A one-step photocatalytic synthesis of 2-(trifluoromethyl)butyrolactones

Ninja Reineke, Naveed A. Zaidi, Manju Mitra, David O'Hagan,* Andrei S. Batsanov, Judith A. K. Howard and Dmitri Y. Naumov†

Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, UK

An efficient one-step procedure is described for the synthesis of 2-(trifluoromethyl)butyrolactone 1 and 4-substituted 2-(trifluoromethyl)butyrolactones by the photocatalytic conjugate addition of primary and secondary alcohols to 2-(trifluoromethyl)acrylic acid 6. With the exception of methanol, the reactions are conducted without a photosensitiser. The diastereoisomers of compounds 8 and 10 were separable by chromatography and their relative configurations were established unambiguously by X-ray analyses of suitable crystals.

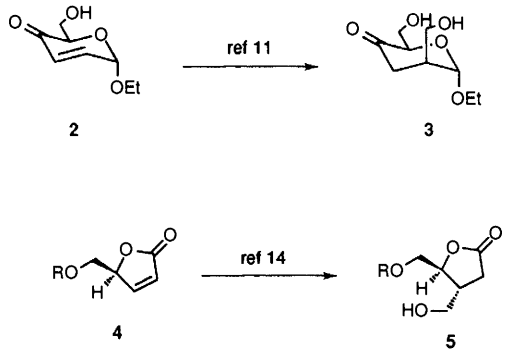
Introduction

The trifluoromethyl group is becoming increasingly prevalent in the structures of fine chemicals,[1] biological[2] and particularly in materials applications.[3] The large dipole moment of the CF_3 group, and its chemical stability, render it attractive as a functional group for incorporation into molecular electronic[4] devices and liquid crystals.[5] We have had an interest in the preparation of trifluoromethyl-containing monomers[6,7] and polymers[8] and have recently turned our attention to 2-(trifluoromethyl)butyrolactone **1** for ring-opening polymerisation studies to generate polyesters as potential piezo-electric materials.

1

In this regard, a number of papers[9,10] have appeared recently which report the synthesis of **1**, however all of these require multiple steps and are not easily amenable to scale-up. Thus, **1** is not a readily available material. In view of this we now report a one-step, photocatalytic process, which we have developed for the synthesis of **1**. The preparation is readily adaptable to a range of 4-substituted 2-(trifluoromethyl)butyrolactones, and is the most straightforward and versatile entry into this class of compounds to date.

The photocatalytic conjugate addition of alcohols to α,β-unsaturated ketones has been described both with[11,12] and without[13,14] photosensitiser and we were attracted by a recent study[14] which extended this methodology to α,β-unsaturated lactones. Thus, when alcohols such as methanol are used as a solvent, reactions with the α-enone **2**[11] and the butenolide **4**[14] generate the corresponding 1,4-adducts **3** and **5** respectively, as shown in Scheme 1. These reactions were mediated by irradiation using a medium-pressure mercury lamp with benzophenone as a photosensitizer. Reaction of propan-2-ol with **4** was achieved without a photosensitiser.[14] The recent commercial (Aldrich Chem Co. Ltd.) availability of 2-(trifluoromethyl)acrylic acid **6** offered a starting material containing a trifluoromethyl moiety α to a carboxylate group and prompted us to explore the photocatalytic conjugate addition of alcohols to **6**. The results of this investigation are discussed below.



