# Conformational Preferences of Titanocene Dichlorides with Ligands Derived from Menthol: Comparison of Structures in Solution and in the Crystal

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A comparison of the structures of three titanocenes, **1**, **2**, and **3**, with ligands derived from menthol in the solid state and in solution determined by X-ray crystallography and by modern NMR methods has been carried out. The respective structures are essentially the same in solution and in the crystal. It seems that an examination of this type has not appeared in the literature as yet. Complexes **1** and **2** are conformationally fixed by interactions of the cyclopentadienyl ring with the menthol substitutents. This remote effect has to the best of our knowledge not been observed before and leads to efficient chirality transfer to the distant part of the chiral pockets. The results are of relevance for catalyst design in metallocene-catalyzed reactions and for structure determination of similar metallocenes both in the solid state and in solution.

## Introduction

A variety of titanocene complexes possessing chirality either in the ligand sphere or at the titanium center have been successfully used in enantioselective catalysis over the last two decades.[1] Especially important in this respect have been *ansa*-metallocenes,[2,3] e.g., in catalytic hydrogenation of imines[4] and Pauson−Khand type reactions.[5] The mechanistic reasoning for both reactions is firmly based on the X-ray structure of Brintzinger's catalyst.[3] To the best of our knowledge no correlation with a measured structure in solution has been described. We have recently employed enantiomerically pure titanocene complexes with the chirality contained in the ligands with success in catalytic enantioselective openings of *meso*-epoxides via electron transfer.[6,7] Three catalysts, **1**, **2**, and **3**, employed in this reaction are depicted in Figure 1.
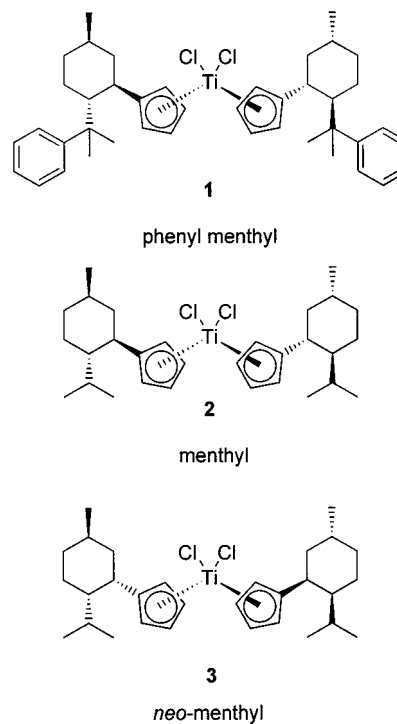


**Figure 1.** Titanocenes used in enatioselective opening of *meso*-epoxides via electron transfer.

The knowledge of structural details of these complexes (no X-ray structures except for **1**[6] and more importantly no NMR studies in solution are available to date) is of central importance for the analysis of this novel epoxide opening via electron transfer.

Zirconocenes on the other hand have been investigated more thoroughly. Erker has studied the conformational behavior of a number of zirconocenes containing indenyl and tetrahydroindenyl ligands derived from

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(3) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. (b) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* **1988**, *342*, 21.

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(5) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688.

(6) Gansäuer, A.; Lauterbach, T.; Bluhm, H.; Noltemeyer, M. *Angew. Chem.* **1999**, *111*, 3112; *Angew. Chem., Int. Ed.* **1999**, *38*, 2909.

(7) For stoichiometric achiral work on this type of epoxide opening see: RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986. (b) For catalytic achiral work see: Gansäuer, A.; Bluhm, H.; Pierobon, M. *J. Am. Chem. Soc.* **1998**, *120*, 12849.

various derivatives of menthol by ^{1}H NMR spectroscopy at different temperatures. The structural focus of this work was to identify torsional isomers of the metallocene rotamers. However, no conformational analysis of the terpene groups with respect to the indenyl system was carried out.[8] Recently a publication describing the design of the chiral ligand sphere around zirconium using myrtanyl ligands has appeared. The structural results are based on X-ray data and modeling studies, however.[9] In a more general context, it is desirable to correlate crystal structures with studies of conformations of metallocenes in solution to gain a detailed understanding of organometallic reaction mechanisms. In this context modern NMR techniques have recently been used with great success in conformational analysis of phosphine-containing complexes, especially in $\pi$-allyl palladium chemistry.[10] The structures obtained by NMR spectroscopy should clearly be more relevant for mechanistic studies and therefore deserve great attention. In this paper we wish to report the realization of these two important goals.

## Results and Discussion

The titanocenes **1**, **2**, and **3** were prepared as described in the literature by Kagan[11] and Vollhardt.[12] We managed to obtain single crystals suitable for X-ray crystallographic[13] analysis by slow evaporation of concentrated solutions in chloroform for **1** and in dichloromethane for **2** and **3**, respectively. Complexes **2** and **3** are $C_2$-symmetrical in the solid state, whereas **1** possesses $C_1$-symmetry. This is due to the presence of one molecule of chloroform in the unit cell, resulting in different conformations for the two phenylmenthol derived ligands. In the structure of **3** the $CH(CH_3)_2$ groups are disordered and two rotamers of the $CH(CH_3)_2$ group are observed. The crystal structures of the three complexes viewed along one of the titanium chlorine bonds are depicted in Figure 2. For the ORTEP drawings see the Supporting Information.

Some characteristic angles and bond distances (numbering according to the menthol nomenclature is used in this article for reasons of clarity, see Figure 3) are summarized in Table 1, and crystal data are summarized in Tables 2 and 3.

The striking structural feature of **1** is the orientation of the phenyl group relative to the cyclopentadienyl ring. Coplanarity is almost achieved. Either a $\pi$-stacking
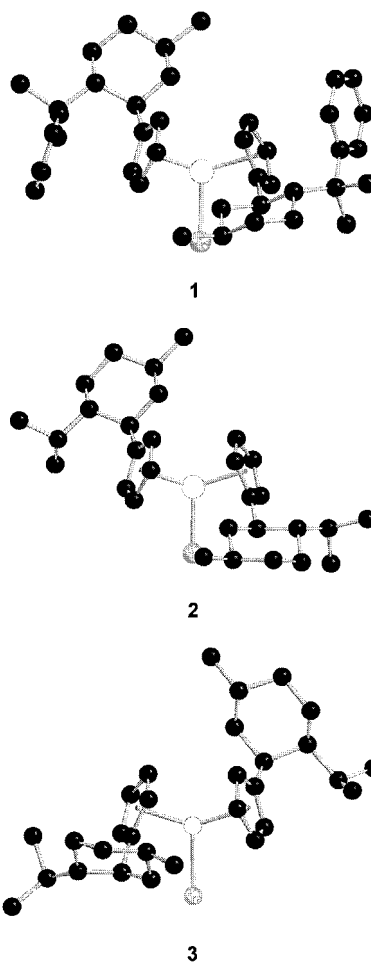
(8) Erker, G.; Aulbach, M.; Knickmeier, M.; Wingermühle, D.; Krüger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590. (b) Knickmeier, M.; Erker, G.; Fox, T. *J. Am. Chem. Soc.* **1996**, *118*, 9623.

