Total Synthesis of Anhydromarasmone

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Dedicated to Prof. Dr. Wolfgang Steglich on the occasion of his 70th birthday

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A synthesis of anhydromarasmone is presented using, as key step, an iridium-catalyzed double-bond isomerization from a homoallyl ether to an allyl ether. Other transition metal complexes employed for double-bond transposition resulted in the vinyl ether as the final product.

Introduction

In the course of our research towards highly functionalized natural products, we recently published our syntheses of kuehneromycin A,[1] mniopetal E,[2] and mniopetal F.[3] Structurally related to these compound are the marasmones (Figure 1), which were isolated some years ago by Ayer and co-workers[4] from *Marasmius oreades*. This fungus seems to be responsible for the so-called "fairy rings" in Canadian golf yards.

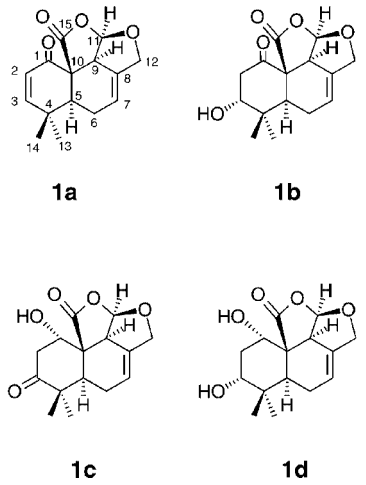

Figure 1. Anhydromarasmone **1a**, marasmone **1b**, isomarasmone **1c** and dihydromarasmone **1d**

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Since kuehneromycin A and the mniopetals are inhibitors of the reverse transcriptase of HIV, we became interested in the question of whether the marasmones also show this biological activity. Therefore, we decided to synthesize anhydromarasmone **1a** as a first target molecule to provide material for biological testing.[5]

Here we wish to report our results towards this end.

Results and Discussion

Our syntheses of kuehneromycin A and the mniopetals were based on a common intermediate **6**, which should be a suitable starting material for the synthesis of **1a**.

In principle, we have two possibilities to convert **6** into **1a** (see Scheme 1). The first strategy consists of the cleavage of the silyl ether **6**, oxidation of **5** with a concomitant double-bond shift to the α,β-unsaturated aldehyde **4**, Luche reduction to the allyl alcohol **3**, intramolecular transacetalization to **2** and, finally, introduction of the 2,3-double bond. The second strategy is shorter and makes use of silyl ether cleavage to give **5**, intramolecular transacetalization leading to **7**, double-bond isomerization to yield **2** and, finally, introduction of the 2,3-double bond. Whereas in the first strategy the double-bond isomerization is driven by establishing an α,β-unsaturated aldehyde from a homoallyl alcohol, there is no such driving force in the second strategy. In that case, it was an interesting question as to whether or not it is possible to use transition metal methodology for this task and, thus, we decided to explore the second strategy in greater detail.

Desilylation of **6** using TBAF was straightforward as was intramolecular transacetalization in the presence of TFA to give **7** (92% over two steps). Acetal **7** crystallized readily upon standing. The structure was confirmed by NMR spectroscopy and X-ray analysis[6] (Figure 2). The next step was

