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Synthesis of New Mono-functionalised Tetrathiafulvalene Derivatives by Reactions of Tetrathiafulvalenyllithium with Aldehydes and Ketones: X-Ray Crystal Structures of TTF-CMe(OH)Fc, TTF-CMe(OMe)Fc and TTF-CH(OMe)TTF (Fc = ferrocenyl)

Martin R. Bryce,* Peter J. Skabara, Adrian J. Moore, Andrei S. Batsanov,
Judith A. K. Howard and Vanessa J. Hoy

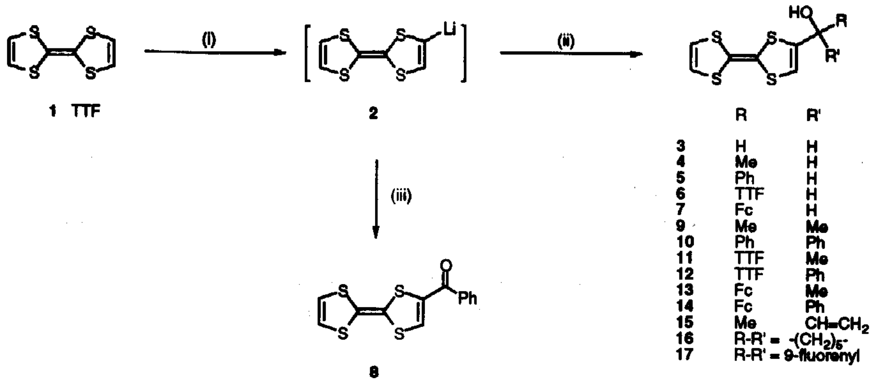
Department of Chemistry, University of Durham, Durham DH1 3LE, U.K

Abstract: Reactions of tetrathiafulvalenyllithium (TTF-Li) with a range of aldehydes and ketones have been explored for the first time, to provide an efficient route to mono-functionalised TTF derivatives of general formulae TTF-CH(OH)R (R = alkyl, phenyl, tetrathiafulvalenyl and ferrocenyl) and TTF-CR(OH)R' (R = alkyl, phenyl, R' = alkyl, phenyl, tetrathiafulvalenyl, ferrocenyl, and R-R' = fluorenyl). Subsequent transformations involving the reactive alcohol group of some of these compounds are reported. The structures of the three title compounds have been established by single-crystal X-ray analysis. © 1997 Elsevier Science Ltd.

INTRODUCTION

Extensive studies on the π-electron donor molecule tetrathiafulvalene (TTF) **1** and its derivatives during the last twenty years[1] have been driven primarily by the quest for new organic metals and organic superconductors, and many charge-transfer complexes (*e.g.* TTF-TCNQ) (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) and radical ion salts of TTF are one-dimensional systems which exhibit unusual conductivity and magnetic properties.[2] It has recently been recognised that functionalised TTF derivatives also have an important role to play as redox sites in several other areas of supramolecular chemistry, *e.g.* catenanes, molecular shuttles, dendritic polymers and cation sensors, and this has highlighted the need to develop efficient synthetic routes to new TTF derivatives.[3] From this viewpoint we have undertaken extensive studies on the mono-lithiation of TTF and subsequent functionalisation with electrophilic reagents[4] and the lithiation chemistry of TTF has recently been reviewed.[5]

We have modified Green's original procedure[6] for the preparation of tetrathiafulvalenyllithium (TTF-Li) **2** and some mono-substituted TTF derivatives can now be obtained in high yield: for example, *N*-methyl-*N*-phenylformamide reacts with TTF-Li **2** to yield TTF-carboxaldehyde in 82% yield, the reduction of which affords TTF-methanol **3**, which is a valuable building block in TTF chemistry.[4f] Other electrophiles that are known to react efficiently with species **2** include acid chlorides,[4a,6] chloroformates,[4d,6] Eschenmoser's salts ($CH_2=NR_2^+ I^-$),[7] isocyanates[4d] and isothiocyanates.[4d] Green first demonstrated that TTF-Li **2** reacted with formaldehyde to afford TTF-methanol **3**[6] and it is remarkable that, until now, extension of this reaction to other aldehydes and ketones has remained unexplored. However, we note that Fourmigué *et al.* have recently observed the *in situ* interception of 3-acetyl-3',4,4'-trimethyltetrathiafulvalene (TriMeTTF = trimethyltetrathiafulvalene) by TriMeTTF-Li (during the reaction of acetyl chloride and TriMeTTF-Li) to afford a bis-TriMeTTF tertiary alcohol.[8] In this paper, we report the reaction of tetrathiafulvalenyllithium **2** with a range of aldehydes and ketones to yield new secondary and tertiary hydroxymethyl-TTF derivatives, and describe



	R	R'
3	H	H
4	Me	H
5	Ph	H
6	TTF	H
7	Fc	H
9	Me	Me
10	Ph	Ph
11	TTF	Me
12	TTF	Ph
13	Fc	Me
14	Fc	Ph
15	Me	CH=CH$_2$
16	R-R' = -(CH$_2$)$_5$-	
17	R-R' = 9-fluorenyl	

Scheme 1. Reagents and conditions: (i) LDA, Et_2O, -78°C, 1.5 h; (ii) RC(O)R', -78°C, 1 h, then warm to 20°C overnight, then H_2O; (iii) PhC(O)Cl, -78°C, 1 h, then warm to 20°C overnight.

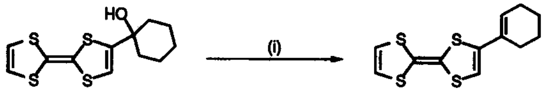
some subsequent transformations of these systems. In the context of TTF-based donor molecules appended with substituents capable of intermolecular hydrogen bonding,[9] a number of donors endowed with hydroxyl groups have been shown to exhibit effective hydrogen bonding leading to novel crystal-packing motifs.[8a,10]

RESULTS AND DISCUSSION

Synthesis

Tetrathiafulvalenyllithium **2**[4f] reacted with the following aldehydes: acetaldehyde, benzaldehyde, TTF-carboxaldehyde[4f] and ferrocenecarboxaldehyde to yield secondary alcohols **4-7**, respectively (47-60% yield) and with the following ketones: acetone, benzophenone, acetyl-TTF,[6] benzoyl-TTF **8** (benzoyl-TTF was prepared by reaction of TTF-Li **2**[4f] with benzoyl chloride in 58% yield), acetylferrocene, benzoylferrocene,[11] methyl vinyl ketone, cyclohexanone and fluorenone to afford tertiary alcohols **9-17**, respectively (44-90% yield) (Scheme 1). It is noteworthy that in these reactions, ketones generally give higher isolated yields of product than aldehydes, and no product derived from Michael addition of anion **2** to methyl vinyl ketone was observed.