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(12) Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883.

(13) Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-118965. (b) The structures of **2** and **3** were measured on a Nonius KappaCCD instrument.

**Figure 2.** Crystal structures of complexes **1**, **2**, and **3**.



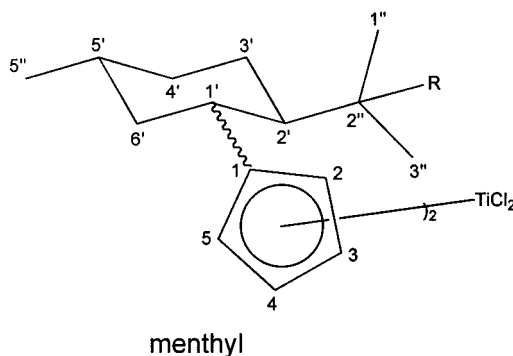**Figure 3.** Numbering of the carbon atoms according to the menthol nomenclature.

**Table 1. Selected Bond Lengths [Å] and Angles [deg] for 1, 2, and 3 (esd's in parentheses)**

|  | **1** | **2** | **3** |
|---|---|---|---|
| Ti−Cl | 2.372(2) | 2.3559(7) | 2.3667(12) |
| Cl−Ti−Cl | 93.47(6) | 93.20(6) | 92.36(5) |
| C5−Ti | 2.396(5) | 2.387(4) | 2.387(2) |
| C5−Ti−C5 | 79.5(2) | 82.81(19) | 82.76(14) |
| C5′−C5″ | 1.562(8) | 1.539(7) | 1.586(7) |
| C1−C1′−C6′ | 111.3(4) | 112.0(4) | 111.8(2) |
| C1′−C2′−C2″ | 115.5(5) | 113.7(4) | 108.8(3) |

interaction or minimization of steric interactions of the $C(CH_3)_2Ph$ and the cyclopentadienyl ligand could be responsible for this positioning. To the best of our knowledge, this type of conformational locking of the ligand has not been observed before in group IV met-

**Table 2. Crystal Data and Structure Refinement for 2**

| | |
|---|---|
| empirical formula | C30 H46 Cl2 Ti |
| fw | 525.47 |
| temperature | 293(2) K |
| wavelength | 0.71074 Å |
| cryst syst, space group | tetragonal, $P42$ |
| unit cell dimens | $a = 15.3002(11)$ Å, $\alpha = 90°$ |
| | $b = 15.3002(11)$ Å, $\beta = 90°$ |
| | $c = 6.4528(2)$ Å, $\gamma = 90°$ |
| volume | 1510.58(16) Å$^3$ |
| $Z$, calcd density | 2, 1.155 Mg/m$^3$ |
| abs coeff | 0.475 mm$^{-1}$ |
| $F(000)$ | 564 |
| crystal size | $0.4 \times 0.1 \times 0.08$ mm |
| $\theta$ range for data collection | 1.88–27.48° |
| limiting indices | $-19 \leq h \leq 19$, $-14 \leq k \leq 13$, |
| | $-6 \leq l \leq 7$ |
| no. of reflns collected/unique | 7669/3174 [$R$(int) = 0.055] |
| completeness to $\theta = 27.48$ | 95.9% |
| abs corr | none |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/params | 3174/0/165 |
| goodness-of-fit on $F^2$ | 1.032 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0494, wR2 = 0.1260 |
| $R$ indices (all data) | R1 = 0.0806, wR2 = 0.1520 |
| absolute structure param | −0.02(6) |
| largest diff peak and hole | 0.287 and −0.454 e Å$^{-3}$ |

**Table 3. Crystal Data and Structure Refinement for 3**

| | |
|---|---|
| empirical formula | C30 H46 Cl2 Ti |
| fw | 525.47 |
| temperature | 293(2) K |
| wavelength | 0.71074 Å |
| cryst system, space group | monoclinic, $C_2$ |
| unit cell dimens | $a = 20.6290(12)$ Å, $\alpha = 90°$ |
| | $b = 6.6952(2)$ Å, $\beta = 131.0583(17)°$ |
| | $c = 13.9570(8)$ Å, $\gamma = 90°$ |
| volume | 1453.55(13) Å$^3$ |
| $Z$, calcd density | 2, 1.201 Mg/m$^3$ |
| abs coeff | 0.494 mm$^{-1}$ |
| $F(000)$ | 564 |
| cryst size | $0.5 \times 0.2 \times 0.2$ mm |
| $\theta$ range for data collection | 1.94–27.47° |
| limiting indices | $-26 \leq h \leq 26$, $-7 \leq k \leq 8$, |
| | $-17 \leq l \leq 18$ |
| no. of reflns collected/unique | 5846/3137 [$R$(int) = 0.029] |
| completeness to $\theta = 27.47$ | 49.7% |
| abs corr | none |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/params | 3137/0/163 |
| goodness-of-fit on $F^2$ | 1.198 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0426, wR2 = 0.1359 |
| $R$ indices (all data) | R1 = 0.0463, wR2 = 0.1420 |
| absolute structure param | −0.01(3) |
| largest diff peak and hole | 0.314 and −0.430 e Å$^{-3}$ |

allocene chemistry.[1] The structural result of this conformational rigidity is the shielding of one of the faces of the titanium chlorine bond by the C5″ methyl group as shown in Figure 2. The distances between these C and Cl atoms are 518.9 and 528.8 pm, respectively. The dihedral angles between C5 of the cyclopentadienyl group and H1′ have values of 157.3° and 171.4° in the solid.

A similar result is observed for the structure of **2**. The conformation of this ligand is also locked. This is due to interactions of the CH(CH$_3$)$_2$ group and the cyclopentadienyl ligand. Presumably due to the minimization of steric interactions of the 2′-propyl group and the cyclopentadienyl ligand, the C−H bond of the CH(CH$_3$)$_2$ group is oriented almost parallel to the plane of the cyclopentadienyl ring. Thus, the H2″ in **2** replaces the phenyl group in **1**. These results suggest that for **1** the
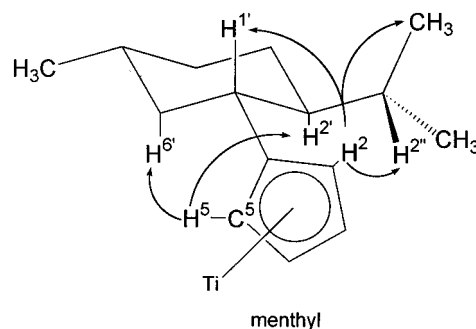


**Figure 4.** Pertinent NOE enhancements (>10%) of **2**.

minimization of steric interactions could be decisive, also. The resulting dihedral angle between C5 and H1′ (148.0°) is smaller than the corresponding angles in **1**. As a consequence, the distance between the C5″ methyl groups and the chlorine atoms is larger in **2** (539.2 pm) than in **1**. Therefore, the chiral pocket of **2** is wider than that of **1**.