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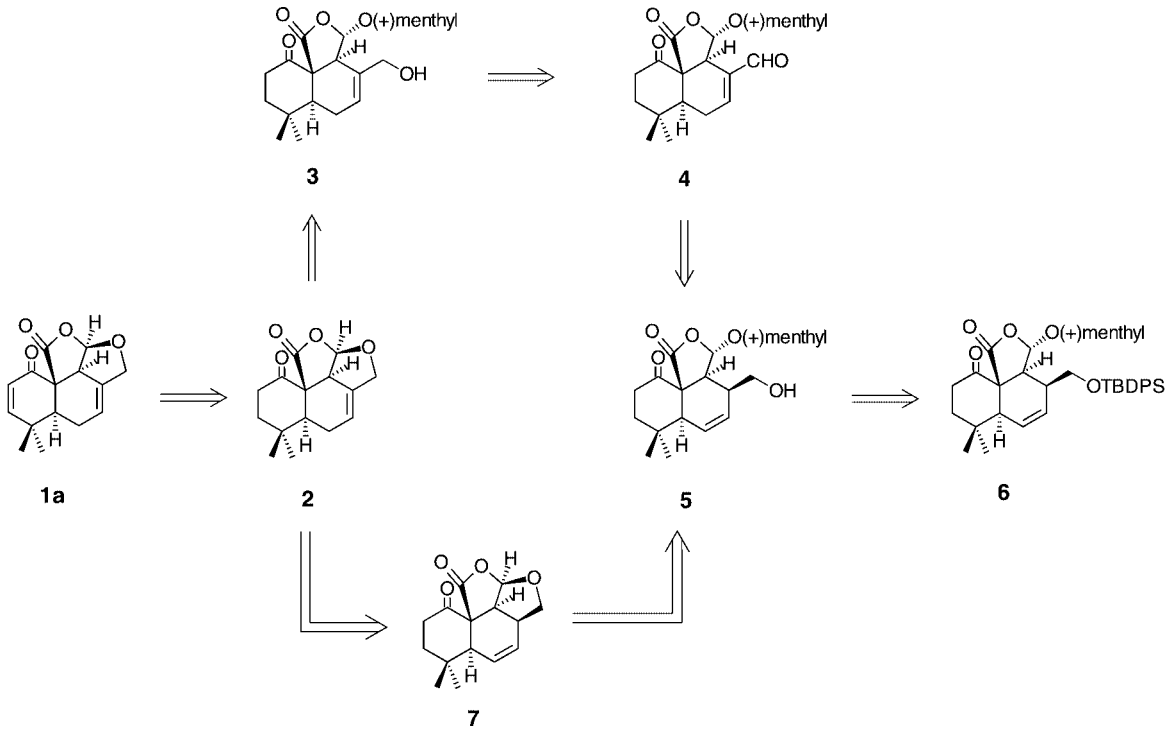
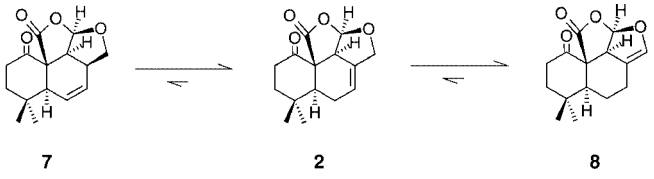


Scheme 1. Retrosynthetic strategies for the synthesis of **1a**

the crucial double-bond isomerization and a survey of the literature[7] offered, as catalysts, Pd/C, $PdCl_2(PhCN)_2$, $PtCl_2(PhCN)_2$, and $RuCl_3{\cdot}3H_2O$, which did not give the desired isomerization. Using $RhCl_3{\cdot}3H_2O$ with or without $CaCO_3$, $[(PPh_3)_3RhCl]$, $[(PPh_3)_3RhH(CO)]$, and $IrCl_3{\cdot}3H_2O$ as catalysts gave the enol ether **8** as the main product (> 80%) (Scheme 2). Compound **2** is produced initially, but soon it isomerizes, so that once the disappearance of **7** has occurred, almost all of **2** has been transformed into **8**.

A solution to this problem would be a catalyst that mediates the first isomerization selectively, but not the second one. After various unsuccessful attempts, we found that Va-



Scheme 2. Double-bond isomerization using various transition metal catalysts (see text)

ska's complex $[(PPh_3)_2Ir(CO)Cl]$[8] is the catalyst of choice in this reaction. After 6 h at 70 °C in toluene/ethanol (4:1, v/v) equilibrium between **7** and **2** was reached [46% of **7**, 50% of **2,** 4% of **8** (GC)]. Interestingly, in all our isomeriz-

