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Frustrated Lewis Pairs

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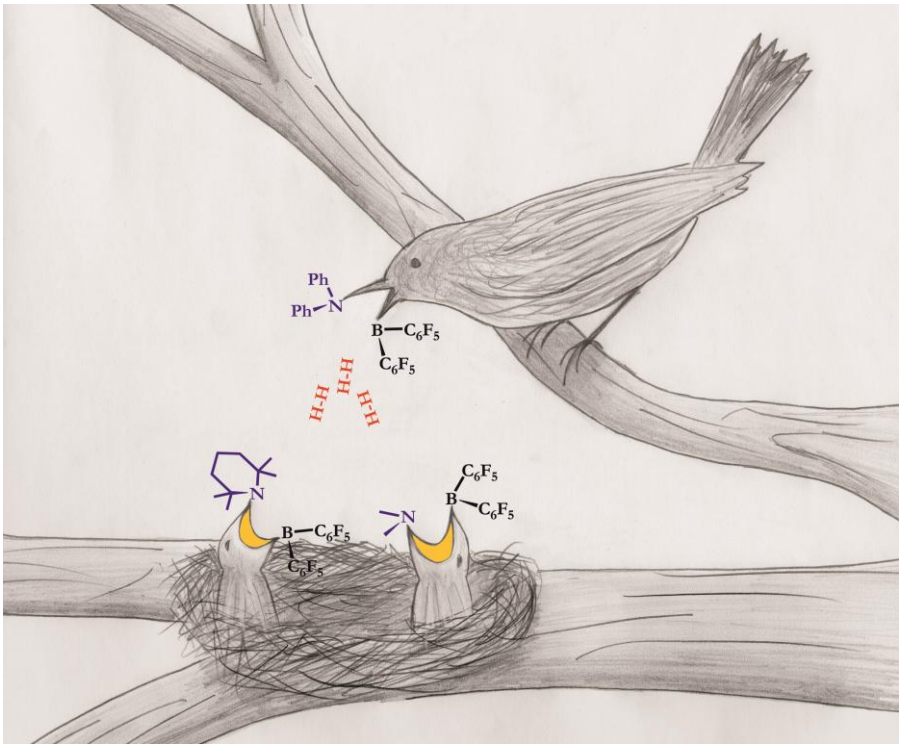

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COMMUNICATION

Novel H_2 activation by a tris[3,5-bis(trifluoromethyl)phenyl]borane frustrated Lewis pair†

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Tris[3,5-bis(trifluoromethyl)phenyl]borane (1, $BArF_{18}$), has been synthesised on a practical scale for the first time. According to the Gutmann–Beckett method it is a more powerful Lewis acid than $B(C_6F_5)_3$. It forms a 'frustrated Lewis pair' with 2,2,6,6-tetramethylpiperidine which cleaves H_2 to form a salt containing the novel anion $[\mu\text{-}H(BArF_{18})_2]^-$.

In recent years the concept and reactivity of "frustrated Lewis pairs" (FLPs) continues to develop apace.[1] Within these systems, dative bond formation is restricted by steric encumbrance about the donor and acceptor atoms which leads to 'unquenched' reactivity. This enables the activation of small molecules such as CO_2,[2] and importantly the heterolytic cleavage of H_2, which has led to application for the metal-free hydrogenation of polar organic substrates (*e.g.* nitriles and imines),[1e] and even the weak oxidant CO_2.[3] Typically, FLPs consist of an electrophilic borane (most commonly $B(C_6F_5)_3$ or derivatives thereof), whose Lewis acidity is promoted by electron-withdrawing substituents, in combination with a hindered phosphine or amine *e.g.* $^tBu_3P$ or 2,2,6,6-tetramethylpiperidine (TMP).