When the cyclopentadienyl group is attached to the menthol-derived six-membered ring in an axial position as in complex **3**, a conformational locking similar to **1** and **2** is not observed. The CH(CH$_3$)$_2$ group is structurally disordered, and therefore several rotamers for this group are accessible in the crystal. This could, however, be due to crystal-packing forces.

The dihedral angle between C5 and H1′ has a value of 151°. This tilt is an indication of the avoidance of steric interactions of the cyclopentadienyl ligand with the rotating CH(CH$_3$)$_2$ group and the cyclohexane ring. The axial positioning of the cyclopentadienyl unit therefore results in a less compact structure compared to **1** and **2** and thus to a distinctly wider chiral pocket of **3**. This is exemplified by the larger distance between the respective chlorine atoms and C5″ (571.7 pm).

To compare these results to the structures of **1**, **2**, and **3** in solution, $^1$H−$^1$H COSY, $^{13}$C−$^1$H COSY, NOE difference spectra, and coupled $^{13}$C spectra of the complexes were recorded in addition to the usual $^1$H and $^{13}$C spectra (see Supporting Information for copies of all spectra). In the spectra of all complexes only one set of signals for the respective ligands is observed at room temperature. Thus, all complexes exhibit $C_2$-symmetry in solution. By measuring the spectra of **2** and **3** at 240 and 190 K we were not able to observe coalescence or a second set of signals expected for conformers differing in rotation about the Ti−Cp axis.[14] However, for **3** line broadening and changes of the chemical shifts were observed at 190 K. Complex **2** did not show these effects. At lower temperatures the complexes start to precipitate.

The ideal starting point for the analysis of the spectra is constituted by the signal of H1′. Combination of the results of both COSY spectra in the usual manner allows for unequivocal assignment of all protons and carbons in the menthol ligands for **1**, **2**, and **3**. Assignment of the cyclopentadienyl protons is possible with the data obtained from the NOE difference spectra. The relevant interactions (NOE > 10%) are shown in Figure 4 for one of the homotopic ligands of **2**. Essentially the

(14) Fritze, C.; Knickmeier, M.; Erker, G.; Zaegel, F.; Gautheron, B.; Meunier, P.; Paquette, L. A. *Organometallics* **1995**, *14*, 5446.

same results were obtained from the analysis of the spectra of **1**.

In **2** H5 showed NOE contacts with H2′$_{ax}$ and H6′$_{ax}$, wheras H2 allowed for the observation of the NOE contacts with H1′$_{ax}$, only one of the CH$_3$ groups, and the proton of the CH(CH$_3$)$_2$ group. In **1** very similar effects were operating: H5 revealed NOE contacts with H2′$_{ax}$ and H6′$_{ax}$, whereas H2 showed the expected signal enhancements with H1′$_{ax}$ and only one of the CH$_3$ groups and the aryl protons of the C(CH$_3$)$_2$Ph moiety. It should be noted that in both complexes only one of the two CH$_3$ groups exhibited an NOE enhancement with H2. Therefore, it seems that one rotamer is strongly preferred over all others for both the C(CH$_3$)$_2$-Ph in **1** and the CH(CH$_3$)$_2$ group in **2** in solution as a consequence of the above-mentioned conformational locking. Additionally for **2** a $^3J_{HH}$ of 2.4 Hz for H2′ and H2″ was measured. According to the Karplus relationship this corresponds to a dihedral angle of 58–68°.[15] This value matches the angle observed in the crystal (67.1°) reasonably well.

The remaining question concerning the conformation of **1** and **2** in solution is the relative magnitude of the dihedral angles between C5 and H1′. For this purpose the respective $^3J_{CH}$ coupling constants were measured. They are related to this angle by a Karplus relation. The value for **1** is bigger (4.2 Hz) than the one of **2** (2.9 Hz), and thus, as in the crystal, **1** should have a tighter chiral pocket than **2** in solution. Unfortunately, no quantitative conclusions can be drawn from these numbers, since to the best of our knowledge no parameters for $^3J_{CH}$ Karplus equations have been reported for systems containing cyclopentadienyl anions. On the basis of the pertinent NOE contacts and the $^3J_{CH}$ values, it is reasonable to assume that the distances between the chlorine atoms and the respective C5″ atoms are at least similar to the values obtained from the crystal structure. The complexes **1** and **2** should therefore be considered structurally equal in solution and in the solid state, with **2** having a wider chiral pocket in both aggregation states.

Thus, for the structure of **1** and **2** in both the solid state and in solution the conformation is governed by interaction of the cyclopentadienyl ring and the 2′-substituent of the menthol-derived ring. This remote effect results in an efficient chirality transfer to distant regions of the chiral pocket. This is exemplified by the shielding of one of the faces of the titanium chlorine bond by the respective C5″ methyl groups.

With the cyclopentadienyl ligand in an axial position a different situation is observed for titanocene **3**. The relevant NOE enhancements are shown in Figure 5. Only one of the homotopic ligands is shown for reasons of clarity.

The contacts between H5 and H5′, H2 and H1′, H2 and H2″, and H2 and (CH$_3$)1″ are expected if the structures in solution and the solid state are assumed to be similar concerning the cp ring and the cyclohexane unit. However, in solution **3** shows a similar conformational locking to that observed in **1** and **2**. Only one of the methyl groups shows an NOE contact, and the $^3J_{HH}$
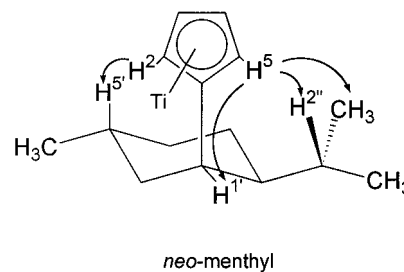


*neo*-menthyl

**Figure 5.** Pertinent NOE enhancements (>10%) of **3**.

coupling constant for H2′ and H2″ has a value of 8.7 Hz, which is larger than the usual values for rotating groups (ca. 7 Hz). As for **1** and **2**, an estimate of the dihedral angle between H1′ and C2 can be obtained from the $^3J_{CH}$ coupling constant of the two nuclei.[16] A value of 6.7 Hz was measured. Compared to the situation observed in **1** and **2**, the magnitude of the coupling constant suggests a somewhat larger angle in solution than in the solid state accounting for the conformational locking.

Structures of **3** in both the solid state and in solution should still be considered similar based on the observed NOE enhancements. Therefore, the assumption that **3** has a less tight chiral pocket compared to **1** and **2** in solution, too, seems valid.