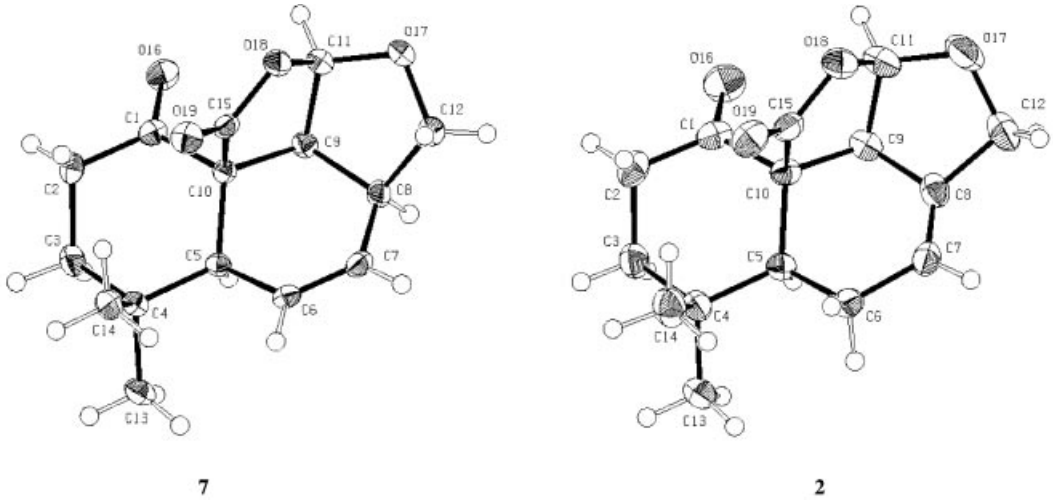
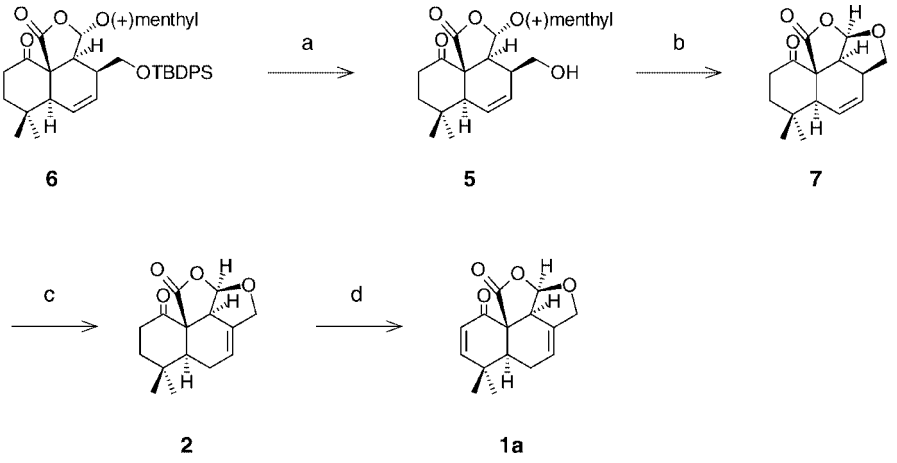


Figure 2. X-ray structures of homoallyl ether **7** and allyl ether **2**



Scheme 3. a) TBAF, THF, room temp., 2 h; b) 20% TFA in CH_2Cl_2, room temp., 10 min, 92% over two steps; c) $[(PPh_3)_2Ir(CO)Cl]$ (50 mol %), toluene/ethanol (4:1, v/v), 70 °C, 6 h, 43% (ca. 35% of **7** was recovered); d) i. LDA, THF, −78 °C, 15 min, ii. PhSeBr, −78 °C, 15 min, iii. H_2O_2, 0 °C to room temp., 2 h, 58%.

ation reactions, the double bond migrates towards the bridgehead carbon C8.

This successful isomerization would be practical only if the two isomers could be separated readily. Indeed, this is possible using flash chromatography. It is essential to use silica gel with 15−40 μm particle size since it gives better separations than the silica gel (40−63 μm particle size) that is usually applied. The separated starting material, as well as the catalyst, could be recycled. Isomerized acetal **2** gave crystals suitable for X-ray analysis (Figure 2).[6]

After having solved the isomerization problem, introduction of the 2,3-double bond using standard methodology (LDA, PhSeBr, H_2O_2)[9] was straightforward. The resulting product was identical in all respects with the published natural product. Furthermore, our synthesis confirms the absolute configuration of anhydromarasmon suggested by Ayer et al.[4]

The complete synthesis of **1a** starting from **6** is shown in Scheme 3.

