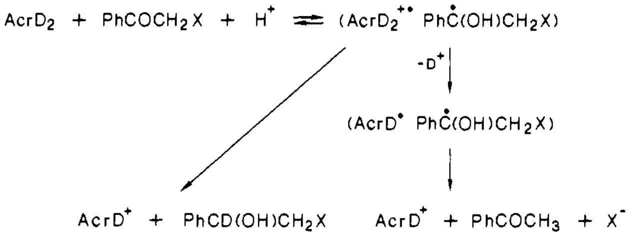
Scheme I



335 K. In the presence of $HClO_4$, however, $PhCOCH_2X$ can be readily reduced by two equivalent amounts of $Fe(MeC_5H_4)_2$ in MeCN to yield only acetophenone (eq 3, Table I). When $Fe(MeC_5H_4)_2$ was replaced by decamethylferrocene $[Fe(Me_5C_5)_2]$, which is a much stronger one-electron reductant than $Fe(MeC_5H_4)_2$,[12] the rates of the acid-catalyzed reduction of α-haloketones were much faster than those by $Fe(MeC_5H_4)_2$, and thus the rates were determined by using a stopped-flow technique at 298 K.[13] The second-order rate constant (k_{et}) increased linearly with an increase in the $HClO_4$ concentration. Such acid catalysis of electron-transfer reactions of α-haloketones is also observed for photoinduced electron transfer from the excited state of $[Ru(bpy)_3]^{2+}$ to α-haloketones.[14,15]

$$2Fe(Me_5H_4)_2 + PhCOCH_2X + H^+ \rightarrow 2Fe(MeC_5H_4)_2{}^+ + PhCOCH_3 + X^- \quad (3)$$

Comparison of the observed and second-order rate constants (k_{obsd} for the acid-catalyzed reduction of various α-haloketones by $AcrH_2$ with the rate constants (k_{et}) for the acid-catalyzed electron-transfer reactions from ferrocene derivatives and $[Ru(bpy)_3]^{2+*}$ (* denotes the excited state) to the same series of α-ketones is shown in Figure 1. There are linear correlations between the k_{obsd} values and the k_{et} values, despite the apparent difference in the products between the reduction by a two-electron reductant ($AcrH_2$) and one-electron reductants (ferrocene derivatives) as shown in Table I. Such correlations strongly suggest that the acid-catalyzed reduction of α-haloketones by $AcrH_2$ to yield the corresponding ketones (eq 1) and halohydrins (eq 2) involves a common activation process, i.e., the acid-catalyzed single electron-transfer from $AcrH_2$ to α-haloketones as shown in Scheme I for the $AcrD_2$–$PhCOCH_2X$ system. Since the one-electron reduction potentials of carbonyl compounds are known to be shifted in the positive direction significantly in the presence of $HClO_4$ in MeCN,[14] the acid-catalyzed electron transfer from $AcrD_2$ to $PhCOCH_2X$ may occur to generate the radical pair ($AcrD_2{}^{\bullet+}$-$Ph\dot{C}(OH)CH_2X$), which disappears either by deuterium (or hydrogen) transfer from $AcrD_2{}^{\bullet+}$ to $Ph\dot{C}(OH)CH_2X$ or second electron transfer from $AcrD^\bullet$, which is formed by the deprotonation of $AcrD_2{}^{\bullet+}$, to $Ph\dot{C}(OH)CH_2X$ (Scheme I). The deuterium transfer yields $PhCD(OH)CH_2X$, while the second electron transfer yields $PhCOCH_3$, accompanied by the reductive dehalogenation (Scheme I). This may be the reason why the deuterium is incorporated into α-halohydrin but not into acetophenone. The observed primary kinetic isotope effects may be ascribed to the hydrogen-transfer process as well as the deprotonation process (Scheme I). In the case of one-electron reductants (ferrocene derivatives), no hydrogen-transfer process is involved, and thus the second electron transfer yields only $PhCOCH_3$.

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[12] The one-electron oxidation potential of $Fe(Me_5C_5)_2$, determined by the cyclic voltammetry in MeCN (−0.08 V vs SCE) is much more negative than that of $Fe(MeC_5H_4)_2$ (0.26 V vs SCE).