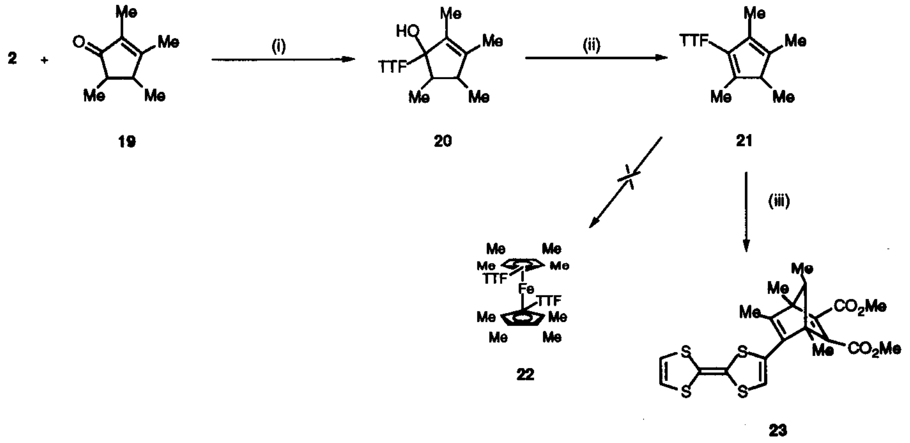
We have observed a decomposition pathway of the TTF alcohols involving the elimination of water (where possible). For example, compound **16** slowly dehydrated under ambient conditions (t.l.c. and ^1H NMR evidence) to afford the cyclohexene derivative **18** (Scheme 2). This process was efficiently catalysed by the



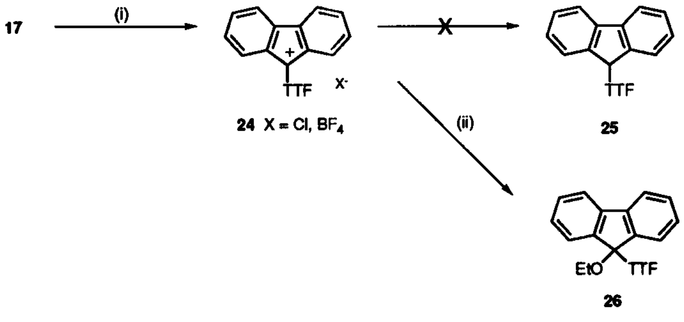
16 **18**

Scheme 2. Reagents and conditions: (i) $HCl.Et_2O$, CH_2Cl_2, 20°C, 1 h.

addition of HCl-etherate. We recognised that this methodology offered a potential route to the bis-(TTF)octamethylferrocene system **22**, which should form charge-transfer complexes with π–electron acceptors which might possess interesting solid-state properties.[12,13] Accordingly, we reacted TTF-Li **2** with 2,3,4,5-tetramethyl-2-cyclopentenone **19** to give alcohol **20** (73% yield), which was dehydrated to yield cyclopentadiene derivative **21** (87% yield) (Scheme 3). Unfortunately, all attempts to convert **21** into the ferrocene system **22** by deprotonation followed by complexation with Fe^{2+}, using a range of bases and iron salts, proved fruitless: compound **21** was recovered unchanged in all cases. Spectroscopic data were entirely consistent with compound **21** existing as the monomer (as opposed to a cyclopentadiene dimer); this was supported by the reaction of compound **21** with dimethyl acetylenedicarboxylate (DMAD) which afforded the expected [4 + 2] cycloadduct **23** (89% yield), for which ^{1}H NMR spectra and CV data (see below) confirm that cycloaddition had occurred across the cyclopentadiene ring of **21** and not to the vinyl-TTF diene unit.[14]



Scheme 3. Reagents and conditions: (i) Et_2O, -78°C, 1 h, then warm to 20°C overnight; then H_2O; (ii) $HCl.Et_2O$, CH_2Cl_2, 20°C, 1 h; (iii) DMAD, PhMe, 50°C, 4 h.

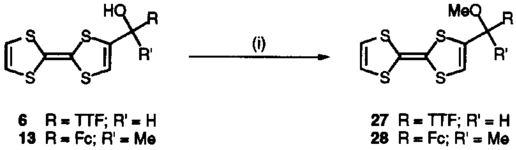


Scheme 4. Reagents and conditions: (i) HBF_4 or $HCl.Et_2O$, CH_2Cl_2, 20°C, 0.5 h; (ii) NaOEt, EtOH, 20°C, 0.25 h.

We attempted to convert compound **17** into compound **25**, *via* cation salt **24** (Scheme 4), following literature precedent for a related ferrocenylfluorene derivative.[15] Reaction of compound **17** with either tetrafluoroboric acid or with HCl-etherate, yielded an intractable black precipitate (presumed to be impure salt **24**) which could not be converted into compound **25** upon attempted reaction with a number of reducing reagents (*viz.* $LiAlH_4$, DIBAL-H and $NaBH_4$). However, addition of sodium ethoxide to the black solid yielded ethoxy derivative **26** (33% yield) providing strong evidence that the black solid contained salt **24**. Compound **25** could also not be isolated from the attempted reduction of **17** with $LiAlH_4$ / $AlCl_3$, which resulted in an inseparable mixture of unidentified products (t.l.c. evidence).

We have successfully deprotonated compounds **6** and **13** using sodium hydride in THF, and the derived alkoxides can be trapped *in situ* with methyl iodide to afford methyl ether derivatives **27** and **28** (Scheme 5).

The X-ray crystal structures of ferrocene-TTF systems **13** and **28** and the bis-TTF derivative **27** are reported below.



Scheme 5. Reagents and conditions: (i) NaH, THF, 20°C, 1 h; then MeI, 20°C, 1 h.