Tetraaryl borate anions $[B(C_6F_5)_4]^-$ and tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate, $[BArF_{24}]^-$, (Fig. 1) have widely gained use as weakly-coordinating counterions for reactive cationic metal centres (*e.g.* in homogeneous olefin polymerisation).[4] Their high stability in acidic and oxidative conditions is attributed to the electron-withdrawing properties of their F-substituents (which lower aromatic π-basicity and hence susceptibility towards electrophilic B–C bond cleavage), and the strength of their C–F bonds.[5] Remarkably, in view of the rich chemistry developed for $B(C_6F_5)_3$ [6] (which can be viewed as the Lewis acid 'parent' of $[B(C_6F_5)_4]^-$) only one report exists for the synthesis of the analogous tris[(3,5-trifluoromethyl)phenyl] borane ($BArF_{18}$), resulting from decomposition of the $[BArF_{24}]^-$ anion by the electrophilic platinum complex *trans*-$[(Ph_3P)_2Pt(Me)(OEt_2)]^+$.[7] Only X-ray crystallographic data

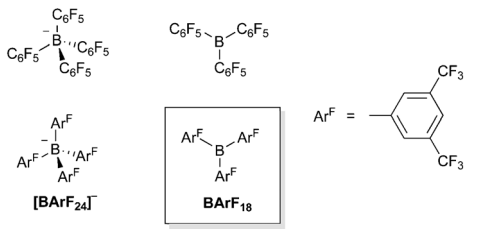
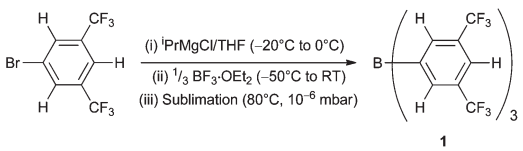


Fig. 1 Commonly used fluorinated aryl borates and their 'parent' Lewis acid boranes.



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Scheme 1 Synthesis of tris[3,5-bis(trifluoromethyl)phenyl]borane, (**1**).

was reported, and no subsequent reactivity studies have been conducted.

In continuation of our interest in FLP-H_2 activation chemistry, we herein report a practical synthesis of $BArF_{18}$ and communicate preliminary findings of its Lewis acidic properties and differing reactivity with H_2 in an FLP system, relative to $B(C_6F_5)_3$.

$Na[BArF_{24}]$ is synthesised *via* reaction of excess [3,5-bis-(trifluoromethyl)phenyl]MgX (X = Cl, Br) with $NaBF_4$ or $BF_3{\cdot}OEt_2$;[5a,8] we reasoned that $BArF_{18}$ should be an intermediate en route to the borate anion and decided to employ a rigid stoichiometry. Accordingly, the Grignard was generated *via* metal-halogen exchange of ^{i}PrMgCl and 1-bromo-3,5-bis-(trifluoromethyl)benzene in THF, which was subsequently reacted *in situ* with $BF_3{\cdot}OEt_2$ (3 : 1) (Scheme 1).[9] Facile work-up followed by high vacuum sublimation (80 °C, 1×10^{-6} mbar) afforded tris[3,5-bis(trifluoromethyl)phenyl]borane (**1**, $BArF_{18}$) in good yield (65–70%, 2–5 gram scale) as a free-flowing white powder (Scheme 1).‡ The reaction solvent appeared to be important; Grignard formation can also be conducted in Et_2O, yet metathesis with $BF_3{\cdot}OEt_2$ led to formation of $[BArF_{24}]^-$, as shown by ^{11}B NMR spectroscopy. It is thought the use of THF may retard the competitive addition of a fourth Grignard equivalent by coordinating to **1** as it is formed in solution; indeed the sublimation step is required to remove THF from the moderately labile adduct **1**·THF, which is the actual

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†Electronic supplementary information (ESI) available: Experimental details, X-ray crystallographic details for **2**·Et_2O, synthetic procedures and NMR spectral data for **1** and **2**, and free volume plots obtained from X-ray crystal structures of $C_5H_5N{\cdot}A$ (A = **1**, $B(C_6F_5)_3$). CCDC 868317. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30384a

product extracted immediately after the Grignard step, as evinced by ^{1}H, ^{19}F and ^{11}B NMR spectroscopy.