Conclusion

In summary, we have synthesized **1a** from **6** in four steps, using an iridium-catalyzed double-bond isomerization as the key transformation. Offering a valuable shortcut, this reaction could be useful for other chemists faced with the problem of double-bond transposition.

Experimental Section

General Procedures: ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 360 at 360 and 90 MHz, respectively. Chemical shifts are reported in ppm and coupling constants are given in Hz. For complete assignments of H and C atoms, HMQC, HMBC, H,H-COSY, HMQC-COSY and NOESY spectra were recorded on a Bruker AV 500 at 500 MHz. Mass spectra were obtained in EI (GC-MS) mode on a Finnigan MAT 8200. THF was filtered through basic alumina to remove peroxides and then dried with K/benzophenone under N_2. Methylene chloride was dried over CaH_2 and diisopropylamine was dried over NaH prior to distillation.

Synthesis of 7: A solution of silyl ether 6 (0.81 g, 1.24 mmol) in THF (10 mL) was cooled to 0 °C and a solution of TBAF in THF (1.2 mL, 1.2 mmol) was added. The cooling bath was removed and the reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated in vacuo and the residue was dissolved in dichloromethane (ca. 10 mL) and evaporated again to remove residual water azeotropically. Crude 5, which was pure enough for the next step, was dissolved in dichloromethane (8.5 mL) and cooled to 0 °C. TFA (2 mL) was then added dropwise with vigorous stirring and after 10 min the cooling bath was removed. Stirring was continued for 1 h at room temperature and then the reaction mixture was poured onto a mixture of crushed ice, saturated $NaHCO_3$ solution and diethyl ether (ca. 50 mL). After separation of the phases, the aqueous phase was extracted once with diethyl ether (50 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. Flash chromatography with pentane/diethyl ether (3:1, v/v) gave 7 (0.3 g, 92%) as a colorless oil, which crystallized upon standing. $[\alpha]_D^{20}$ = + 97.8 (c = 0.99, CH_2Cl_2). ^1H NMR (360 MHz, $CDCl_3$): δ = 6.11 (d, J = 4.6 Hz, 1 H, H-11), 5.98 (dt, J = 9.8, 3.3 Hz, 1 H, H-7), 5.74 (dt, J = 9.8, 2.6 Hz, 1 H, H-6), 4.41 (t, J = 8.8 Hz, 1 H, H-12), 3.76 (t, J = 8.4 Hz, 1 H, H-12), 3.41 (dd, J = 11.3, 4.5 Hz, 1 H, H-9), 3.01−2.88 (m, 1 H, H-8), 2.95 (td, J = 14.0, 5.2 Hz, 1 H, H-3), 2.39 (ddd, J = 11.7, 4.5, 3.9 Hz, 1 H, H-3), 2.37 (d, J = 3.3 Hz, 1 H, H-5), 2.00 (dt, J = 14.3, 4.9 Hz, 1 H, H-2), 1.69 (td, J = 13.6, 3.9 Hz, 1 H, H-2), 1.48 (s, 3 H, H-14), 1.08 (s, 3 H, H-13) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 205.1 (C-1), 169.7 (C-15), 129.1 (C-6), 128.3 (C-7), 106.7 (C-11), 73.3 (C-12), 64.8 (C-10), 49.0 (C-9), 48.9 (C-5), 39.8 (C-2), 36.0 (C-3), 34.6 (C-8), 32.1 (C-4), 31.8 (C-13), 21.9 (C-14) ppm. MS (EI, 80 °C): m/z (%) = 262 ([M^+], 5), 218 ([$M - CO_2$]$^+$, 39), 189 (49), 162 (62), 132 (100), 119 (63), 91 (68), 55 (12). HRMS (EI, 80 °C): calcd. 262.1205; found 262.1216.