Solution Electrochemistry

The solution redox chemistry of compounds **4-18**, **20**, **23**, **27** and **28** has been studied by cyclic voltammetry in acetonitrile solution. The TTF ring system in all the new compounds displays the expected two reversible one-electron redox couples ($E_1^{1/2} = 0.24$ - 0.43 V; $E_2^{1/2} = 0.63$ - 0.85 V) (*cf.* TTF **1**, $E_1^{1/2} =$

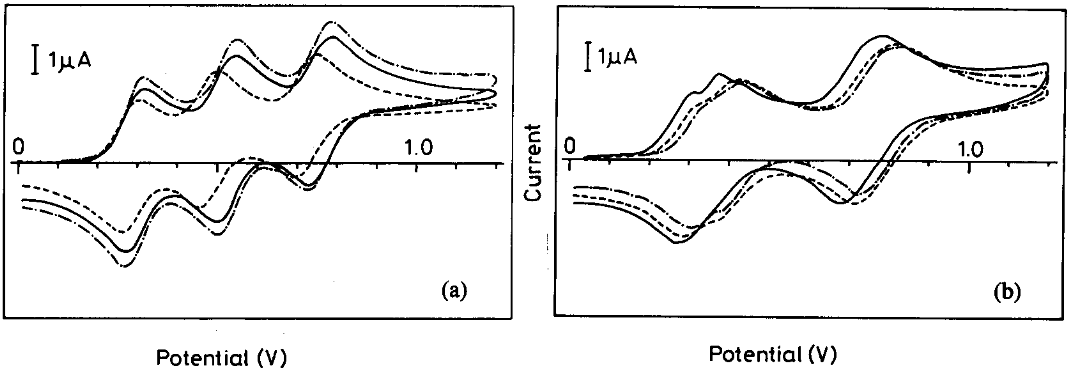


Figure 1. Cyclic voltammograms of (a) compounds **7** (-----), **13** (——) and **14** (—·—·—); and, (b) compounds **6** (-----), **11** (——) and **12** (—·—·—).

0.34 V; $E_2^{1/2}$ = 0.74 V). Compound **9** is the easiest derivative to oxidise by virtue of the geminal dimethyl groups which stabilise the TTF cation radical and dication states. Ferrocene derivatives **7**, **13**, **14** and **28** exhibit an additional reversible wave ($E^{1/2}$ = 0.47 - 0.52 V) corresponding to the ferrocene / ferrocenium redox couple (Figure 1a). For the bis-TTF derivatives **6**, **11**, **12** and **27**, two close-lying reversible one-electron oxidations are observed ($E^{1/2}$ = 0.30 - 0.43 V) followed by a reversible two-electron oxidation at higher potential ($E^{1/2}$ = 0.74 - 0.85 V) (Figure 1b). These data are consistent with the sequential formation of the mono- and dicationic species, followed by a further two-electron oxidation to afford the tetracationic species. These features, already reported in a number of bis-TTF derivatives[16] with organic[4b,17] or organometallic[18] linkers, have been ascribed to a through-space coulombic intermolecular interaction between the two redox moieties.[17a] It is noteworthy that the similarity between the cyclic voltammogram of compound **23** and other TTF derivatives provides further evidence that cycloaddition has occurred to the cyclopentadiene unit of **21**, leaving the TTF ring system intact.

X-Ray Crystal Structures of Compounds 13, 27 and 28

In the crystal structure of compound **13** the asymmetric unit (Figure 2) comprises two molecules (A and B). In molecule A, the hydroxy H atom is directed towards the midpoint (X) of the ferrocenyl C(6)-C(7) bond. This can be interpreted as a weak O-H---π H-bond, as observed earlier in some α-ferrocenylcarbinols,[19a] although the H···X distance (2.88 Å for the idealised O-H bond length of 0.97 Å, the O-H···X angle being 151°) is much longer than in O-H···alkyne H-bonds,[19b] where it can be as short as 2.26 Å. This interaction may be responsible for 'fixing' the Cp-ring in an ordered position, while in molecule B, whose OH group, in contrast, is engaged in *inter*molecular O-H···O bonding (O···O 3.075 Å), the unsubstituted Cp ring is rotationally disordered. In both molecules A and B, the TTF moiety is almost perpendicular to the Cp rings. In A, TTF adopts a boat conformation with rings *E* and *F* folding along S---S vectors by 13.9° and 11.2°, respectively. In B, TTF adopts smaller, chair-like folding by 3.3° (ring *G*) and -3.0° (ring *H*). The C(OH)Me groups of molecules A and B are almost coplanar with each other and show strong libration (or minor disorder) in their mean plane, probably in concerted motion. The molecules of **13** in the crystal stack parallel to the [1 1 0] direction, in the succession ...A..A..B..B..A... and in head-to-tail fashion, so that the ferrocene moiety of each molecule is sandwiched between the TTF moieties of the adjacent two molecules, and *vice versa* (Figure 3).

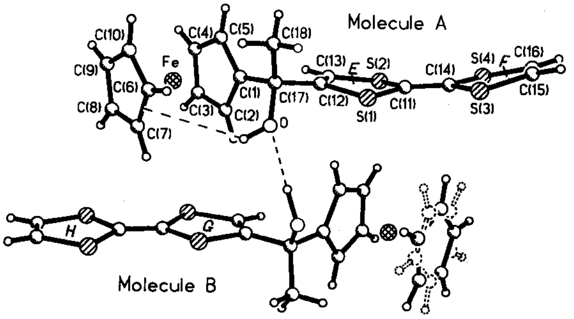


Figure 2. Two independent molecules (A and B) in the structure of **13**, showing the atom numbering scheme for molecule A. For molecule B, two positions of the disordered Cp ring are shown.

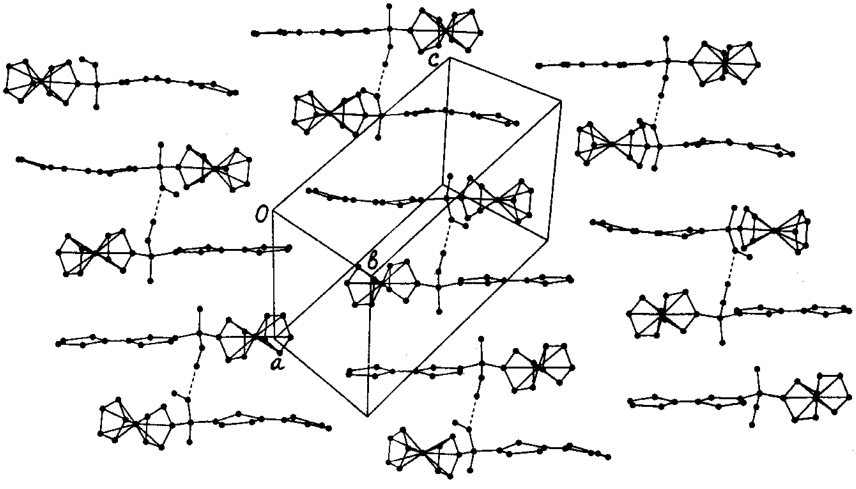


Figure 3. Crystal packing of **13**.