1 is practically insoluble in aliphatic hydrocarbons, moderately so in aromatic solvents and displays optimum solubility in CH_2Cl_2 or $CHCl_3$; this property contrasts with $B(C_6F_5)_3$ (soluble in most common non-donor media). This behaviour may be attributed to intermolecular H···F bond interactions between the *para* proton and CF_3 groups on neighbouring molecules in the solid-state for **1**; a distance of 2.63 Å is found in the reported crystal structure [sum of vdW radii, $r_w(F) + r_w(H) = 2.67$ Å], which would obviously be lacking for $B(C_6F_5)_3$.[7,10]

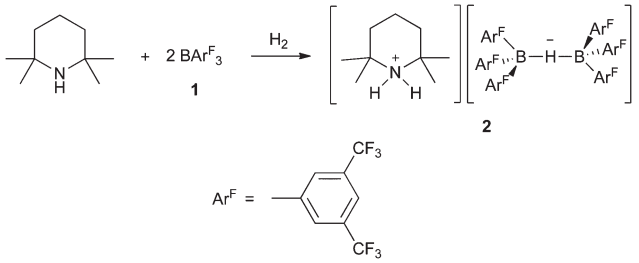
1 has been fully characterised by ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectroscopy; the latter shift (δ 68.1 ppm; CD_2Cl_2) lends support for a three-coordinate geometry in the solution-phase and is noticeably deshielded in comparison with that found for $B(C_6F_5)_3$ (δ 61.2 ppm; CD_2Cl_2). Whilst $B(C_6F_5)_3$ has been shown to be inert to pure oxygen at room temperature,[11] admission of dry O_2 to a CD_2Cl_2 solution of **1** led to rapid decomposition (numerous uncharacterisable resonances in the ^{1}H, ^{19}F and ^{11}B NMR spectra). Despite strongly electron-withdrawing CF_3 groups in **1** (rationalised to contribute to the observed oxidative stability of the $[BArF_{24}]^-$ anion), it is possible that the *ortho*-F substituents in $B(C_6F_5)_3$ are more important in suppressing reaction with O_2; the absence of this structural feature in **1** might then lead to the heightened reactivity observed for this trigonal borane in this case. Interestingly, H_2O reversibly forms the dative complex **1**·OH_2; the donor can be removed under vacuum or through addition of 3 Å molecular sieves in CH_2Cl_2 solution, in contrast with the tightly bound analogue $(C_6F_5)_3B{\cdot}OH_2$.[12]

In order to better understand the reactivity of **1**, Lewis acidity assessments were performed by employing the Gutmann–Beckett (Et_3PO probe; ^{31}P NMR) and Childs (*trans*-crotonaldehyde; ^{1}H NMR of H_3 resonance) methods; both rely on respective chemical shift differences ($\Delta\delta$) upon complexation of the probe to the Lewis acid, which is proportional to the Lewis acid strength of the acceptor site.[13] The results, compared with data acquired for $B(C_6F_5)_3$, are tabulated in Table 1. It can be seen that **1** displays a Lewis acidity *ca.* 6% greater than that for $B(C_6F_5)_3$ using the former method, which contrasts markedly with a *ca.* 38% reduction observed employing the Childs. A linear correlation is usually documented between methods,[14] although an increasing number of boron systems oppose this observation.[15] Notably, Britovsek *et al.* reported a non-linear trend for the series $B(C_6F_5)_{3-x}(OC_6F_5)_x$ (x = 1–3), where preference for Et_3PO binding over crotonaldehyde is observed as x increases.[15b] This was rationalised using Pearson's HSAB principle where the covalent (softer) C═O bond is a preferable donor to $B(C_6F_5)_3$ compared with the more ionic (harder) P═O bond, favoured by $B(OC_6F_5)_3$.

Table 1 ^{31}P and ^{1}H NMR spectral data derived for Lewis acidity measurements of **1** and $B(C_6F_5)_3$

	Et_3PO		*trans*-Crotonaldeyde	
Lewis acid	^{31}P NMR/ppm[a]	$\Delta\delta$/ppm[b]	^{1}H NMR/ppm[a]	$\Delta\delta$/ppm[c]
None	50.7	—	6.85	—
$B(C_6F_5)_3$	77.3	26.6	7.93	1.08
1	78.9	28.2	7.52	0.67

[a] CD_2Cl_2 at room temperature. [b] $\Delta\delta$ = [Et_3PO(coordinated) − Et_3PO-(CD_2Cl_2)]. [c] $\Delta\delta$ = [H_3(coordinated) − $H_3(CD_2Cl_2)$].