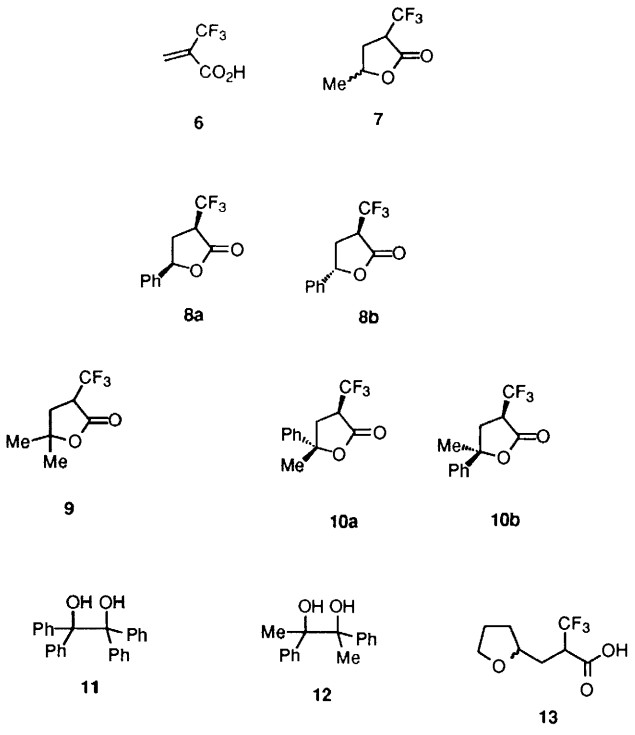
2 **3** **4** **5**

Scheme 1

Results and discussion

Irradiation of **6** with methanol in the presence of benzophenone as a photosensitiser generated 2-(trifluoromethyl)-butyrolactone **1**, the parent compound of the series, in a single step. The reaction course could be followed directly by ^{19}F NMR spectroscopy and complete conversion was achieved after 5 h. Distillation of the product resulted in *in situ* cyclisation and direct isolation of the lactone in good yield. Similarly reactions with ethanol and benzyl alcohol generated the corresponding 4-substituted 2-(trifluoromethyl)butyrolactones **7** and **8**, respectively, and reactions of isopropylalcohol and phenethanol with **6** generated the 4,4-dimethylbutyrolactone **9** and 4-methyl-4-phenylbutyrolactone **10**, respectively. The isolation and chromatographic purification of these compounds was to some extent hampered by the presence of benzophenone and its dimerisation product **11**. Thus, we investigated these reactions without the addition of the photosensitiser. All of the transformations, with the exception of the methanol reaction, proceeded smoothly and with complete conversion as judged by ^{19}F NMR analysis of the crude products, to generate product lactones. The reactions without benzophenone were slower (~20 h *versus* ~5 h) however this modification considerably simplified the purification of those products which are isolated by chromatography. In the absence of the photosensitiser the methanol reaction did not proceed to complete conversion and, with time, multiple fluorinated products became apparent by ^{19}F NMR analysis.

† On leave from the Institute of Solid State Chemistry, Novosibirsk, 630128, Kutateladze, 18, Russia.



Thus, straightforward preparation of **1** requires the photosensitiser.

Compounds **7** and **8** were isolated as mixtures of diastereoisomers, as expected. In the case of **7** the diastereoisomers (1:1) could not be separated by chromatography. Diastereoisomers **8a**:**8b** (2:1) were separable and each was isolated as a white crystalline solid. X-Ray analysis of suitable crystals allowed unambiguous assignment of the relative configurations of **8a** and **8b** as shown in Fig. 1. The small stereochemical bias in favour of **8a** will clearly reflect transition-state energies. In the structure of **8a** the 1,3-diaxial interaction between the hydrogen at C-2 and the axial hydrogen on C-4 is of little significance, but in **8b** the lactone ring flattens to some extent to minimise the repulsion of the C-2 hydrogen and the *ortho* hydrogen of the aromatic ring.

Reactions with the secondary alcohols propan-2-ol and phenethanol generated **9** and **10** (**10a**:**10b**, 2:1) again in good yield. The dimer of phenethanol **12** emerged as a significant side product in the phenethanol reaction, a phenomenon observed in a previous study.[13] This was apparent as a mixture of (*RR* and *SS*:*meso*) diastereoisomers in a 1:1 ratio. However, chromatography allowed the separation of this side product and the isolation of each of the product diastereoisomers **10a** and **10b**. Product **10b** was an oil but the major diastereoisomer **10a** was a solid material and X-ray analysis of a suitable crystal again allowed unambiguous assignment of the *syn* relative stereochemistry as shown in Fig. 2.

A reaction of (*R*)-phenethanol with **6** was conducted to assess if the homochiral reagent (and solvent) would retain any level of asymmetry. This was assayed by assessing the ratio of *RR* and *SS*:*meso* diastereoisomers **12** which accumulate as a side product in the reaction. The resultant ratio is readily identified by ^{1}H NMR analysis of the crude reaction mixture by integration of the CH_3 signals from the two sets of diastereoisomers. If the stereochemical integrity of the phenethanol radical is retained then *RR*-**12** will predominate over the *meso* diastereoisomer. In the event, the resultant product was racemic, *i.e.* the ratio of *RR* and *SS*:*meso* in **12** remained at 1:1, and thus the phenethanol radical racemised rapidly.