The structure of compound **28** comprises centrosymmetric dimers (Figure 4) in which essentially planar TTF moieties overlap in a ring-over-bond fashion, with an interplanar separation of 3.50 Å. Such overlap is common for dimers of TTF derivatives[4d,g] but usually the TTF systems therein are folded in a boat fashion, their central C_2S_4 moieties remaining planar with an interplane separation of 3.33 to 3.47 Å and the peripheral C=C bonds bending outwards. Ring-over-bond overlap of planar TTF moieties is typical for infinite stacking motifs rather than for separate dimers. It is not clear whether the peculiarity of **28** is due to a (rather small) increase of intermolecular spacing or to electronic influence of the ferrocene part of the molecule. In any case, *ab initio* MO calculations[4g] have shown high conformational flexibility of the TTF molecule, energy costs of folding both rings by 5, 10, 15 and 20° being 0.016, 0.1, 0.4 and 1.0 kcal mol^{-1} only. Dimers, related by a translation in the *y* direction, form a ribbon with short interdimer contacts S(1)...S(2) 3.47, S(3)...S(2) 3.50, S(3)...S(4) 3.51 Å, close to the lower end of the range for such contacts.

In the molecule of compound **27** (Figure 5) both TTF moieties show the usual distortions from planarity with minor folding of the rings along S...S lines (by 2.6 - 11.2°). Mean planes of the TTF moieties form a

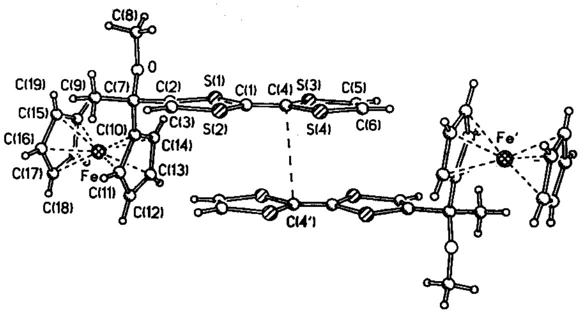


Figure 4. Dimer of molecules of **28** (primed atoms are inversion-related).

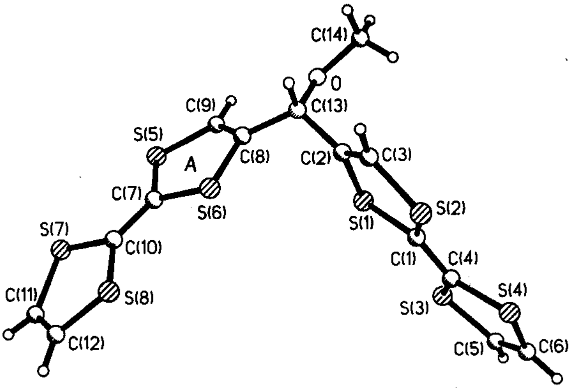


Figure 5. Molecular structure of **27**.

dihedral angle of 87° and are inclined by 63° and 44° to the C(2)-C(13)-C(8) plane. Such a conformation precludes the formation of molecular stacks. The shortest intermolecular contacts occur between the molecules related *via* a translation in the *x* direction, *viz.* S(2)...S(1) 3.76, S(2)...O 3.18, S(6)...S(5) 3.75, S(8)...S(5) 3.56 and S(8)...S(7) 3.79Å. Molecules related via the (-x, -y, -z) inversion have their respective rings *A* overlapping [S(6) is located over the centre of the ring] with an interplanar separation of *ca.* 3.5 Å.

CONCLUSIONS

New reactions of monolithiated-TTF **2** with aldehydes and ketones have been shown to provide efficient access to secondary and tertiary hydroxymethyl-TTF derivatives. Tertiary alcohol **13** is an interesting system, as it comprises covalently linked TTF and ferrocene units, and it has been converted into the methyl ether derivative **28**. The X-ray crystal structures of **13** and **28** reveal very different packing motifs, with intermolecular hydrogen bonding being a notable feature of the solid state structure of the former compound. The versatile synthetic methodology reported herein should prove useful in the search for new mono-functionalised TTF derivatives which possess unusual solid state properties.

Acknowledgements. This work was funded by EPSRC. We thank Dr. S. T. A. K. Daley (Zeneca F.C.M.O.) for helpful discussions.

EXPERIMENTAL

General Methods. ^{1}H NMR spectra were obtained on a Bruker AC 250 spectrometer operating at 250.134 MHz. Mass spectra were recorded on a VG7070E spectrometer operating at 70 eV. Infra-red spectra were recorded on a Perkin-Elmer 1615 FTIR operated from a Grams Analyst 1600. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. All reagents were of commercial quality and solvents were dried, where necessary, using standard procedures. All column chromatography was performed using distilled solvents. Cyclic voltammetric data were measured with iR compensation using a BAS 100 Electrochemical Analyser. The experiments were carried out under an argon atmosphere at 20 °C at a platinum disc electrode (1.6 mm diameter) with a platinum gauze counter electrode in 5 mL of a *ca.* 10^{-4} M solution of the compound containing 0.2 M tetrabutylammonium hexafluorophosphate (Fluka, puriss, electrochemical grade) as the supporting electrolyte. The solvent, acetonitrile, was dried and freshly distilled prior to use. The potentials were measured versus Ag / AgCl and corrected *versus* ferrocene / ferrocene$^+$ as $E^{1/2}$ = +0.36 V by adding ferrocene to the studied solution after the experiment and referenced *versus* Ag / AgCl.