[13] Rates of the acid-catalyzed electron transfer from ferrocene derivatives to α-haloketones were determined by the increase in the absorbance due to the corresponding ferricenium ions in the long-wavelength region (650–750 nm).

[14] Fukuzumi, S.; Ishikawa, K.; Hironaka, K.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1987**, 751.

[15] The rate constants (k_{et}) of photoinduced acid-catalyzed electron transfer from $[Ru(bpy)_3]^{2+*}$ to α-haloketones were determined by quenching experiments of the $[Ru(bpy)_3]^{2+*}$ luminescence by α-haloketones in the presence of $HClO_4$ in MeCN.[14] It was confirmed that the luminescence intensity in the absence of α-haloketones was unaffected by the presence of $HClO_4$ up to 2.0 M.

A Total Synthesis of (±)-Trichodermol

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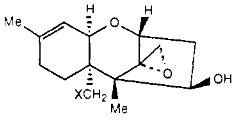
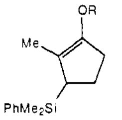
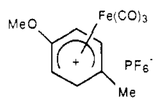
Trichothecenes, exemplified by the simpler members trichodermol (**1**) and verrucarol (**2**), have attracted considerable interest for total synthesis,[2] owing to their diverse biological activity,[3] which ranges from antifungal to cytotoxic. They serve as useful, moderately complex, target molecules to illustrate the application of new synthesis technology. The fact that trichodermin (**1** acetate)[2a] and trichodermol[2b] have already succumbed to total synthesis introduces special challenges: any new approach must employ fewer synthetic steps, all of which should be high yielding; the synthesis must not involve difficult transformations, and it should not utilize functional groups that become redundant in the later stages.[4] This paper describes a short highly stereocontrolled route to (±)-trichodermol that was designed to achieve such objectives. The synthesis utilizes the newly discovered regiocontrolled addition of tin enolates[5] to cyclohexadienyl–iron complexes, it does not require protecting groups and it also illustrates the usefulness of the dimethylphenylsilyl group as a hydroxyl equivalent.[6]



1 X = H
2 X = OH



3 (a) R = SiMe$_3$
(b) R = SnBu$_3$



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Dimethylphenylsilyl-substituted silyl enol ether **3a** was generated in 80–90% yield from 2-methylcyclopentanone in two synthetic operations (1) sulfuryl chloride, CCl_4, followed by distillation;[7] (2) $2Me_2PhSiLi$, CuCN, THF, −23 °C then 0 °C, 2 h, followed by enolate trapping with Me_3SiCl, Et_3N, room temperature, 3 h). Conversion of **3a** to the corresponding tin enolate **3b** (1.2 equiv of MeLi, DME, room temperature, 45 min; 1.2 equiv of Bu_3SnCl, −78 °C, 1 h) followed by in situ reaction with complex **4**[8] afforded

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[1] (a) Case Western Reserve University. (b) University of Toledo.

[2] (a) Colvin E. W.; Malchenko, S.; Raphael, R. A.; Roberts, J. S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1989. (b) Still, W. C.; Tsai, M. *J. Am. Chem. Soc.* **1980**, *102*, 3654. (c) A recent review summarizes the total synthesis of trichothecenes: McDougal, P. G.; Schmuff, N. R. *Prog. Chem. Org. Nat. Prod.* **1985**, *47*, 153.

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[4] Previous work in our laboratory has resulted in total syntheses of trichothecene analogues. An ester group was used to generate suitably reactive enolates, but this does not allow elegant approaches to the natural products because of the cumbersome reduction of ester to methyl group that is required: (a) Pearson, A. J.; Ong, C. W. *J. Am. Chem. Soc.* **1981**, *103*, 6686. (b) Pearson, A. J.; Chen, Y. S. *J. Org. Chem.* **1986**, *51*, 1939.

[5] Pearson, A. J.; O'Brien, M. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1445.

[6] Hayashi, T.; Ito, Y.; Matsumoto, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5579. Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229. Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520.