In order to explore the product range further, tetrahydrofuran was used as a solvent in the reaction with **6**. This gave the expected adduct **13** as a 1:1 mixture of diastereoisomers in good yield. Investigations with polyols both with and without benzophenone were less satisfactory. Reactions with ethylene glycol, butane-1,4-diol and glycerol resulted in the complete consumption of **6**, however the product mixtures were complex and they could not be adequately purified and characterised.

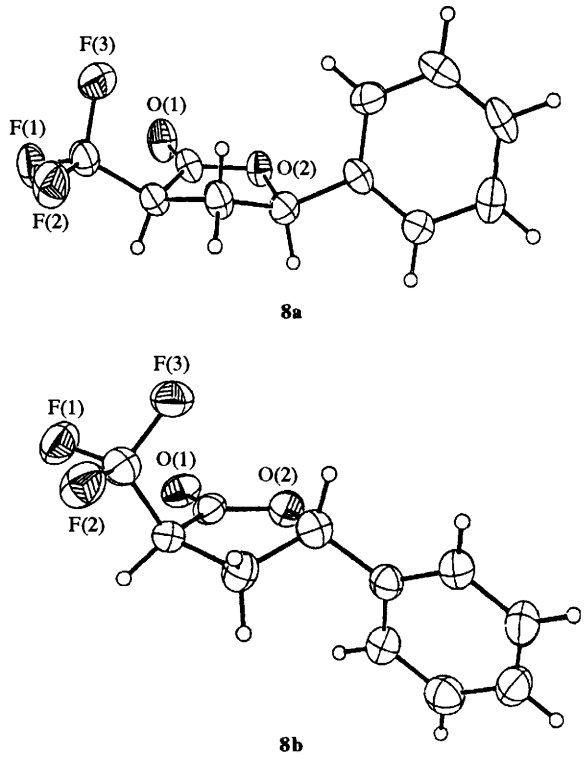


Fig. 1 X-Ray structures of **8a** and **8b**. Thermal ellipsoids are drawn at 50% probability

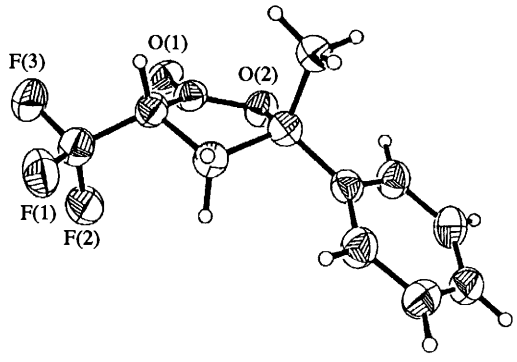


Fig. 2 X-Ray structure of **10a**. Thermal ellipsoids are drawn at 50% probability

In summary, we present an efficient one-step process for the synthesis of 2-(trifluoromethyl)butyrolactone **1** and a series of 4-substituted derivatives. The major diastereoisomers in these reactions have a *syn* relationship between the CF_3 group and the larger substituent at C-4. It is noteworthy that the only alternative general route reported[10] for the preparation of **7**, **8** and **9** (as diastereoisomeric mixtures), involves a four-step process.

Experimental

All photolytic reactions were carried out using a 1 kW Honovia UVS lamp. NMR spectra were recorded in solutions of $CDCl_3$ on either a Varian Gemini 200 MHz (^{1}H at 199.9 MHz, ^{13}C at 50.29 MHz), a Varian VXR 400S (^{1}H at 399.95 MHz, ^{13}C at 100.577 MHz) or a Bruker 250AC (^{19}F at 235.42) instruments. ^{1}H and ^{13}C chemical shifts are quoted in ppm relative to TMS (Me_4Si) and ^{19}F chemical shifts are quoted relative to fluorotrichloromethane. *J* Values are recorded in Hz. IR spectra were recorded on Perkin-Elmer FT 1720X or 1600

spectrometers as films or KBr plates. Mass spectra were obtained using a VG Analytical 7070E Organic mass spectrometer operating at 70 eV. Chromatography was carried out using silica gel-60 (35 μm) (Fluka) or Sorbsil-C60-H (40–60 μm). All solvents were distilled and dried before use.