Double-Bond Isomerization by Using Vaska's Complex: A solution of 7 (145 mg, 0.55 mmol) and $(PPh_3)_2Ir(CO)Cl$ (225 mg, 0.29 mmol, 0.5 equiv.) in dry toluene (4 mL) and dry ethanol (1 mL) and stirred for 6 h at 70 °C. After cooling to room temperature, the reaction mixture was filtered (ca. 200 mg of Vaska's com-

plex was recovered) and the solvents were evaporated to dryness. Flash chromatography on silica gel (15−40 μm, Merck) as the stationary phase and pentane/diethyl ether (5:1, v/v) as the eluent gave 2 (62 mg, 0.24 mmol, 43%) as a colorless oil that crystallized upon standing $[\alpha]_D^{20} = +30.8$ ($c = 0.2$, Et_2O); ref.[4a] $[\alpha]_D^{20} = +28$ ($c = 0.4$, MeOH)). Additionally, 7 (50 mg, 0.19 mmol, 35%) was recovered and 8 (6 mg, 4%) was isolated. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 6.14 (d, $J = 4.2$ Hz, 1 H, H-11), 5.95 (m, 1 H, H-7), 4.53 (br. d, $J = 10.2$ Hz, 1 H, H-12), 4.45 (br. d, $J = 10.6$ Hz, 1 H, H-12), 3.37 (m, 1 H, H-9), 2.91 (td, $J = 14.6$, 5.1 Hz, 1 H, H-2), 2.48−2.28 (m, 2 H, H-6), 2.38 (dt, $J = 14.2$, 3.3 Hz, 1 H, H-2), 2.04 (dd, $J = 11.4$, 5.9 Hz, 1 H, H-5), 1.95 (dt, $J = 13.5$, 4.5 Hz, 1 H, H-3), 1.74 (td, $J = 14.6$, 3.4 Hz, 1 H, H-3), 1.45 (s, 3 H, H-14), 1.06 (s, 3 H, H-13) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 205.5 (C-1), 169.3 (C-15), 131.2 (C-8), 125.9 (C-7), 105.3 (C-11), 72.2 (C-12), 64.7 (C-10), 48.7 (C-9), 47.9 (C-5), 41.4 (C-3), 36.4 (C-2), 32.7 (C-4), 31.4 (C-13), 25.3 (C-6), 21.5 (C-14) ppm. MS (EI, 80 °C): *m/z* (%) = 247 ($[M - CH_3]^+$, 2), 234 ($[M - CO]^+$, 2), 218 ($[M - CO_2]^+$, 100), 161 (44), 147 (25), 134 (25), 120 (36), 119 (40), 91 (40).

Synthesis of 1a: *n*BuLi in hexane (89 μL, 133.6 μmol) was added to dry diisopropylamine (14.0 mg, 18.2 μL, 138.9 μmol) dissolved in THF (0.5 mL) under N_2 at −78 °C. The resulting solution was stirred for 15 min at that temperature, and then a solution of 2 (28.0 mg, 106.8 μmol) in THF (0.5 mL) was added dropwise. After 15 min at −78 °C, a dark-red solution of phenylselenyl bromide (32.8 mg, 138.9 μmol) in THF (0.7 mL) was added dropwise (PhSeBr reacted immediately and the red color disappeared. The color of the reaction mixture changed from yellow to red after 1 equiv. of PhSeBr had been added). The reaction mixture was quenched with saturated NH_4Cl solution (ca. 5 mL), warmed to room temperature and then it was extracted with diethyl ether (3 × ca. 10 mL). 30% H_2O_2 (0.5 mL) was added to the combined organic extracts and the mixture was stirred at room temperature for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ (ca. 10 mL) and the aqueous layer was extracted with diethyl ether (2 × ca. 10 mL). The combined organic phases were dried with $MgSO_4$, filtered and the solvents evaporated to leave a yellow residue, which was purified by flash chromatography with pentane/diethyl ether (2:1, v/v) as eluent. Yield: 16 mg of pure 1 (58%). $[\alpha]_D^{20} = -68$ ($c = 0.3$, MeOH); ref.[4a] $[\alpha]_D^{20} = -59.8$ ($c = 0.4$, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.86 (d, $J = 10.5$ Hz, 1 H, H-3), 6.40 (d, $J = 4.5$ Hz, 1 H, H-11), 6.00 (d, $J = 10.0$ Hz, 1 H, H-2), 5.99 (m, 1 H, H-7), 4.54 (br. d, $J = 10.0$ Hz, 1 H, H-12), 4.47 (d, $J = 10.5$ Hz, 1 H, H-12), 3.29 (br. s, 1 H, H-9), 2.48−2.28 (m, 3 H, H-5, H-6), 1.47 (s, 3 H, H-14), 1.22 (s, 3 H, H-13) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 193.5 (C-1), 169.6 (C-15), 162.6 (C-3), 131.2 (C-8), 125.5 (C-7), 123.9 (C-2), 105.9 (C-11), 72.1 (C-12), 59.9 (C-10), 49.4 (C-9), 41.9 (C-5), 35.5 (C-4), 30.8 (C-13), 24.7 (C-6), 23.9 (C-14) ppm. MS (EI, 70 eV): *m/z* (%) = 260 (M^+, 1), 216 ($[M - CO_2]^+$, 54), 201 ($[M - CO_2 - CH_3]^+$, 38), 187 (30), 173 (20), 120 (100), 96 (34).