[7] Gassman, P. G.; Pascone, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 7801.

[8] This complex is readily prepared on large scale (>100 g) in three steps from *p*-methylanisole, see: Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, *1882*. An improved procedure avoiding mixture formation, uses four steps: see ref 4a.

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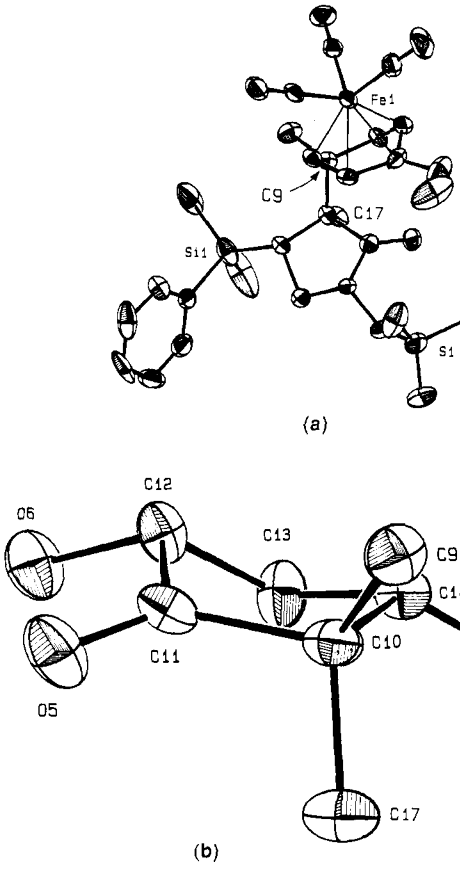


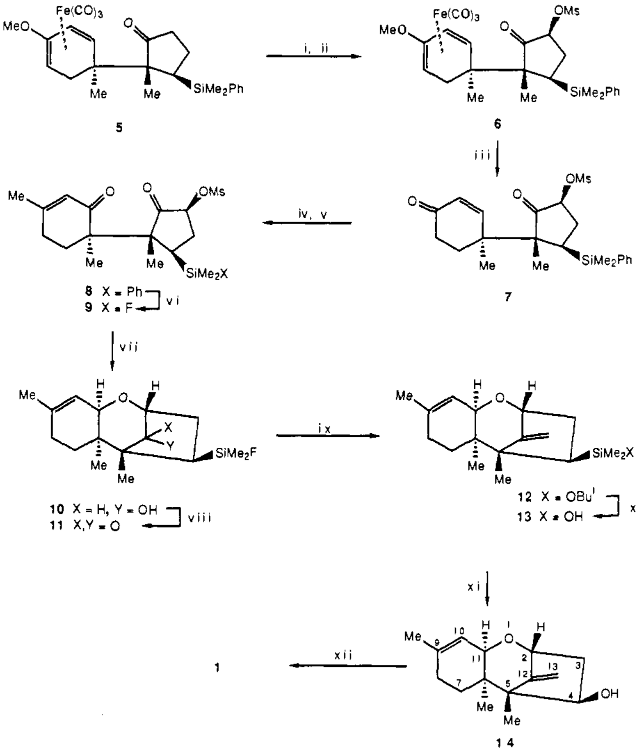
Figure 1. (a) Drawing of a single molecule of **6** showing 30% probability ellipsoids. (b) Simplified view of the five-membered ring of **6**, illustrating the stereochemical relationships.

complex **5** in 72% yield after separation from minor amounts of diastereomeric byproduct[9] by flash chromatography. Hydroxylation of **5** (LDA, THF, −78 °C, 15 min; MoOPH,[10] −78 °C, then −60 °C, 1 h) followed by mesylation (CH_3SO_2Cl, pyridine, room temperature, overnight) afforded complex **6** in 80% overall yield.[11] That the stereochemistry of **6** was indeed as shown was established at this juncture by X-ray crystal structure determination (Figure 1), which clearly demonstrates that the diastereoselective reaction of **3b** with **4** produces the relative stereochemistry between the newly established quaternary carbon centers required for trichodermol synthesis. Treatment of **6** with copper(II) chloride in ethanol[12] (room temperature, 2–4 h) afforded enone **7** in 87% yield.