General Procedure for Compounds 4-17 and 20. To a solution of tetrathiafulvalene **1**,[20] in diethyl ether (100 mL) at -78°C under argon, was added lithium diisopropylamide mono(tetrahydrofuran) (1.05 equiv., 1.5 M in cyclohexane), and TTF-Li **2** allowed to form over 1.5 h.[4f] The relevant aldehyde, ketone or acid chloride was then added neat in one portion against a flow of argon, and the reaction was stirred at -78°C for a further 1 h before warming slowly to room temperature overnight. Water (100 mL) was added, the organic layer separated and the aqueous phase extracted with dichloromethane (2 x 30 mL). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography (silica gel, 70-230 mesh) of the residue eluting initially with hexane - dichloromethane (3:1 $^{v}/_{v}$) removed unchanged tetrathiafulvalene. Subsequent elution with dichloromethane afforded products **4-17** and **20**. All solids were recrystallised from hexane - dichloromethane. There was thus obtained:

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]ethanol 4. Tetrathiafulvalene (600 mg, 2.94 mmol) and acetaldehyde (0.2 mL, 3.58 mmol) afforded compound **4** as an orange oil (440 mg, 60%); υ_{max} (Nujol) / cm^{-1}: 3358 (br, OH), 3045, 1681, 1134, 888, 796, 733 and 647; δ_H (d_6-acetone): 6.60 (2 H, s), 6.39 (1 H, s), 4.67 (1 H, q, *J* 6.5), 2.92 (1 H, br, exch.), and 1.38 (3 H, d, *J* 6.5); *m/z* (DCI): 249 (M^++1), HRMS found 247.9445, $C_8H_8OS_4$ requires 247.9458; CV (MeCN) / V: $E_1^{1/2}$ 0.29, $E_2^{1/2}$ 0.69.

[2,2'-Bi(1,3-dithiolylidene)-4-yl]phenylmethanol 5. Tetrathiafulvalene (600 mg, 2.94 mmol) and benzylaldehyde (0.4 mL, 3.94 mmol) afforded compound **5** as an orange oil (490 mg, 54%); υ_{max} (neat) / cm^{-1}: 3383 (br, OH), 3066, 1689, 1492, 1452, 1254, 1015, 794, 777, 700 and 644; δ_H ($CDCl_3$): 7.50 - 7.37 (5 H, s), 6.26 (2 H, s), 6.09 (1 H, s), 5.47 (1 H, s), and 3.09 (1 H, br, exch.); *m/z* (DCI): 311 (M^++1), HRMS found 309.9588, $C_{13}H_{10}OS_4$ requires 309.9615; CV (MeCN) / V: $E_1^{1/2}$ 0.31, $E_2^{1/2}$ 0.70.

Bis[2,2'-bi(1,3-dithiolylidene)-4-yl]methanol 6. Tetrathiafulvalene (250 mg, 1.23 mmol) and tetrathiafulvalenecarboxaldehyde[4f] (300 mg, 1.29 mmol) afforded compound **6** as a pale orange solid (250 mg, 47%); m.p. 45-48°C (Found: C, 35.8; H, 1.9. $C_{13}H_8OS_8$ requires C, 35.8; H, 1.9%); υ_{max} (KBr) / cm^{-1}: 3420 (br, OH), 3060, 2958, 1636, 1431, 1361, 1231, 1156, 1083, 794, 775, 756 and 641; δ_H ($CDCl_3$): 6.38 (2 H, s), 6.30 (4 H, s), 5.30 (1 H, d, *J* 4.2), and 2.47 (1 H, d, *J* 4.2, exch.); *m/z* (DCI): 437 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.32, $E_2^{1/2}$ 0.36, $E_3^{1/2}$ 0.76 (2e).

[1-Cyclopentadienyl(cyclopentadienyl)iron][2,2'-bi(1,3-dithiolylidene)-4-yl]methanol 7. Tetrathiafulvalene (250 mg, 1.23 mmol) and ferrocenecarboxaldehyde (400 mg, 1.87 mmol) afforded compound **7** as a brown solid (240 mg, 47%); m.p. 137-139°C (Found: C, 49.0; H, 3.5. $C_{17}H_{14}FeOS_4$ requires C, 48.8; H, 3.4%); υ_{max} (KBr) / cm^{-1}: 3549, 3433 (br, OH), 3062, 1090, 1009, 824, 793, 641 and 487; δ_H ($CDCl_3$): 6.30 (2 H, s), 6.12 (1 H, s), 5.20 (1 H, d, *J* 3.8), 4.32 (2 H, m), 4.25 (5 H, s), 4.23 (2 H, m), 2.42 (1 H, d, *J* 3.8, exch.); *m/z* (DCI): 419 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.28, $E_2^{1/2}$ 0.47, $E_3^{1/2}$ 0.72 (2e).

2,2'-Bi[1,3-dithiolylidene)-4-yl]phenylmethanone 8. Tetrathiafulvalene (750 mg, 3.67 mmol) and benzoyl chloride (0.85 mL, 7.35 mmol) afforded compound **8** as a purple solid (655 mg, 58%); m.p. 126°C (Found: C, 50.7; H, 2.6. $C_{13}H_8OS_4$ requires C, 50.6; H, 2.6%); υ_{max} (KBr) / cm^{-1}: 3058, 1688, 1616, 1527, 1516, 1298, 834, 806, 782, 711 and 650; δ_H ($CDCl_3$): 7.71 - 7.44 (5 H, m), 7.16 (1 H, s) and 6.34 (2 H, s); *m/z* (DCI): 309 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.51, $E_2^{1/2}$ 0.88.

2-[2,2'-Bi(1,3-dithiolylidene)-4-yl]propan-2-ol 9. Tetrathiafulvalene (250 mg, 1.23 mmol) and acetone (0.5 mL, 10.90 mmol) afforded compound **9** as a yellow solid (230 mg, 72%); m.p. 93-94°C (Found: C, 41.1; H, 3.9. $C_9H_{10}OS_4$ requires C, 41.2; H, 3.8%); υ_{max} (KBr) / cm^{-1}: 3295 (br, OH), 2978, 1156, 936, 794 and 758; δ_H ($CDCl_3$): 6.31 (2 H, s), 6.13 (1 H, s), 3.22 (1 H, s, exch.), and 1.53 (6 H, s); *m/z* (DCI): 263 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.24, $E_2^{1/2}$ 0.63.

[2,2'-Bi(1,3-dithiolylidene)-4-yl]diphenylmethanol 10. Tetrathiafulvalene (600 mg, 2.94 mmol) and benzophenone (700 mg, 3.85 mmol) afforded compound **10** as an orange oil (980 mg, 86%); υ_{max} (neat) / cm^{-1}: 3448 (br, OH), 3062, 1654, 1597, 1446, 1318, 1279, 763, 742, 700 and 638; δ_H ($CDCl_3$): 7.85-7.28 (10 H, m), 6.26 (2 H, s), 5.86 (1 H, s) and 3.24 (1 H, s, exch.); *m/z* (EI): 386 (M^+), HRMS found 385.9928, $C_{19}H_{14}OS_4$ requires 385.9928; CV (MeCN) / V: $E_1^{1/2}$ 0.35, $E_2^{1/2}$ 0.76.