2-(Trifluoromethyl)butyrolactone 1

A solution of 2-(trifluoromethyl)acrylic acid **6** (1.04 g, 7.5 mmol) and benzophenone (1.30 g, 7.2 mmol) in methanol (30 cm^3) was placed in a Schlenk tube and degassed using a stream of nitrogen. The mixture was irradiated for 5 h after which the solvent was removed and distillation (50 °C, 0.2 mmHg) gave **1** as a colourless oil (64%, 0.58 g); δ_H 2.3–2.6 (m, 2 H, CH_2), 3.2–3.4 (m, 1 H, CH) and 4.1–4.4 (m, 2 H, CH_2O); δ_C 23.9 (s), 44.4 (q, J_{CF} 30.4, CH), 66.87 (s), 119.4 (q, J_{CF} 277.7, CF_3) and 170.1 (s); δ_F −69.5 (s); ν_{max}/cm^{-1} 1780vs; *m/z* 155 (M + 1, 29.3%) (Found: C, 39.3; H, 3.3. Calc. for $C_5H_5F_3O_2$: C, 38.96; H, 3.25%).

General procedure for the preparation of 7–10 and 13

A solution of 2-(trifluoromethyl)acrylic acid **6** (1.04 g, 7.4 mmol) in the appropriate alcohol (30 cm^3) was placed in a Schlenk tube and degassed using a stream of nitrogen. The solution was irradiated using a medium-pressure mercury lamp for ~20 h after which the solvent was removed under reduced pressure and the crude products were either directly distilled and/or chromatographed to afford the desired products (62–98%).

4-Methyl-2-(trifluoromethyl)butyrolactone 7. By the general procedure and with ethanol as solvent compound **7** was obtained as a 2:1 mixture of diastereoisomers in 77% yield after distillation; δ_H 1.5–1.59 (2 × d, 3 H, CH_3's), 2.1–2.4 (m, 1 H, CH_2's), 2.6–2.8 (m, 1 H, CH_2's), 3.4–3.7 (m, 1 H, $CHCF_3$) and 4.5–4.9 (2 × m, 1 H, HCO); δ_F −68.9 (s, major) and −69.2 (s, minor); ν_{max}/cm^{-1} 1775vs; *m/z* 169 (M + 1, 100%); ν_{max}(KBr, film)/cm^{-1} (Found: C, 42.7; H, 4.2. Calc. for $C_6H_7F_3O_2$: C, 42.86; H, 4.17%).

4-Phenyl-2-(trifluoromethyl)butyrolactone 8a and 8b. By the general procedure and with benzyl alcohol as solvent compound **8** was obtained (93%, 1.58 g) after distillation (25 °C, 0.1 mmHg) as a 2:1 mixture of diastereoisomers **8a** and **8b**. Chromatography over silica gel, with gradient elution (light petroleum→light petroleum–dichloromethane→dichloromethane), allowed separation of diastereoisomers **8a** (34.5%, 0.59 g) and **8b** (32.3%, 0.51 g) as white crystalline solids.

Compound **8a**, mp 86.6–87.6 °C; δ_H 2.41 (dd, 1 H, C*H*^{a}H^b), 2.94 (m, 1 H, CH^a*H*^{b}), 3.62 (m, 1 H, CH), 5.45 (q, 1 H, HCO) and 7.26–7.44 (m, 5 H, Ph); δ_F −69.09; δ_C 32.3 (s, CH_2), 46.8 (q, CH), 79.1 (s, CO), 119.3–127.7 (q, CF_3), 125.6 (s, C-3′ + C-5′), 129.0 (s, C-2′ + C-6′), 129.2 (s, C-4′), 137.2 (s, C-1′) and 168.2 (s, OCO); ν_{max}/cm^{-1} 2940 and 1733; *m/z* (CI+) 248 (M + NH_4, 14.1%) (Found: C, 57.1; H, 3.9. Calc. for $C_{11}H_9F_3O_2$: C, 57.39; H, 3.91%).

Compound **8b**, mp 76.4–77.3 °C; δ_H 2.54 (m, 1 H, C*H*^{a}H^b), 2.89 (dd, 1 H, CH^a*H*^{b}), 3.45 (m, 1 H, CH), 5.65 (t, 1 H, HCO) and 7.28–7.42 (m, 5 H, Ph); δ_F −68.56; δ_C($CDCl_3$) 31.4 (s, CH_2), 44.6 (q, CH), 79.3 (s, CO), 119.9–128.2 (q, CF_3), 125.0 (s, C-3′ + C-5′), 128.9 (s, C-4′), 129.0 (s, C-2′ + C-6′), 136.1 (s, C-1′) and 169.0 (s, OCO); ν_{max}/cm^{-1} 2929 and 1767; *m/z* (CI+) 248 (M + NH_4, 24.5%) (Found: C, 57.55; H, 3.9. Calc. for $C_{11}H_9F_3O_2$: C, 57.39; H, 3.91%).