There are several points at which the dimethylphenylsilyl group might be converted to hydroxyl. The following sequence proved to be the most effective and serves to illustrate the ability to carry the silyl group through a number of transformations without detriment to its efficacy as an OH surrogate.

Conversion of **7** to **8** was accomplished in 58% overall yield as shown, and **8** was subsequently treated with tetrafluoroboric acid[6] to effect conversion to fluorosilane derivative **9**. Reduction of the enone in **9** proceeded with concomitant intramolecular displacement of the mesylate to give **10**, which was oxidized to give **11** in greater than 95% overall yield.[13] Wittig olefination of **11**, according to Raphael's procedure,[2a] was accompanied by conversion of the fluorosilyl group to *tert*-butoxysilyl, giving **12** in 90% yield (containing ca. 10% of intact $SiMe_2F$ group).[14]

Scheme I[a]



[a] Reagents (Yield): (i) a. LDA, THF, −78 °C, 15 min; b. MoOPH, −60 °C, 1 h. (ii) MsCl, C_5H_5N, room temperature, overnight (80% overall for two steps). (iii) Saturated $CuCl_2$ in EtOH, room temperature, 2–4 h monitored by infrared spectroscopy (87%). (iv) 6 equiv of MeMgBr, THF, −78 °C, 3 h (70%). (v) Pyridinium chlorochromate, CH_2Cl_2, room temperature, 2–3 h (83%). (vi) 10 equiv of $HBF_4{\cdot}Et_2O$, CH_2Cl_2, 45–50 °C, 20 h, (90%). (vii) 3.0 equiv of $(i\text{-}Bu)_2AlH$, CH_2Cl_2, 0 °C, room temperature, 30 min (95%). (viii) Pyridinium chlorochromate, NaOAc, CH_2Cl_2, room temperature, 2–3 h (95%). (ix) 6 equiv of Ph_3PCH_3Br, 6 equiv of $KOBu^t$, Bu^tOH, Et_2O, reflux, 18 h (90%). (x) Excess Bu^nNF, THF, room temperature, 2 h (70%). (xi) 30% aqueous H_2O_2 (24 equiv), KF (6 equiv), $NaHCO_3$ (6 equiv), THF/MeOH (1:1), 60 °C, 24 h (80%). (xii) MCPBA, Na_2HPO_4, CH_2Cl_2, room temperature, (65% based on recovered pure starting material at 66% conversion).

Conversion of **12** to the penultimate intermediate **14** was accomplished by treatment with excess tetra-*n*-butylammonium fluoride in THF (wet) to give **13**, followed by reaction with H_2O_2 at elevated temperature in the presence of potassium fluoride and sodium hydrogen carbonate.[6] This sequence produced **14** in 48% overall yield from **11** without purification of intermediates. Epoxidation[2a] of **14** gave (±)-trichodermol (**1**) as anticipated.[15] This work illustrates the use of an inexpensive organometallic complex as a starting material for total synthesis, which is more efficient

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(9) All new compounds were fully characterized by NMR, IR, and mass spectrometry. Compounds containing fluorine were further characterized with ^{19}F NMR spectroscopy.

(10) Vedejs, E. *J. Am. Chem.* Soc. **1974**, *96*, 5944.

(11) The hydroxylation of **5** does not go to completion; the yield of **6** is based on recovered pure **5**, the conversion being ca. 80%.

(12) Thompson, D. J. *J. Organomet. Chem.* **1976**, *108*, 381.

(13) The DIBAL reduction of **9** can be partially controlled to give **11** directly, but this was always contaminated with **10**. It was found to be more efficient to overreduce and reoxidize **10**.

(14) The conditions used for the Wittig reaction in this work were by far the best that we have examined, but the *tert*-butoxide present in the equilibrium readily displaces fluoride from the $SiMe_2F$ group. The use of $[Ph_3PCH_3]^+Br^-/BuLi$ in THF gave only ca. 5% conversion of ketone to olefin after prolonged reaction. Since the introduction of the *t*-BuO group as in **12** did not prevent conversion to **14**, further experimentation with alternative methylenation procedures was not pursued.