1,1-Bis[2,2'-bi(1,3-dithiolylidene)-4-yl]ethanol 11. Tetrathiafulvalene (400 mg, 1.96 mmol) and acetyltetrathiafulvalene[6] (250 mg, 1.02 mmol) afforded compound **11** as a pale orange solid (320 mg, 70%); m.p. 128-130°C (Found: C, 37.1; H, 2.2. $C_{14}H_{10}OS_8$ requires C, 37.3; H, 2.2%); υ_{max} (KBr) / cm^{-1}: 3442 (br, OH), 3060, 1654, 820, 786 and 625; δ_H ($CDCl_3$): 6.33 (6 H, br s), 2.56 (1 H, br, exch.), and 1.90 (3 H, s); *m/z* (DCI): 451 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.30, $E_2^{1/2}$ 0.34, $E_3^{1/2}$ 0.74 (2e).

Bis[2,2'-bi(1,3-dithiolylidene)-4-yl]phenylmethanol 12. Tetrathiafulvalene (250 mg, 1.23 mmol) and benzoyltetrathiafulvalene **8** (250 mg, 0.81 mmol) afforded compound **12** as a pale orange solid (200 mg, 48%); m.p. 94-96°C (Found: C, 44.6; H, 2.5. $C_{19}H_{12}OS_8$ requires C, 44.5; H, 2.4%); υ_{max} (KBr) / cm^{-1}: 3446 (br, OH), 3063, 1654, 795, 775, 713 and 645; δ_H ($CDCl_3$): 7.58 - 7.50 (2 H, m), 7.45 - 7.38 (3 H, m), 6.31 (4 H, s), 6.22 (2 H, s) and 2.97 (1 H, s, exch.); *m/z* (DCI): 513 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.30, $E_2^{1/2}$ 0.36, $E_3^{1/2}$ 0.75 (2e).

1-[1-Cyclopentadienyl(cyclopentadienyl)iron]-1-[2,2'-bi(1,3-dithiolylidene)-4-yl]ethanol 13. Tetrathiafulvalene (1.00 g, 4.90 mmol) and acetylferrocene (1.30 g, 5.70 mmol) afforded compound **13** as a yellow solid (1.91 g, 90%); m.p. 139-141°C (Found: C, 50.2; H, 3.6. $C_{18}H_{16}FeOS_4$ requires C, 50.0; H, 3.7%); υ_{max} (KBr) / cm^{-1}: 3543, 3495 (br, OH), 3074, 2978, 1104, 1029, 820, 794, 776, 642, 513, 498 and 484; δ_H ($CDCl_3$): 6.28 (2 H, s), 5.96 (1 H, s), 4.33 (1 H, m), 4.27-4.19 (8 H, m), 2.70 (1 H, s, exch.), and 1.80 (3 H, s); *m/z* (EI): 432 (M^+); CV (MeCN) / V: $E_1^{1/2}$ 0.29, $E_2^{1/2}$ 0.51, $E_3^{1/2}$ 0.75.

[1-Cyclopentadienyl(cyclopentadienyl)iron][2,2'-bi(1,3-dithiolylidene)-4-yl]phenylmethanol 14. Tetrathiafulvalene (500 mg, 2.45 mmol) and benzoylferrocene[11] (500 mg, 1.72 mmol) afforded compound **14** as an orange solid (540 mg, 63%); m.p. 66-67°C (Found: C, 55.5; H, 3.7. $C_{23}H_{18}FeOS_4$ requires C, 55.9; H, 3.7%); υ_{max} (KBr) / cm^{-1}: 3489 (br, OH), 3064, 2922, 1105, 1048, 1001, 821, 794, 775, 729, 699, 644 and 488; δ_H ($CDCl_3$): 7.42-7.32 (5 H, m), 6.29 (2 H, s), 5.82 (1 H, s), 4.47 (1 H, m), 4.33 (1 H, m), 4.25 (5 H, s), 4.24 (1 H, m), 3.89 (1 H, m) and 3.41 (1 H, s, exch.); *m/z* (DCI): 495 (M^++1), HRMS found 493.9560, $C_{23}H_{18}FeOS_4$ requires 493.9590; CV (MeCN) / V: $E_1^{1/2}$ 0.29, $E_2^{1/2}$ 0.52, $E_3^{1/2}$ 0.75.

3-[2,2'-Bi(1,3-dithiolylidene)-4-yl]-1-buten-3-ol 15. Tetrathiafulvalene (500 mg, 2.45 mmol) and methyl vinyl ketone (0.2 mL, 2.45 mmol) afforded compound **15** as a yellow solid (443 mg, 66%); m.p. 69-

71°C (Found: C, 44.0; H, 3.8. $C_{10}H_{10}OS_4$ requires C, 43.8; H, 3.7%); ν_{max} (KBr) / cm^{-1}: 3284 (br, OH), 3066, 2978, 924, 792, 776 and 642; δ_H ($CDCl_3$): 6.30 (2 H, s), 6.16 (1 H, s), 6.03, 5.41 and 5.22 (each 1 H, ABX, J_{AX} 17.1, J_{BX} 10.7, J_{AB} 1.9), 2.14 (1 H, s, exch.) and 1.59 (3 H, s); *m/z* (DCI): 275 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.30, $E_2^{1/2}$ 0.70.

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]cyclohexanol 16. Tetrathiafulvalene (600 mg, 2.94 mmol) and cyclohexanone (0.62 mL, 6 mmol) afforded compound **16** as an unstable yellow solid (390 mg, 44%); m.p. 92-94°C (Found: C, 48.1; H, 5.2. $C_{12}H_{14}OS_4$ requires C, 47.6; H, 4.7%); ν_{max} (KBr) / cm^{-1}: 3260 (br, OH), 3178, 2931, 2856, 1059, 963, 792, 774 and 650; δ_H ($CDCl_3$): 6.40 - 6.35 (3 H, br s), 2.14 (1 H, s, exch.) and 1.85 - 1.55 (10 H, m); *m/z* (DCI): 303 (M^++1), HRMS found 301.9893, $C_{12}H_{14}OS_4$ requires 301.9928; CV (MeCN) / V: $E_1^{1/2}$ 0.27, $E_2^{1/2}$ 0.68.