4,4-Dimethyl-2-(trifluoromethyl)butyrolactone 9. By the general procedure and with propan-2-ol as solvent compound **9** was obtained (79%) as a colourless oil; δ_H 1.49 (s, 3 H, CH_3), 1.57 (s, 3 H, CH_3), 2.2–2.3 (m, 1 H, CH_2), 2.4–2.5 (m, 1 H, CH_2) and 3.6–3.7 (m, 1 H, $CHCF_3$); δ_C 27.2 (s), 28.3 (s), 35.5 (s), 45.6 (q, J_{CF} 30.4, CH), 82.9 (s), 125 (q, J_{CF} 278, CF_3) and 168.5 (s); δ_F −69.1 (s); ν_{max}/cm^{-1} 1775vs; *m/z* 183 (M + 1, 100%) (Found: C, 44.8; H, 5.4. Calc. for $C_7H_9F_3O_2$: C, 45.28; H, 5.19%).

4-Methyl-4-phenyl-2-(trifluoromethyl)butyrolactone 10a and 10b. By the general procedure and with phenethanol as solvent compound **10** was obtained after distillation (75 °C, 0.1 mmHg) as a 2:1 mixture of diastereoisomers **10a** and **10b** together with the dimer **12**. Chromatography over silica gel with gradient elution (petroleum→light petroleum–dichloromethane→dichloromethane), allowed separation of diastereoisomer **10a** (13.9%, 0.25 g) as a white crystalline solid and **10b** (31.8%, 0.58 g) as a colourless oil. The phenethanol dimer **12** was isolated as a white amorphous solid (0.25 g, 13.87%).

Compound **10a**, mp 72.4–73.5 °C; δ_H 1.73 (s, 3 H, $COCH_3$), 2.80 (dd, 1 H, C*H*^{a}H^b), 2.65 (dd, 1 H, CH^a*H*^{b}) 3.65 (m, 1 H, CH) and 7.26–7.40 (m, 5 H, Ph); δ_F −68.77; δ_C 28.8 (s, CH_3), 36.6 (s, CH_2), 45.2 (q, CH), 84.9 (s, CO), 119–130.0 (q, CF_3), 123.7 (s, C-3′ + C-5′), 128.1 (s, C-4′), 128.8 (s, C-2′ + C-6′), 143.4 (s, C-1′) and 168.5 (s, OCO); ν_{max}/cm^{-1} 2983, 2957, 1761, 947 and 700; *m/z* (CI+) 262 (M + NH_4, 69.1%) (Found: C, 59.2; H, 4.57. Calc. for $C_{12}H_{11}F_3O_2$: C, 59.02; H, 4.51%).

Compound **10b**, δ_H 1.81 (s, 3 H, $COCH_3$), 2.56 (dd, 1 H, C*H*^{a}H^b), 2.89 (dd, 1 H, CH^a*H*^{b}), 3.25 (m, 1 H, CH) and 7.33–7.38 (m, 5 H, Ph); δ_F −68.74; δ_C 29.8 (s, CH_3), 37.5 (s, CH_2), 44.9 (q, CH), 85.1 (s, CO), 121.6–130.1 (q, CF_3), 123.9 (s, C-3′ + C-5′), 128.2 (s, C-4′), 128.9 (s, C-2′ + C-6′), 142.0 (s, C-1′) and 168.0 (s, OCO); ν_{max}/cm^{-1} 2983, 2934, 1792, 953 and 701; *m/z* (CI+) 262 (M + NH_4, 85.9%) (Found: C, 59.0; H, 4.7. Calc. for $C_{12}H_{11}F_3O_2$: C, 59.02; H, 4.51%).

3-(2′-Furyl)-2-(trifluoromethyl)propanoic acid 13. By the general procedure, with tetrahydrofuran replacing the alcohol, compound **13** was obtained as a 1:1 diastereoisomeric mixture in 85% yield; δ_H 1.6–1.8 (m, 1 H, C*H*H), 1.9–2.0 (m, 3 H, CH*H*, CH_2), 2.1–2.2 (m, 2 H, CH_2), 3.2–3.6 (2 × m, 1 H, $CHCF_3$), 3.8–3.9 (m, 2 H, CH_2O), 4.1–4.2 (m, 1 H, CHO) and 11.4 (s, 1 H, OH); δ_F −69 (s); *m/z* 213 (M + 1, 1.71%); ν_{max}/cm^{-1} 3500 (OH) and 1730 (Found: C, 46.2; H, 5.1. Calc. for $C_8H_{11}F_3O_3$: C, 46.15; H, 4.95%).