In conclusion we have demonstrated that **1**, **2**, and **3** show similar conformational preferences in solution and in the solid state by comparing the results of the X-ray crystallographic analysis and the results of a variety of NMR experiments. Thus, applications of these complexes in catalysis in solution can be discussed on the basis of the structural data obtained from X-ray crystallography. In a more general sense, data obtained from sophisticated NMR measurements should be as relevant as crystallographic data for the structural discussion of these titanocene complexes. It remains to be seen if this conclusion can be generalized for the analysis of other metallocene complexes also. It should be noted that even though the first metallocene described with chiral ligands, Kagan's cyclopentadienyl (menthylcyclopentadienyl) titanium dichloride,[11] contained a menthylcyclopentadienyl ligand showing a similar conformation, the conformational locking was not described and not investigated in solution. In zirconocene chemistry similar ligands containing the *neo*-menthyl and menthyl derived ligands have also been described by Erker[8,17] and Marks.[18] However, these complexes show different behavior due to sterically demanding cyclopentadienyl unit, e.g., dimethylsilyl-bridged and tetrahydroindenyl ligands.

## Experimental Section

All spectra were recorded on a Bruker DRX 500 spectrometer. The $^1$H–$^1$H COSY 45, the $^{13}$C–$^1$H COSY, the NOE difference NMR, and the gated coupled $^{13}$C programs were used to record the spectra.

(15) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870. (b) Friebolin, H. *Ein- und zweidimensionale NMR-Spektroskopie*; VCH: Weinheim, 1988; pp 71–80.

(16) Thomas, W. A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1997**, *30*, 183. (b) For examples of hydrocarbons where assignments are possible see: Aydin, R.; Loux, J.-P.; Günther, H. *Angew. Chem.* **1982**, *94*, 451; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 449.

(17) Thiele, S.; Erker, G.; Fritze, C.; Psior, Z., Fröhlich, R. *Z. Naturforsch. B* **1995**, *50*, 982.