Acknowledgments

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[5] These tests are currently under way and will be reported elsewhere.

[6] [6a] Crystal structure analysis of **7**: $C_{15}H_{18}O_4$, $M_r = 262.29$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 8.0967(1)$, $b = 10.3170(1)$, $c = 15.5077(1)$ Å, $V = 1295.41(2)$ Å^3; $Z = 4$; $\rho_{calcd.} = 1.345$ g cm^{-3}, $F_{000} = 560$, $\mu = 0.097$ mm^{-1}. A single crystal suitable for the X-ray diffraction study was obtained from an Et_2O/pentane solution (slow evaporation). The selected crystal was coated with perfluorinated ether, fixed in a capillary and transferred to the diffractometer under a cold nitrogen flow (Oxford Cryosystems). Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) at the window of a rotating anode (NONIUS FR591) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 123 K within the Θ range of $2.37° < \Theta < 25.34°$. A total of 19359 reflections were integrated and corrected for Lorentz and polarization effects. After merging ($R_{int} = 0.033$), 2368 [2293: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 245 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions were found in the difference Fourier map calculated from the model containing all non-hydrogen atoms. The hydrogen atoms' positions were refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $w(F_o^2 - F_c^2)^2$ and converged with $R1 = 0.0242$ [$I_o > 2\sigma(I_o)$], $wR2 = 0.0621$ [all data], $GOF = 1.036$ and shift/error < 0.001. The correct enantiomer is proved by the chemical synthesis. [6b] Crystal structure analysis of **2**: $C_{15}H_{18}O_4$, $M_r = 262.29$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 8.5170(1)$, $b = 10.4650(2)$, $c = 14.4239(3)$ Å, $V = 1285.61(4)$ Å^3; $Z = 4$; $\rho_{calcd.} = 1.355$ g cm^{-3}, $F_{000} = 560$, $\mu = 0.098$ mm^{-1}. A single crystal suitable for the X-ray diffraction study was obtained from an Et_2O/pentane solution (slow evaporation). The selected crystal was coated with perfluorinated ether, fixed in a capillary and transferred to the diffractometer under a cold nitrogen flow (Oxford Cryosystems). Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) at the window of a rotating anode (NONIUS FR591) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 153 K within the Θ range of $2.40° < \Theta < 25.42°$. A total of 25579 reflections were integrated, corrected for Lorentz and polarization effects. After merging ($R_{int} = 0.042$), 2372 [2152: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 244 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions were found in the difference Fourier map calculated from the model containing all non-hydrogen atoms. The hydrogen atoms' positions were refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $w(F_o^2 - F_c^2)^2$ and converged with $R1 = 0.0297$ [$I_o > 2\sigma(I_o)$], $wR2 = 0.0696$ [all data], $GOF = 1.064$ and shift/error < 0.001. CCDC-199736 (**7**) and CCDC-199737 (**2**) contain the supplementary crystallographic data for

this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].[6c] Data Collection Software for Nonius Kappa-CCD devices, Delft (The Netherlands), **2001**. [6d]Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307. [6e] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *SIR92 J. Appl. Crystallogr.* **1994**, *27*, 435−436. [6f] *International Tables for Crystallography*, Vol. C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2 (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht (The Netherlands), **1992**. [6g] A. L. Spek, PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht (The Netherlands), **2001**. [6h] G. M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen (Germany), **1998**.

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