9-Hydroxy-9-[2,2'-bi(1,3-dithiolylidene)-4-yl]fluorene 17. Tetrathiafulvalene (500 mg, 2.45 mmol) and 9-fluorenone (500 mg, 2.78 mmol) afforded compound **17** as a yellow solid (730 mg, 77%); m.p. 72-74°C (Found: C, 59.5; H, 3.4. $C_{19}H_{12}OS_4$ requires C, 59.4; H, 3.2%); ν_{max} (KBr) / cm^{-1}: 3416 (br, OH), 3063, 1448, 768, 743, 731 and 636; δ_H ($CDCl_3$): 7.65 - 7.25 (8 H, m), 6.27 (2 H, s), 6.21 (1 H, s), and 2.66 (1 H, s, exch.); *m/z* (DCI): 385 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.38, $E_2^{1/2}$ 0.79.

1-Hydroxy-1-[2,2'-bi(1,3-dithiolylidene)-4-yl]-2,3,4,5-tetramethyl-2-cyclopentene 20. Tetrathiafulvalene (500 mg, 2.45 mmol) and 2,3,4,5-tetramethyl-2-cyclopentenone **19** (0.4 mL, 2.52 mmol, mixture of *cis* and *trans* isomers) afforded compound **20** (isolated as an inseparable mixture of diastereomers and used directly in the preparation of **21**) as an orange oil (610 mg, 73%); ν_{max} (neat) / cm^{-1}: 3502 (br, OH), 3067, 2964, 2925, 2868, 796, 778, 733 and 643; *m/z* (EI): 342 (M^+), HRMS found 342.0253, $C_{15}H_{18}OS_4$ requires 342.0241; CV (MeCN) / V: $E_1^{1/2}$ 0.37, $E_2^{1/2}$ 0.74.

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]cyclohexene 18. To a solution of compound **16** (200 mg, 0.66 mmol) in dry dichloromethane (30 mL) was added slowly $HCl.Et_2O$ (0.3 mL, 1.0 M, 0.30 mmol) and the solution stirred under argon at 20°C for 1 h. After evaporation of the solvent *in vacuo*, the residue was chromatographed (silica gel, 70 - 230 mesh) eluting with hexane - dichloromethane (1:1 $^v/_v$) to afford compound **18** as a yellow solid (160 mg, 85%); m.p. 115 - 117°C (Found: C, 50.6; H, 4.3. $C_{12}H_{12}S_4$ requires C, 50.7; H, 4.3%); δ_H ($CDCl_3$): 6.31 (2 H, s), 6.13 (1 H, s), 5.78 (1 H, t, *J* 4.5), 2.27 - 2.18 (4 H, m) and 1.69 - 1.57 (4 H, m); *m/z* (DCI): 285 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.30, $E_2^{1/2}$ 0.70.

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]-2,3,4,5-tetramethyl-2,4-cyclopentadiene 21. To a solution of **20** (mixture of diastereomers, 200 mg, 0.58 mmol) in dry dichloromethane (20 mL) was added $HCl.Et_2O$ (0.60 mL, 1.0 M, 0.60 mmol) and the mixture stirred under argon at 20°C for 1 h. Column chromatography (silica gel, 70 - 230 mesh) eluting with dichloromethane afforded compound **21** as an orange oil (165 mg, 87%); δ_H ($CDCl_3$): 6.33 (2 H, s), 5.89 (1 H, s), 2.86 (1 H, m), 2.05 (3 H, d, *J* 1.7), 1.87 (3 H, s), 1.80 (3 H, d, *J* 1.7) and 1.11 (3 H, d, *J* 7.5); *m/z* (EI): 324 (M^+), HRMS found 324.0119, $C_{15}H_{16}S_4$ requires 324.0135.

Dimethyl 5-[2,2'-bi(1,3-dithiolylidene)-4-yl]-1,4,6,7-tetramethylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate 23. To a solution of compound **21** (200 mg, 0.62 mmol) in toluene (30 mL) was added dimethyl acetylenedicarboxylate (0.1 mL, 0.81 mmol) and the reaction was stirred at 50°C for 4 h. After cooling, the solvent was removed *in vacuo* and column chromatography (neutral alumina, 70 - 230 mesh) of the residue eluting with dichloromethane - hexane (1:1 $^v/_v$) afforded compound **23** as an orange solid (255 mg, 89%); m.p. 42-44°C (from hexane - dichloromethane at 0°C) (Found: C, 54.0; H, 5.1. $C_{21}H_{22}O_4S_4$ requires C, 54.1; H, 4.8%); ν_{max} (KBr) / cm^{-1}: 3069, 2949, 1716, 1432, 1293 and 1236; δ_H ($CDCl_3$): 6.30 (2 H, s), 6.19 (1 H, s), 3.77 (3 H, s), 3.75 (3 H, s), 2.68 (1 H, q, *J* 6.3), 1.92 (3 H, q, *J* 1.4), 1.67 (3 H, q, *J* 1.4), 1.30 (3 H, s) and 0.82 (3 H, d, *J* 6.3); *m/z* (DCI): 467 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.38, $E_2^{1/2}$ 0.78.

9-[2,2'-Bi(1,3-dithiolylidene)-4-yl]fluorenium - chloride (X = Cl) and - tetrafluoroborate (X = BF_4). To a solution of compound **17** (460 mg, 1.20 mmol) in dry dichloromethane (10 mL) was added $HCl.Et_2O$ (1.2 mL, 1.0 M, 1.2 mmol) at 20°C under argon and the reaction stirred for 0.5 h. Diethyl ether (100 mL) was added affording a brown / black precipitate (450 mg), presumed to be cation salt **24** (X = Cl), which was collected by filtration. Alternatively, to a solution of compound **17** (200 mg, 0.52 mmol) in dry dichloromethane (10 mL) was added dropwise tetrafluoroboric acid at 20°C under argon, until deposition of a solid ceased. Diethyl ether (100 mL) was added to the reaction mixture and the brown / black precipitate (170 mg), presumed to be cation salt **24** (X = BF_4), was isolated by filtration. For both salts **24** (X = Cl and BF_4) satisfactory elemental analysis could not be obtained; salt **24** (X = BF_4) was used directly in the next reaction.