Crystal structure determination

X-Ray single-crystal diffraction experiments were performed at 150 K on a Siemens SMART CCD detector with an Oxford Cryosystems open-flow N_2 gas cryostat. Data collection was controlled by the SMART[15] software and reflection intensities were obtained using SAINT[16] software.

$C_{11}H_9F_3O_2$ **8a**: M = 230.18, orthorhombic, space group *Iba*2, a = 10.0784(9), b = 22.470(2), c = 8.9385(8) Å, V = 2024.3(3) Å^3 (from 481 reflections, 12 < θ < 21°), Z = 8, D_c = 1.511 g cm^{-3}, F(000) = 944, graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å, μ = 1.4 cm^{-1}, crystal size 0.4 × 0.20 × 0.16 mm, ω scan mode, 2θ ⩽ 52.3°, 4273 total and 1738 unique data, R_{int} = 0.0379. The structure was solved by direct methods (SHELXS-86).[17] Least-squares refinement (SHELXL-93):[18] full-matrix of 154 variables (all non-H atoms anisotropic, H(1) and H(3) were refined without constraints, all other hydrogen atoms were refined using geometric constraints) against F^2 of all data with Chebyshev weighting scheme, converging at $wR(F^2)$ = 0.1034 and goodness-of-fit 1.283 for all data, $R(F)$ = 0.0460 for 1624 'observed' data with $I \geqslant 2\sigma(I)$; residual $\Delta\rho_{max}$ = 0.260, $\Delta\rho_{min}$ = −0.206 e Å^{-3}.

$C_{11}H_9F_3O_2$ **8b**: M = 230.18, orthorhombic, space group $P2_12_12_1$, a = 6.3124(8), b = 8.5420(11), c = 18.526(3) Å, V = 998.9(2) Å^3 (from 366 reflections, 12 < θ < 21°), Z = 4, D_c = 1.531 g cm^{-3}, F(000) = 472, graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å, μ = 1.4 cm^{-1}, crystal size 0.3 × 0.12 × 0.07 mm, ω scan mode, 2θ ⩽ 52.3°, 4069 total and 1679 unique data, R_{int} = 0.0650. The structure was solved by direct methods (SHELXS-86).[17] Least-squares refinement (SHELXL-93):[18] full-matrix of 154 variables (all non-H atoms anisotropic, H(1) and H(3) were refined without constraints, all other hydrogen atoms were refined using geometric constraints) against F^2 of all data with Chebyshev weighting scheme, converging at $wR(F^2)$ = 0.1403 and goodness-of-fit 1.285 for

all data, $R(F) = 0.0722$ for 1348 'observed' data with $I \geqslant 2\sigma(I)$; residual $\Delta\rho_{max} = 0.189$, $\Delta\rho_{min} = -0.217$ e Å^{-3}.

$C_{12}H_{11}F_3O_2$ **10a**: $M = 244.21$, monoclinic, space group $P2_1/n$ (No. 14), $a = 8.237(1)$, $b = 5.574(1)$, $c = 24.507(4)$ Å, $\beta = 98.38(1)°$, $V = 1113.2(4)$ Å^3 (from 141 reflections, $10 < \theta < 21°$), $Z = 4$, $D_c = 1.46$ g cm^{-3}, $F(000) = 504$, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $\mu = 1.3$ cm^{-1}, crystal size $0.18 \times 0.22 \times 0.6$ mm, ω scan mode, $2\theta \leqslant 52.3°$, 4479 total and 1925 unique data, $R_{int} = 0.057$. The structure was solved by direct methods (SHELXS-86).[17] Least-squares refinement (SHELXL-93):[18] full matrix of 199 variables (all non-H atoms anisotropic, H atoms isotropic) against F^2 of all data with Chebyshev weighting scheme, converging at $wR(F^2) = 0.150$ and goodness-of-fit 1.114 for all data, $R(F) = 0.051$ for 1653 'observed' data with $I \geqslant 2\sigma(I)$; residual $\Delta\rho_{max} = 0.25$, $\Delta\rho_{min} = -0.19$ e Å^{-3}.

For **8a**, **8b** and **10a** all atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre; see *J. Chem. Soc., Perkin Trans. 1*, 1995, issue 1, Instructions for Authors, (1995).

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