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**NMR of 1.** ^{1}H NMR (500 MHz, C$H$Cl$_3$ as internal standard in CDCl$_3$): $\delta$ 7.00−7.09 (m, 2‴-H, 3‴-H, 5‴-H, 6‴-H); 6.96 (dddd, $^3J_{4‴-H,3‴-H} \approx {}^3J_{4‴-H,5‴-H} \approx 7.0$ Hz, $^4J_{4‴-H,2‴-H} \approx {}^4J_{4‴-H,6‴-H} \approx 1.3$ Hz, 4‴-H); 6.22 (ddd, $^3J_{3-H,2-H} \approx {}^3J_{3-H,4-H} \approx 3.0$ Hz, $^4J_{3-H,5-H} = 2.1$ Hz, 3-H); 6.11 (ddd, $^3J_{2-H,3-H} = 3.0$ Hz, $^4J_{2-H,4-H} \approx {}^4J_{2-H,5-H} \approx 2.1$ Hz, 2-H); 5.60 (ddd, $^3J_{4-H,3-H} \approx {}^3J_{4-H,5-H} \approx 2.7$ Hz, $^4J_{4-H,2-H} = 2.5$ Hz, 4-H); 2.68 (ddd, $^3J_{1'-H,2'-H} \approx {}^3J_{1'-H,6'-H(ax)} \approx 11.0$ Hz, $^3J_{1'-H,6'-H(eq)} = 2.5$ Hz, 1'-H); 1.89 (ddd, $^3J_{2'-H,1'-H} \approx {}^3J_{2'-H,3'-H(ax)} \approx 11.0$ Hz, $^3J_{2'-H,3'-H(eq)} = 2.5$ Hz, 2'-H); 1.79 (dddd, $^2J_{3'-H(eq),3'-H(ax)} = 13.2$ Hz, $^3J_{3'-H(eq),2'-H} \approx {}^3J_{3'-H(eq),4'-H(ax)} \approx {}^3J_{3'-H(eq),4'-H(eq)} \approx 3.0$ Hz, 3'-H$_{eq}$); 1.75 (ddd, $^2J_{4'-H(eq), 4'-H(ax)} = 12.9$ Hz, $^3J_{4'-H(eq),3'-H(ax)} \approx {}^3J_{4'-H(eq),3'-H(eq)} \approx {}^3J_{4'-H(eq),5'-H(ax)} \approx 2.8$ Hz, 4'-H$_{eq}$); 1.43 (dddd, $^2J_{6'-H(eq),6'-H(ax)} = 12.3$ Hz, $^3J_{6'-H(eq),1'-H} \approx {}^3J_{6'-H(eq),5'-H} \approx {}^4J_{6'-H(eq),4'-H(eq)} \approx 2.5$ Hz, 6'-H$_{eq}$); 1.36 (m$_c$, 5'-H); 1.25 (dddd, $^2J_{3'-H(ax),3'-H(eq)} \approx {}^3J_{3'-H(ax),2'-H} \approx {}^3J_{3'-H(ax),4'-H(ax)} \approx 12.5$ Hz, $^3J_{3'-H(ax),4'-H(eq)} = 2.8$ Hz, 3'-H$_{ax}$); 1.15 (s, 3″-H$_3$); 1.09 (s, 1″-H$_3$); 0.98 (ddd, $^2J_{6'-H(ax),6'-H(eq)} \approx {}^3J_{6'-H(ax),1-H} \approx {}^3J_{6'-H(ax),5'-H} \approx 11.7$ Hz, 6'-H$_{ax}$); 0.93 (dddd, $^2J_{4'-H(ax),4'-H(eq)} \approx {}^3J_{4'-H(ax),3'-H(ax)} \approx {}^3J_{4'-H(ax),5'-H} \approx 12.1$ Hz, $^3J_{4'-H(ax),3'-H(eq)} \approx 3.2$ Hz, 4'-H$_{ax}$); 0.84 (d, $^3J_{5'-CH_3,5'-H} = 6.5$ Hz, 5'-C$H_3$). ^{13}C NMR (125 MHz, $C$DCl$_3$ as internal standard in CDCl$_3$): $\delta$ 151.43 (C-1‴); 145.54 (C-1); 127.75 (C-3‴, C-5‴); 127.75 (C-3‴, C-5‴); 127.75 (C-3‴, C-5‴); 126.95 (C-3); 125.64 (C-2‴, C-6‴); 125.64 (C-2‴, C-6‴); 124.78 (C-4‴); 123.24 (ddddd, $^1J_{C-2,2-H} = 176.8$ Hz, $^3J_{C-2,4-H} \approx {}^3J_{C-2,1'-H} \approx 7.6$ Hz, $^2J_{C-2,3-H} \approx {}^2J_{C-2,5-H} \approx 4.2$ Hz, C-2); 115.91 (C-5); 109.02 (C-4); 54.12 (C-2'); 43.86 (C-6'); 41.85 (C-1'); 40.82 (C-2″); 35.77 (C-4'); 32.36 (C-5'); 30.45 (C-3″); 28.90 (C-3'); 23.59 (C-1″); 22.56 (5'-$C$H$_3$). H,H-correlation (500 MHz, C$H$Cl$_3$ as internal standard in CDCl$_3$): $\delta$ 7.00−7.09 (2‴-H, 3‴-H, 5‴-H, 6‴-H) $\leftrightarrow$ 6.96 (4‴-H); 6.96 (4‴-H) $\leftrightarrow$ 7.00−7.09 (2‴-H, 3‴-H, 5‴-H, 6‴-H); 6.22 (3-H) $\leftrightarrow$ 6.11 (2-H), 6.05 (5-H), 5.60 (4-H); 6.11 (2-H) $\leftrightarrow$ 6.22 (3-H), 6.05 (5-H), 5.60 (4-H); 6.05 (5-H) $\leftrightarrow$ 6.22 (3-H), 6.11 (2-H), 5.60 (4-H); 5.60 (4-H) $\leftrightarrow$ 6.22 (3-H), 6.11 (2-H), 6.05 (5-H); 2.68 (1'-H) $\leftrightarrow$ 1.89 (2'-H), 1.43 (6'-H$_{eq}$), 0.98 (6'-H$_{ax}$); 1.89 (2'-H) $\leftrightarrow$ 2.68 (1'-H), 1.79 (3'-H$_{eq}$), 1.25 (3'-H$_{ax}$); 1.79 (3'-H$_{eq}$) $\leftrightarrow$ 1.89 (2'-H), 1.75 (4'-H$_{eq}$), 1.25 (3'-H$_{ax}$), 0.93 (4'-H$_{ax}$); 1.75 (4'-H$_{eq}$) $\leftrightarrow$ 1.79 (3'-H$_{eq}$), 1.43 (6'-H$_{eq}$), 1.25 (3'-H$_{ax}$), 0.93 (4'-H$_{ax}$); 1.43 (6'-H$_{eq}$) $\leftrightarrow$ 2.68 (1'-H), 1.75 (4'-H$_{eq}$), 0.98 (6'-H$_{ax}$); 1.43 (6'-H$_{eq}$) $\leftrightarrow$ 2.68 (1'-H), 1.75 (4'-H$_{eq}$), 0.98 (6'-H$_{ax}$); 1.36 (5'-H) $\leftrightarrow$ 0.84 (5'−C$H_3$); 1.25 (3'-H$_{ax}$) $\leftrightarrow$ 1.89 (2'-H), 1.79 (3'-H$_{eq}$), 1.75 (4'-H$_{eq}$); 1.15 (3″-H$_3$) $\leftrightarrow$ 1.09 (1″-H$_3$); 1.09 (1″-H$_3$) $\leftrightarrow$ 1.15 (3″-H$_3$); 0.98 (6'-H$_{ax}$) $\leftrightarrow$ 2.68 (1'-H), 1.43 (6'-H$_{eq}$); 0.93 (4'-H$_{ax}$) $\leftrightarrow$ 1.79 (3'-H$_{eq}$) and 1.75 (4'-H$_{eq}$); 0.84 (5'-C$H_3$) $\leftrightarrow$ 1.36 (5'-H). C,H-correlation: 127.75 (C-3‴, C-5‴) $\leftrightarrow$ 7.00−7.09 (3‴-H, 5‴-H); 126.95 (C-3) $\leftrightarrow$ 6.22 (3-H);. 125.64 (C-2‴,C-6‴) $\leftrightarrow$ 7.00−7.09 (2‴-H, 6‴-H); 124.78 (C-4‴) $\leftrightarrow$ 6.96 (4‴-H); 123.24 (C-2) $\leftrightarrow$ 6.11 (2-H); 115.91 (C-5) $\leftrightarrow$ 6.05 (5-H); 109.02 (C-4) $\leftrightarrow$ 5.60 (4-H); 54.12 (C-2') $\leftrightarrow$ 1.89 (2'-H); 43.86 (C-6') $\leftrightarrow$ 1.43 (6'-H$_{eq}$) and 0.98 (6'-H$_{ax}$); 41.85 (C-1') $\leftrightarrow$ 2.68 (1'-H); 35.77 (C-4') $\leftrightarrow$ 1.75 (4'-H$_{eq}$) and 0.93 (4'-H$_{ax}$); 32.36 (C-5') $\leftrightarrow$ 1.36 (5'-H); 30.45 (C-3″) $\leftrightarrow$ 1.15 (3″-H$_3$); 28.90 (C-3') $\leftrightarrow$ 1. 79 (3'-H$_{eq}$) and 1.25 (3'-H$_{ax}$); 23.59 (C-1″) $\leftrightarrow$ 1.09 (1″-H$_3$); 22.56 (5'-C$H_3$) $\leftrightarrow$ 0.84 (5'-C$H_3$). NOE-difference spectra (500 MHz, C$H$Cl$_3$ as internal standard in CDCl$_3$); only significant enhancements (>10%) are given: irradiation at 7.00−7.09, 6.96 ppm leads to enhancement at 6.22, 6.11, 1.89, 1.15, 1.09 ppm; ir-

radiation at 6.22 ppm $\leftrightarrow$ 7.00−7.09, 6.96, 6.11, 6.05, 5.60 ppm; irradiation at 6.11 ppm $\leftrightarrow$ 7.00−7.09, 6.96, 6.22, 2.68, 1.15, 1.09 ppm; irradiation at 6.05 ppm $\leftrightarrow$ 6.22, 5.60, 1.89, 0.98 ppm; irradiation at 5.60 ppm $\leftrightarrow$ 6.22, 6.05, 1.43 ppm; irradiation at 2.68 ppm $\leftrightarrow$ 6.11, 1.43, 1.36, 1.25, 1.15, 1.09 ppm; irradiation at 1.89 ppm $\leftrightarrow$ 7.00−7.09, 6.96, 6.05, 1.15, 1.09 ppm; irradiation at 1.15 ppm $\leftrightarrow$ 7.00−7.09, 6.96, 6.11, 2.68, 1.89, 1.09 ppm; irradiation at 1.09 ppm $\leftrightarrow$ 7.00−7.09, 6.96, 6.11, 2.68, 1.89, 1.79, 1.75, 1.15 ppm; irradiation at 0.84 ppm $\leftrightarrow$ 1.75, 1.43, 1.36 ppm.