(15) Spectral data for intermediate **14** and for synthetic trichodermol (**1**) are as follows. **14**: mp 122–124 °C (lit.[2a] mp 125–126 °C). IR ($CHCl_3$) ν_{max} 3600, 1672 cm^{-1}. 200 MHz ^1H NMR ($CDCl_3$) δ 5.35 (1 H, dq, J = 5.56, 1.52 Hz, H10), 5.13 (1 H, d, J = 0.49 Hz, H13), 4.71 (1 H, d, J = 0.96 Hz, H13′), 4.39 (1 H, d, J = 3.26 Hz, H2), 4.39 (1 H, obscured, m, H4), 3.56 (1 H, d, br, J = 5.37 Hz, H11), 2.59 (1 H, dd, J = 15.38, 7.43 Hz, H3), 2.0–1.7 (3 h, m), 1.68 (3 H, br s, Me), 1.61 (1 H, ddd, J = 15.38, 5.38, 3.04, H3′), 1.5–1.11 (2 H, m), 1.02 (3 H, s, Me), 0.85 (3 H, s, Me). **1**: mp 124–126 °C (lit.[2] mp 124–125 °C). IR ($CHCl_3$) ν_{max} 3580, 2962, 2925, 1680, 1070 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.39 (1 H, dq, J = 5.59, 1.52 Hz, vinyl), 4.34 (1 H, m, H4), 3.83 (1 H, d, J = 5.37 Hz, H2), 3.51 (1 H, d, br, J = 5.4 Hz, H11), 3.11 (1 H, d, J = 3.9 Hz, H13), 2.81 (1 H, d, J = 3.9 Hz, H13′), 2.61 (1 H, dd, J = 15.67, 7.43 Hz, H3), 1.94 (1 H, d, br) 1.97 (2 H, s, br, allylic CH_2), 1.91 (1 H, ddd, J = 15.67, 5.41, 2.19 Hz, H3′), 1.71 (3 H, s, br, Me), 1.6 (s, OH, exch. D_2O), 1.6–1.2 (1 H, d, br), 0.858 (3 H, s), 0.802 (3 H, s).

than using "standard" carbon–carbon bond forming techniques.[16]

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Supplementary Material Available: Structural report for compound **6** giving methods for data collection, data reduction, structure solution and refinement, tables of crystal data, intensity measurements, structure solution and refinement, positional and thermal parameters, general temperature factor expressions, bond distances, bond angles, and intensity data, and a drawing of a single molecule showing 30% probability ellipsoids (22 pages); listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(16) This is the shortest total synthesis of (±)-trichodermol so far recorded, requiring 16 steps from 4-methylanisole, which augurs well for the future use of **4** and related complexes. For comparison, Raphael's synthesis of trichodermin uses 19 steps from 4-methylanisole and was plagued by a difficult internal aldol reaction to generate the C ring. Still's synthesis of trichodermol elegantly overcomes this problem, but it involves 24 steps from 4-methylanisole (ref 2).

Spiropentane as a Tensile Spring

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Highly strained compounds are especially suitable for revealing relationships between structure and reactivity.[2] The synthesis and exact structure determination of molecules comprising unusual topologies, i.e., compounds that contain bond distances and bond angles which deviate substantially from normal values is of prime importance. Structure determinations of spiropentane (**1**)—the parent system—and the ethano- and benzene-bridged spiropentanes **2**[3] and **3**,[4] respectively, provide the opportunity to test the limits of current theoretical work dealing with calculations of structure and physical data of "unusual" molecules. To study the influence of spiropentane (**1**) on the ethano bridge C4–C4′ in **2** and the corresponding benzene bond C4–C5 in **3** we performed single-crystal X-ray structure determinations of **1**, **2**, and **3** including X–X electron density determinations.

According to ab initio calculations, in **1** twisting by ψ is energetically more favorable than bending by Φ.[5] Connecting C2 and C5 or C3 and C4 of **1** with an ethano bridge in a trans fashion yielding **2** should, therefore, lead to additional stress through twisting and bending (Figure 1).

