molecular sieves (4 Å, 1.60 g) were added. The reaction mixture was refluxed overnight. After cooling to room temperature, the mixture was filtered and the solvent was evaporated in vacuo. The residue was purified by flash chromatography using a short column (P). Compound **13** (29 mg, 34%) was isolated as a colorless liquid, together with small amounts of the dehydration products **18** and **19**. In addition, the starting material **22** (50.0 mg, 52%) was recovered. R_f = 0.87 (P). IR (film): $\tilde{\nu}$ = 2925 (s, CH), 2845 (m, CH), 1445 (m, CH), 910 (m), 735 (m). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.09 (s, 3 H, CH$_3$), 1.25 (br. s, 1 H, aliph. H), 1.48−1.57 (m, 1 H, H-9), 1.80−1.94 (m, 3 H, H-10, H-7), 2.03−2.35 (m, 7 H, H-7, H-9), aliph. H), 2.72 (pseudo q, *J* = 6.9 Hz, 1 H, H-8). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 23.8 (q, CH$_3$), 24.2 (t, C-9), 25.1 (t, CH$_2$), 28.3 (t, CH$_2$), 29.6 (t, CH$_2$), 32.4 (t, C-10), 36.4 (t, C-7), 48.2 (s, C-1), 49.2 (d, C-8), 144.1 (s, C-6), 151.2 (s, C-2). MS (70 eV): *m*/*z* (%) = 148 (27) [M$^+$], 133 (37) [(M − CH$_3$)$^+$], 120 (100) [(M − C$_2$H$_4$)$^+$], 105 (80) [C$_8$H$_9^+$], 92 (40) [C$_7$H$_8^+$], 91 (42) [C$_7$H$_7^+$]. HRMS: calcd. for C$_{11}$H$_{16}$ 148.1252; found 148.1253.

1-Methyltricyclo[7.2.0.0^{2,7}]undec-2(7)-ene (14): The reaction was carried out as described in Typical Procedure D, with 2-hydroxy-1-methyltricyclo[7.2.0.0^{2,7}]undecane (210 mg, 1.16 mmol) (**22**). Compounds **14** and **23** (149 mg, 79%) were isolated as an 83:17 mixture. The analytical data for compound **14** are given below. R_f = 0.87 (P). IR (film): $\tilde{\nu}$ = 2925 cm^{-1} (s, CH), 2860 (m, CH), 2830 (m, CH), 1685 (w, C=C), 1445 (m, CH), 1365 (w, CH). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.08 (s, 3 H, CH$_3$), 1.38−1.48 (m, 1 H, H-10), 1.50−1.70 (m, 4 H, CH$_2$), 1.82−1.88 (m, 4 H, CH$_2$, H-11), 1.89−1.93 (m, 1 H, H-8), 1.95−1.99 (m, 2 H, CH$_2$), 2.06 (dddd, *J* = 4.3 Hz, *J* = 9.2 Hz, *J* = 11.7 Hz, *J* = 12.0 Hz, 1 H, H-10), 2.31−2.39 (m, 1 H, H-9), 2.45−2.52 (m, 1 H, H-8). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 20.8 (t, CH$_2$), 23.1 (t, CH$_2$), 23.2 (t, CH$_2$), 23.6 (q, CH$_3$), 24.0 (t, C-10), 26.3 (t, CH$_2$), 32.3 (t, C-11), 41.7 (d, C-9), 42.9 (t, C-8), 53.5 (s, C-1), 132.7 (s, C-7), 139.4 (s, C-2). MS (70 eV): *m*/*z* (%) = 162 (9) [M$^+$], 147 (8) [(M − CH$_3$)$^+$], 134 (100) [(M − C$_2$H$_4$)$^+$], 119 (47) [C$_9$H$_{11}^+$], 106 (23) [C$_8$H$_{10}^+$], 105 (35) [C$_8$H$_9^+$]. HRMS: calcd. for C$_{12}$H$_{18}$ 162.1409; found 162.1406.

Hydrogenation of 1-Methyltricyclo[6.2.0.0^{2,6}]dec-2(6)-ene (13)

Typical Procedure E: A solution of 1-methyltricyclo[6.2.0.0^{2,6}]dec-2(6)-ene (**13**) with minor amounts of the elimination products **18** and **19** (ratio: 80:14:6, 29.0 mg, 0.20 mmol) in 1 mL of glacial acetic acid was subjected to catalytic hydrogenation in the presence of platinum(IV) oxide hydrate (20.0 mg, 0.09 mmol). After stirring at room temperature overnight, the mixture was diluted with 1 mL of water. Solid Na$_2$CO$_3$ (0.25 g) was then added cautiously and the mixture was extracted with CH$_2$Cl$_2$ (3 × 5 mL). The organic layers were washed with saturated NaHCO$_3$ (5 mL) and brine. After removal of the solvent in vacuo, the residue was purified by flash chromatography using a short column (P). Compound **11b** (20.0 mg, 69%) was obtained as a colorless liquid and as a single product, which proved identical to the photocycloaddition product previously obtained from substrate **5b**.

Hydrogenation of 1-Methyltricyclo[7.2.0.0^{2,7}]undec-2(7)-ene (14): The reaction was carried out as described in Typical Procedure E, with 1-methyltricyclo[7.2.0.0^{2,7}]undec-2(7)-ene (**14**) and rearranged product **23** (ratio: 83:17) (63.0 mg, 3.88 mmol). A mixture of compound **12b** and compound **24** (46.0 mg, 72%, ratio: 83:17) was obtained as a colorless liquid. The NMR and GC-MS data of compound **12b** proved identical to those of the compound previously obtained from the photocycloaddition of substrate **6b**.

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