**NMR of 2.** ^{1}H NMR (500 MHz, C$H$Cl$_3$ as internal standard in CDCl$_3$): $\delta$ 6.73 (ddd, $^3J_{3-H,2-H} \approx {}^3J_{3-H,4-H} \approx 3.0$ Hz, $^4J_{3-H,5-H} = 2.2$ Hz, 3-H); 6.40 (br d, $^4J_{5-H,3-H} = 2.2$ Hz, 5-H); 6.28 (ddd, $^3J_{2-H,3-H} = 3.0$ Hz, $^4J_{2-H,4-H} \approx {}^4J_{2-H,5-H} \approx 2.2$ Hz, 2-H); 6.19 (ddd, $^3J_{4-H,3-H} \approx {}^3J_{4-H,5-H} \approx 2.7$ Hz, $^4J_{4-H,2-H} = 2.5$ Hz, 4-H); 2.74 (ddd, $^3J_{1'-H,2'-H(ax)} \approx {}^3J_{1'-H,6'-H(ax)} \approx 11.4$ Hz, $^3J_{1'-H,6'-H(eq)} = 2.8$ Hz, 1'-H); 1.77 (ddddd, $^2J_{4'-H(eq),4'-H(ax)} = 10.1$ Hz, $^3J_{4'-H(eq),3'-H(ax)} \approx {}^3J_{4'-H(eq),3'-H(eq)} \approx {}^3J_{4'-H(eq),5'-H} \approx {}^4J_{4'-H(eq),6'-H(eq)} \approx 2.5$ Hz, 4'-H$_{eq}$); 1.69 (dddd, $^2J_{3'-H(eq),3'-H(ax)} = 13.1$ Hz, $^3J_{3'-H(eq),2'-H} \approx {}^3J_{3'-H(eq),4'-H(ax)} \approx {}^3J_{3'-H(eq),4'-H(eq)} \approx 3.2$ Hz, 3'-H$_{eq}$); 1.60 (dddd, $^2J_{6'-H(eq),6'-H(ax)} = 12.0$ Hz, $^3J_{6'-H(eq),1'-H} \approx {}^3J_{6'-H(eq),5'-H} \approx 5.1$ Hz, $^4J_{6'-H(eq),4'-H(eq)} = 2.9$ Hz, 6'-H$_{eq}$); 1.48 (ttd, $^3J_{2″-H,1″-H3} \approx {}^3J_{2″-H(eq),3″-H3} \approx 6.8$ Hz, $^3J_{2″-H,2'-H} = 2.4$ Hz, 2″-H); 1.36−1.44 (m, 5'-H); 1.14 (dddd, $^2J_{3'-H(ax),3'-H(eq)} \approx {}^3J_{3'-H(ax),2'-H} \approx {}^3J_{3'-H(ax),4'-H(ax)} \approx 12.6$ Hz, $^3J_{3'-H(ax),4'-H(eq)} = 3.3$ Hz, 3'-H$_{ax}$); 1.04 (ddd, $^2J_{6'-H(ax),6'-H(eq)} \approx {}^3J_{6'-H(ax),1'-H} \approx {}^3J_{6'-H(ax),5'-H} \approx 11.8$ Hz, 6'-H$_{ax}$); 0.98 (dddd, $^3J_{2'-H,1'-H} \approx {}^3J_{2'-H,3'-H(ax)} \approx 11.4$ Hz, $^3J_{2'-H,3'-H(eq)} \approx {}^3J_{2'-H,2″-H} \approx 2.7$ Hz, 2'-H); 0.87−0.94 (m, 4'-H$_{ax}$); 0.89 (d, $^3J_{5'-CH_3,5'-H} = 6.5$ Hz, 5'−C$H_3$); 0.85 (d, $^3J_{3″-H3,2″-H} = 6.9$ Hz, 3″-H$_3$); 0.79 (d, $^3J_{1″-H3,2″-H} = 6.9$ Hz, 1″-H$_3$). ^{13}C NMR (125 MHz, $C$DCl$_3$ as internal standard in CDCl$_3$): $\delta$ 145.54 (C-1); 126.82 (C-3); 121.14 (ddddd, $^1J_{C-2,2-H} = 176.5$ Hz, $^3J_{C-2,4-H} \approx {}^3J_{C-2,5-H} \approx 7.6$ Hz, $^2J_{C-2,3-H} = 4.9$ Hz, $^3J_{C-2,1'-H} = 2.7$ Hz, C-2); 115.08 (C-5); 109.54 (C-4); 50.91 (C-2'); 50.91 (C-2'); 42.14 (C-1'); 40.87 (C-6'); 35.22 (C-4'); 32.43 (C-5'); 27.45 (C-2″); 24.72 (C-3); 22.81 (5'-CH$_3$); 21.70 (C-1″); 15.60 (C-3″). H,H-correlation (500 MHz, C$H$Cl$_3$ as internal standard in CDCl$_3$): $\delta$ 6.73 (3-H) $\leftrightarrow$ 6.40 (5-H), 6.28 (2-H), 6.19 (4-H), 0.85 (3″-H$_3$); 6.40 (5-H) $\leftrightarrow$ 6.73 (3-H), 6.28 (2-H), 6.19 (4-H); 6.28 (2-H) $\leftrightarrow$ 6.73 (3-H), 6.40 (5-H), 6.19 (4-H), 0.85 (3″-H$_3$); 6.28 (2-H) $\leftrightarrow$ 6.73 (3-H), 6.40 (5-H), 6.19 (4-H), 0.85 (3″-H$_3$); 6.19 (4-H) $\leftrightarrow$ 6.73 (3-H), 6.40 (5-H), 6.28 (2-H); 2.74 (1'-H) $\leftrightarrow$ 1.60 (6'-H$_{eq}$), 1.04 (6'-H$_{ax}$), 0.98 (2'-H); 1.77 (4'-H$_{eq}$) $\leftrightarrow$ 1.69 (3'-H$_{eq}$), 1.60 (6'-H$_{eq}$), 1.14 (3'-H$_{ax}$), 0.87−0.94 (4'-H$_{ax}$), 1.36−1.44 (5'-H); 1.69 (3'-H$_{eq}$) $\leftrightarrow$ 1.77 (4'-H$_{eq}$), 1.14 (3'-H$_{ax}$), 0.98 (2'-H), 0.87−0.94 (4'-H$_{ax}$); 1.60 (6'-H$_{eq}$) $\leftrightarrow$ 2.74 (1'-H), 1.77 (4'-H$_{eq}$), 1.04 (6'-H$_{ax}$), 1.36−1.44 (5'-H); 1.48 (2″-H) $\leftrightarrow$ 0.85 (3″-H$_3$), 0.79 (1″-H$_3$); 1.36−1.44 (5'-H) $\leftrightarrow$ 0.87−0.94 (4'-H$_{ax}$), 0.89 (5'-CH$_3$), 1.77 (4'-H$_{eq}$), 1.60 (6'-H$_{eq}$), 1.04 (6'-H$_{ax}$); 1.14 (3'-H$_{ax}$) $\leftrightarrow$ 1.77 (4'-H$_{eq}$), 1.69 (3'-H$_{eq}$), 0.98 (2'-H), 0.87−0.94 (4'-H$_{ax}$); 1.04 (6'-H$_{ax}$) $\leftrightarrow$ 2.74 (1'-H), 1.60 (6'-H$_{eq}$), 1.36−1.44 (5'-H); 0.98 (2'-H) $\leftrightarrow$ 2.74 (1'-H), 1.69 (3'-H$_{eq}$), 1.14 (3'-H$_{ax}$); 0.87−0.94 (4'-H$_{ax}$) $\leftrightarrow$ 1.77 (4'-H$_{eq}$), 1.69 (3'-H$_{eq}$), 1.36−1.44 (5'-H), 1.14 (3'-H$_{ax}$), 0.89 (5'-C$H_3$); 0.89 (5'-C$H_3$) $\leftrightarrow$ 1.36−1.44 (5'-H), 1.14 (3'-H$_{ax}$), 0.87−0.94 (4'-H$_{ax}$); 0.85 (3″-H$_3$) $\leftrightarrow$ 1.48 (2″-H), (3-H), 6.28 (2-H); 0.79 (1″-H$_3$) $\leftrightarrow$ 1.48 (2″-H). C,H-correlation: 126.82 (C-3) $\leftrightarrow$ 6.73 (3-H); 121.14 (C-2) $\leftrightarrow$ 6.28 (2-H); 115.08 (C-5) $\leftrightarrow$ 6.40 (5-H); 109.54 (C-4) $\leftrightarrow$