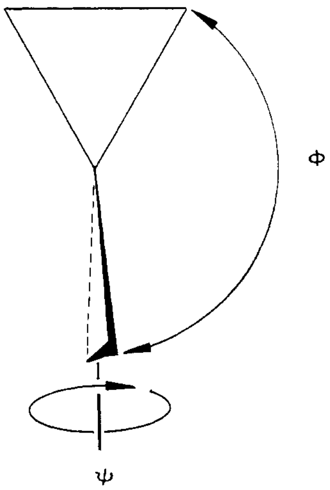

Figure 1. *Twisting* by ψ is performed by rotating the lower three-membered ring against the upper; *bending* by Φ is performed by buckling the 2-fold axis at the spiro atom. By both operations the nonspiro atoms are brought closer together.

The strain energy of **2** has been calculated to be 80 kcal/mol,[5] thus, exceeding that of **1** by ca. 17 kcal/mol.[6] The considerable strain is also reflected in an unusual rearrangement of **2** when exposed to a platinum complex.[7] One furthermore expects that the C4–C4′ bridge in **2** is expanded by the spiropentane unit working like a tensile stress inducing spring.

Electron diffraction studies of spiropentane (**1**)[8] and tricyclo[4.1.0.0^{1,3}]heptane (**2**) are known.[9] To interpret the PE spectrum of **2**, MO calculations were performed.[10] The length of the C4–C4′ bond was calculated to be only 1.500 Å in contrast to the electron structure determination.[9]

It has been shown that annulation of small rings to benzene does *not* lead to alternating bond distances in the aromatic ring[11] in the sense of a Mills–Nixon effect.[12] However, if like in **3**, instead of a three- or four-membered ring a spiropentane is connected to benzene, alternating bond distances might be expected.

The crystallization of **1** (mp −115 °C), **2** (mp −105 °C), and **3** (mp +15 °C) were performed according to a previously described procedure.[13] The results of the X-ray structure and the X–X electron density determinations are shown in Figures 2 and 3.[14]

The slight distortion from the ideal C_{2v} symmetry of **1** (Φ = 179.6° and ψ = 90.2°) in the crystal is probably due to packing effects (lowest intermolecular H···H 2.321 Å with H atoms im-

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(14) Crystal structure determination at −163 °C, Mo Kα radiation, Nicolet R3 diffractometer. **1**: crystallization at −121 °C, rhombohedral, $R\bar{3}$, $a = b$ = 19.346 (2) Å, c = 6.285 (1) Å, $\alpha = \beta$ = 90°, γ = 120°, V = 2037.2 (5) Å^3, Z = 18, D_x = 1.000 g/cm^3, 1847 observed independent intensities, $2\theta_{max}$ = 80°, $F_o \geq 4\sigma(F)$, R = 0.040, R_w = 0.045 for 953 observed reflexions ($2\theta_{max}$ = 55°). **2**: crystallization at −112 °C, orthorhombic, $Pbcn$, a = 7.940 (3) Å, b = 11.254 (4) Å, c = 6.417 (2) Å, $\alpha = \beta = \gamma$ = 90°, V = 573.4 (3) Å^3, Z = 4, D_x = 1.094 g/cm^3, 800 observed independent intensities, $2\theta_{max}$ = 70°, $F_o \geq 4\sigma(F)$, R = 0.041, R_w = 0.048 for 595 observed reflexions ($2\theta_{max}$ = 55°). **3**: crystallization at 11 °C, monoclinic, $P2_1/c$, a = 6.169 (1) Å, b = 17.812 (3) Å, c = 7.587 (1) Å, $\alpha = \gamma$ = 90°, β = 112.51 (1)°, V = 770.0 (2) Å^3, Z = 4, D_x = 1.203 g/cm^3, 3898 independent observed intensities, $2\theta_{max}$ = 85°, $F_o \geq 4\sigma(F)$, R = 0.043, R_w = 0.049 for 1562 observed reflexions ($2\theta_{max}$ = 55°).

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