9-Ethoxy-9-[2,2'-bi(1,3-dithiolylidene)-4-yl]fluorene 26. To a suspension of crude salt **25** (X = BF_4) (100 mg, 0.22 mmol) in dry ethanol (20 mL) was added sodium ethoxide in ethanol (2.5 mL, 0.1 M, 0.25 mmol), and the mixture stirred for 15 min at 20°C under argon. The solvent was evaporated under reduced pressure; column chromatography (silica gel, 70 - 230 mesh) eluting with dichloromethane afforded compound **26** as an orange oil (30 mg, 33%, based upon crude salt **24** (X = BF_4); δ_H ($CDCl_3$): 7.70 - 7.59 (4 H, m), 7.45 - 7.28 (4 H, m), 6.27 (2 H, s), 6.00 (1 H, s), 2.99 (2 H, q, *J* 7.0) and 1.09 (3 H, t, *J* 7.0); *m/z* (DCI): 413 (M^++1), HRMS found 412.0160, $C_{21}H_{16}OS_4$ requires 412.0084.

Bis[2,2'-bi(1,3-dithiolylidene)-4-yl]methyl methyl ether 27. To a solution of compound **6** (300 mg, 0.7 mmol) in dry THF (50 mL) was added sodium hydride (35 mg, 60% dispersion in oil, 0.85 mmol), and the mixture stirred for 1 h at 20°C under argon. Methyl iodide (0.3 mL, 5.36 mmol) was then added, and the solution stirred for a further 1 h at 20°C. After evaporation of the solvent under reduced pressure, column chromatography (silica gel, 70 - 230 mesh) of the residue eluting with hexane - toluene (1:1 $^v/_v$) afforded compound **27** as an orange solid (235 mg, 75%); m.p. 151-153°C (from hexane - dichloromethane) (Found: C, 37.5; H, 2.3. $C_{14}H_{10}OS_8$ requires C, 37.3; H, 2.2%); δ_H ($CDCl_3$): 6.36 (2 H, d, *J* 1.1), 6.32 (4 H, s), 4.75 (1 H, t, *J* 1.1), and 3.42 (3 H, s); *m/z* (DCI): 451 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.40, $E_2^{1/2}$ 0.43, $E_3^{1/2}$ 0.85 (2e).

1-[1-Cyclopentadienyl(cyclopentadienyl)iron]-1-[2,2'-bi(1,3-dithiolylidene)-4-yl]ethyl methyl ether 28 was prepared analogously to compound **27** from compound **13** (300 mg, 0.69 mmol), sodium hydride (35 mg, 60% dispersion in oil, 0.85 mmol) and methyl iodide 0.3 mL, 5.36 mmol). Column chromatography (silica gel, 70 - 230 mesh) eluting with toluene afforded compound **28** as an orange solid (266 mg, 86%); m.p. 148-149°C (from toluene) (Found: C, 51.0; H, 4.2. $C_{19}H_{18}FeOS_4$ requires C, 51.1; H, 4.1%); δ_H ($CDCl_3$): 6.29 (2 H, s); 6.25 (1 H, s), 4.20 (2 H, m), 4.18 (5 H, s), 4.15 (2 H, m), 3.20 (3 H, s), 1.82 (3 H, s); *m/z* (DCI): 447 (M^++1); CV (MeCN) / V: $E_1^{1/2}$ 0.35, $E_2^{1/2}$ 0.56, $E_3^{1/2}$ 0.82.

Crystal Structure Determinations. Low-temperature single-crystal X-ray diffraction experiments were carried out on Rigaku AFC6S (compounds **13** and **27**) and Siemens P4 (compound **28**) four-circle diffractometers (graphite-monochromated Mo-Kα radiation λ = 0.71073 Å, 2θ / ω scan mode) with Cryostream open-flow N_2 gas cryostats.[21] The structures were solved by direct methods (SHELXS-86 programs)[22] and refined by full-matrix least squares against F^2 of all reflections with Chebyshev weighting scheme, using SHELXL-93 software.[23] Non-hydrogen atoms (except the disordered ones in **13**) were refined

Table 1. Crystal Data.

Compound	**13**	**27**	**28**
Formula	$C_{18}H_{16}FeOS_4$	$C_{14}H_{10}OS_8$	$C_{19}H_{18}FeOS_4$
M	432.40	450.70	446.42
Symmetry	triclinic	triclinic	monoclinic
a / Å	9.804(3)	6.431(9)	15.630(5)
b / Å	13.579(4)	10.84(2)	6.090(1)
c / Å	15.700(4)	13.47(2)	19.793(2)
α / °	102.59(2)	105.66(16)	90
β / °	106.32(2)	93.18(14)	93.24(2)
γ / °	108.09(2)	95.57(14)	90
U / Å^3	1797(1)	897(3)	1881.0(7)
Reflections / unit cell	24	25	24
θ range / °	13.6 - 14.4	13 - 15	14.1 - 14.3
T, K	150	150	150
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	4	2	4
D_c / g cm^{-3}	1.60	1.67	1.58
μ(Mo-Kα) / cm^{-1}	13.1	9.9	12.5
F(000)	888	460	920
Crystal size / mm	0.07x0.26x0.27	0.15x0.2x0.5[a]	0.08x0.11x0.6
max. 2θ / °	50	55	50
Data total	6420	4159	4353
Data unique	6129	3944	3317
R_{int}	0.025	0.076	0.087
Data observed[b]	4371	1264	2581
Absorption correction	Semi-empirical[c]	-	Analytical[d]
T_{min}: T_{max}	0.8212:1	-	0.8040:0.9195
Data used in l.s.	6124	3935	3313
$wR(F^2)$, all data	0.154	0.35	0.102
$R(F)$, observed data	0.042	0.086	0.037
No. of variables	437	209	298
Goodness-of-fit	1.04	1.58	0.92
$\Delta\rho_{max.}$, eÅ^{-3}	0.55	1.17	0.48
$\Delta\rho_{min.}$, eÅ^{-3}	-0.49	-1.57	-0.53

[a] Twinned crystal; [b] $F^2 > 2\sigma(F^2)$; [c] 108 ψ-scans of 3 reflections, TEXSAN software;[24] [d] 6 crystal faces were indexed, ABSPSI software.[25]

with anisotropic displacement parameters; all H atoms in 28 were refined in isotropic approximation, in 27 they were treated as 'riding', and in 13 the hydroxy H atoms were refined isotropically, others were treated as 'riding'. In 13 the C_5H_5 ring of molecule B is disordered over two positions with essentially equal occupancies (as shown by refinement); all atomic parameters were refined independently in isotropic approximation. Crystal data and experimental details are listed in Table 1; atomic coordinates and thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

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