6.19 (4-H); 50.91 (C-2′) ↔ 0.98 (2′−H); 42.14 (C-1′) ↔ 2.74 (1′-H); 40.87 (C-6′) ↔ 1.60 (6′-H$_{eq}$) and 1.04 (6′-H$_{ax}$); 35.22 (C-4′) ↔ 1.77 (4′-H$_{eq}$) and 0.87−0.94 (4′-H$_{ax}$); 32.43 (C-5′) ↔ 1.36−1.44 (5′-H); 27.45 (C-2″) ↔ 1.48 (2″-H); 24.72 (C-3′) ↔ 1.69 (3′-H$_{eq}$) and 1.14 (3′-H$_{ax}$); 22.81 (5′-C$H_3$) ↔ 0.89 (5′-C$H_3$); 21.70 (C-1″) ↔ 0.79 (1″-H$_3$); 15.60 (C-3″) ↔ 0.85 (3″-H$_3$). NOE-difference spectra (500 MHz, C$H$Cl$_3$ as internal standard in CDCl$_3$); only significant enhancements (>10%) are given: irradiation at 6.73 ppm leads to significant enhancement (>10%) at 6.28, 6.19, 1.60 ppm; irradiation at 6.40 ppm ↔ 6.19, 1.04 ppm; irradiation at 6.28 ppm ↔ 6.73, 2.74, 1.48, 0.85 ppm; irradiation at 6.19 ppm ↔ 6.73, 6.40, 1.60 ppm; irradiation at 2.74 ppm ↔ 6.28, 1.60, 1.36−1.44, 1.14, 0.85 ppm; irradiation at 1.77 ppm ↔ at 1.36−1.44, 1.14, 0.87−0.94 ppm; irradiation at 1.69 ppm ↔ 1.14, 0.98, 0.87−0.94, 0.79 ppm; irradiation at 1.60 ppm ↔ 6.73, 6.28, 6.19, 2.74, 1.36−1.44, 1.04 ppm; irradiation at 1.48, 1.36−1.44 ppm ↔ 6.28, 2.74, 0.98, 0.89, 0.85, 0.79 ppm; irradiation at 1.14 ppm ↔ 2.74, 1.77, 1.69, 0.85 ppm; irradiation at 0.89 ppm ↔ 1.77, 1.69, 1.60, 1.36−1.44 ppm; irradiation at 0.85 ppm ↔ 6.28, 2.74, 1.77, 1.36−1.44, 1.14 ppm; irradiation at 0.79 ppm ↔ 1.69, 1.48, 0.98 ppm.

**NMR of 3**: $^1$H NMR (500 MHz, C$H$Cl$_3$ as internal standard in CDCl$_3$): δ 6.69 (ddd, $^3J_{5−H,4−H}$ = 2.8 Hz, $^4J_{5−H,3−H} ≈ {}^4J_{5−H,2−H} ≈$ 2.2 Hz, 5-H); 6.60 (ddd, $^3J_{3−H,4−H} ≈ {}^3J_{3−H,2−H} ≈$ 3.0 Hz, $^4J_{3−H,5−H}$ = 2.1 Hz, 3-H); 6.25 (ddd, $^3J_{2−H,3−H}$ = 3.0 Hz, $^4J_{2−H,5−H} ≈ {}^4J_{2−H,4−H} ≈$ 2.2 Hz, 2-H); 6.19 (ddd, $^3J_{4−H,5−H} ≈ {}^3J_{4−H,3−H} ≈$ 2.8 Hz, $^4J_{4−H,2−H}$ = 2.5 Hz, 4-H); 3.54 (ddd, $^3J_{1′−H,2′−H(ax)} ≈ {}^3J_{1′−H,6′−H(ax)} ≈$ 3.8 Hz, $^3J_{1′−H,6′−H(eq)}$ = 3.2 Hz, 1′−H); 2.05 (dddd, $^2J_{6′−H(eq),6′−H(ax)}$ = 14.0 Hz, $^3J_{6′−H(eq),5′−H}$ = 6.1 Hz, $^3J_{6′−H(eq),1′−H}$ = 4.1 Hz, $^4J_{6′−H(eq),4′−H(eq)}$ = 2.4 Hz, 6′-H$_{eq}$); 1.92 (m$_c$, 5′-H); 1.78−1.86 (m, 4′-H$_{eq}$); 1.58−1.66 (m, 3′-H$_{eq}$); 1.33 (dtt, $^3J_{2″−H,2′−H}$ = 8.7 Hz, $^3J_{2″−H,3″−H3}$ = $^3J_{2″−H(eq),1″−H3}$ = 6.5 Hz, 2″-H); 1.24 (m$_c$, 2′-H, superimposed by 6′−H$_{ax}$); 1.21 (ddd, $^2J_{6′−H(ax),6′−H(eq)}$ = 14.0 Hz, $^3J_{6′−H(ax),5′−H}$ = 12.3 Hz, $^3J_{6′−H(ax),1′−H}$ = 5.0 Hz, 6′-H$_{ax}$); 1.00 (d, $^3J_{1″−H3, 2′−H}$ = 6.5 Hz, 1″-H3); 0.91−0.97 (m, 3′-H$_{ax}$, 4′-H$_{ax}$); 0.89 (d, $^3J_{5′−CH3,5′−H}$ = 6.5 Hz, 5′-C$H_3$); 0.71 (d, $^3J_{3″−H3,2″−H}$ = 6.5 Hz, 3″-H$_3$). $^{13}$C NMR (125 MHz, C$D$Cl$_3$ as internal standard in CDCl$_3$): δ 142.04 (C-1); 122.70 (dddd, $^1J_{C−5,5−H}$ = 175.0 Hz, $^3J_{C−5,3−H}$ = 6.7 Hz, $^2J_{C−5,4−H} ≈ {}^3J_{C−5,2−H} ≈$ 6.4 Hz, C-5); 121.85 (C-2); 120.16 (C-3); 110.62 (C-4); 49.99 (C-2′); 39.51 (C-6′); 38.27 (C-1′); 35.64 (C-4′); 29.24 (C-2″); 28.68 (C-5′); 24.63 (C-3′); 22.88 (5′-C$H_3$); 22.30 (C-1″); 20.78 (C-3″).

H,H−Correlation (500 MHz, C$H$Cl$_3$ as internal standard in CDCl$_3$): δ = 6.69 (5-H) ↔ 6.60 (3-H), 6.25 (2-H), 6.19 (4-H); 6.60 (3-H) ↔ 6.69 (4-H), 6.25 (2-H), 6.19 (4-H); 6.25 (2-H) ↔ 6.69 (4-H), 6.60 (3-H), 6.19 (4-H) and 0.91−0,97 (3′-H$_{ax}$); 6.19 (4-H) ↔ 6.69 (5-H), 6.60 (3-H), 6.25 (2-H) and 0.71 (3″-H$_3$); 3.54 (1′-H) ↔ 2.05 (6′-H$_{eq}$), 1.58−1.66 (3′-H$_{eq}$), 1.24 (2′-H) and 1.21 (6′-H$_{ax}$); 2.05 (6′-H$_{eq}$) ↔ 3.54 (1′-H), 1.92 (5′-H), 1.78−1.86 (4′-H$_{eq}$), 1.24

(2′-H) and 1.21 (6′-H$_{ax}$); 1.92 (5′-H) ↔ 2.05 (6′-H$_{eq}$), 1.24 (2′-H), 1.21 (6′-H$_{ax}$) and 0.89 (5′−C$H_3$); 1.78−1.86 (4′-H$_{eq}$) ↔ 2.05 (6′-H$_{eq}$), 1.58−1.66 (3′-H$_{eq}$), 1.24 (2′-H) and 0.91−0,97 (3′-H$_{ax}$, 4′-H$_{ax}$); 1.58−1.66 (3′-H$_{eq}$) ↔ 3.54 (1′-H), 1.78−1.86 (4′-H$_{eq}$), 1.24 (2′-H) and 0.91−0,97 (3′-H$_{ax}$, 4′-H$_{ax}$); 1.33 (2″-H) ↔ 1.24 (2′-H), 1.00 (1″-H$_3$) and 0.71 (3″-H$_3$); 1.24 (2′-H) ↔ 3.54 (1′-H), 2.05 (6′-H$_{eq}$), 1.92 (5′-H), 1.78−1.86 (4′-H$_{eq}$), 1.58−1.66 (3′-H$_{eq}$), 1.33 (2″-H) and 0.91−0,97 (3′-H$_{ax}$, 4′-H$_{ax}$); 1.21 (6′-H$_{ax}$) ↔ 3.54 (1′-H), 2.05 (6′-H$_{eq}$) and 1.92 (5′-H); 1.00 (1″-H$_3$) ↔ 1.33 (2″-H), 0.91−0,97 (3′-H$_{ax}$) and 0.71 (3″-H$_3$); 0.91−0,97 (3′-H$_{ax}$, 4′-H$_{ax}$) ↔ 1.78−1.86 (4′-H$_{eq}$), 1.58−1.66 (3′-H$_{eq}$), 1.24 (2′-H) and 1.00 (1″-H$_3$); 0.89 (5′-C$H_3$) ↔ 1.92 (5′-H), 1.00 (1″-H$_3$) and 0.71 (3″-H$_3$); 0.71 (3″-H$_3$) ↔ 1.33 (2″-H), 1.00 (1″-H$_3$) and 0.91−0,97 (3′-H$_{ax}$). C,H-correlation: 122.70 (C-5) ↔ 6.69 (5-H); 121.85 (C-2) ↔ 6.25 (2-H); 120.16 (C-3) ↔ 6.60 (3-H); 110.62 (C-4) ↔ 6.19 (4-H); 49.99 (C-2′) ↔ 1.24 (2′-H); 39.51 (C-6′) ↔ 2.05 (6′-H$_{eq}$) and 1.21 (6′-H$_{ax}$); 38.27 (C-1′) ↔ 3.54 (1′-H); 35.64 (C-4′) ↔ 1.78−1.86 (4′-H$_{eq}$) and 0.91−0.97 (4′-H$_{ax}$); 29.24 (C-2″) ↔ 1.33 (2″-H); 28.68 (C-5′) ↔ 1.92 (5′-H); 24.63 (C-3′) ↔ 1.58−1.66 (3′-H$_{eq}$) and 0.91−0.97 (3′-H$_{ax}$); 22.88 (5′-C$H_3$) ↔ 0.89 (5′-C$H_3$); 22.30 (C-1″) ↔ 1.00 (1″-H$_3$); 20.78 (C-3″) ↔ 0.71 (3″-H$_3$). NOE-difference spectra (500 MHz, C$H$Cl$_3$ as internal standard in CDCl$_3$); only significant enhancements (>10%) are given: irradiation at 6.69 ppm leads to significant enhancement (>10%) at 6.19, 2.05, 1.92 ppm; irradiation at 6.60 ↔ 6.25, 6.19 ppm; irradiation at 6.25 ppm ↔ 6.60, 3.54, 1.33, 1.00 ppm; irradiation at 6.19 ppm ↔ 6.69, 6.60, 2.05 ppm; irradiation at 3.54 ppm ↔ 6.25, 2.05, 1.33, 1.24, 1.21, 1.00 ppm; irradiation at 2.05 ↔ 6.69, 3.54, 1.21, 0.89 ppm; irradiation at 1.92 ppm ↔ 6.69, 0.89 ppm; irradiation at 1.78−1.86 ppm ↔ 0.91−0.97[1] ppm; irradiation at 1.58−1.66 ppm ↔ 1.24, 0.91−0.97[1], 0.71 ppm; irradiation at 1.33 ppm ↔ 6.25, 3.54, 0.71 ppm; irradiation at 1.00[2] ppm ↔ 6.25, 3.54, 1.78−1.86, 1.58−1.66, 1.33, 1.24, 0.71 ppm; irradiation at 0.91−0.97[1,2] ppm ↔ 1.78−1.86, 1.58−1.66, 1.21, 1.33 ppm; irradiation at 0.89 ppm ↔ 1.92, 1.78−1.86, 1.58−1.66, 1.21 ppm; irradiation at 0.71 ppm ↔ 1.78−1.86, 1.58−1.66, 1.33, 1.00 ppm. [1] unambiguous assignment impossible, [2] low selectivity.

**Supporting Information Available:** Crystallographic tables for **2** and **3** and copies of the NMR spectra of **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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