Scheme 2 Generation of **2** from heterolytic activation of H_2 by **1** and TMP.

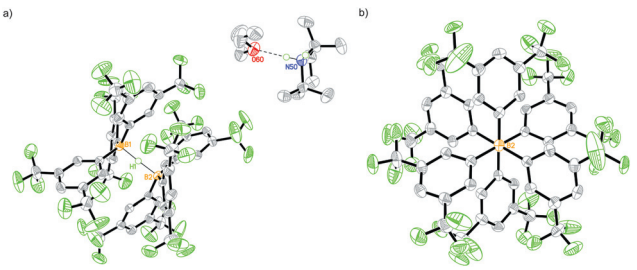


Fig. 2 (a) Diagram of **2**·Et_2O. H atoms (except attached to B and N) have been removed for clarity; thermal ellipsoids are shown at 50% probability. (b) View showing staggered geometry along the B2–H1–B1 axis.

Since Lewis acidity is a composite of both steric and electronic factors at the acceptor site, it would be useful to compare the steric profile of **1** with $B(C_6F_5)_3$; however, to date no solid-state structure of the latter has been reported. Fortunately the pyridine adducts, $C_5H_5N{\cdot}A$ (A = **1**, $B(C_6F_5)_3$), have been crystallographically characterised for both boranes in which both have virtually identical B–N bond lengths (1.63 Å, within e.s.u.), permitting valid comparison.[16] Excision of the pyridine ligand enabled a comparison of the relative free volume from the B centre, at a given radius, for the remaining pyramidalised borane fragments.† The results show that **1** is less hindered in the 2–4 Å region (*i.e.* that occupied by the pyridine molecule), as anticipated from the smaller size of the *ortho*-H in **1** relative to the *ortho*-F in $B(C_6F_5)_3$; in conjunction with the ^{11}B NMR spectroscopic data (an electronic probe at the B atom)[15a] this supports the Gutmann–Beckett assignment that **1** is more Lewis acidic than $B(C_6F_5)_3$.

Addition of **1** to 2,2,6,6-tetramethylpiperidine (TMP) in CD_2Cl_2 (1 : 1) demonstrated the formation of an FLP, as evidenced by unchanged resonances in the ^{1}H, ^{19}F and ^{11}B NMR spectra relative to the species in isolation. Subsequent admission of H_2 (1 atm) led to the rapid precipitation of a white solid, and ^{1}H NMR spectroscopy revealed exactly half of the initial TMP remained in solution, whereas ^{11}B NMR showed complete consumption of **1**, indicating complete sequestration of the borane. Elemental analysis of the solid was consistent with the molecular formula unit (**1**)$_2$(TMP)(H_2) (**2**, Scheme 2).‡ Remarkably, H_2 activation occurs even in Et_2O, and led to the generation of large single crystals suitable for study by X-Ray diffraction, which solved as the novel [TMPH][μ-H($BArF_{18}$)$_2$]·Et_2O (**2**·Et_2O; Fig. 2). The anion geometry approximates to D_3

symmetry, and the bridging borohydride unit is virtually linear (BĤB = 176.3°). The B–H bond lengths (1.40 and 1.42 Å) are similar to those for seen in Li[μ-H(BEt$_3$)$_2$] (1.376(6) Å)[17] yet distinct from [TMPH][H–B(C$_6$F$_5$)$_3$] (1.18(2) Å);[18] the longer bonds reflect the electron-deficient B–H–B interactions relative to terminal B–H. The aryl rings adopt an almost staggered conformation (torsion angles 58.7–61.5°). The [TMPH] cation shows H-bonding to an Et$_2$O molecule with N···O and H···O separations of 2.869(4) and 1.97 Å respectively, the N–H···O angle being *ca.* 178°. Evidently the ammonium ion binds the neutral O atom in preference to the charged borohydride anion. This is the first example of H_2 cleavage by an FLP to produce a bridging borohydride salt.

The only other example of arylborane-mediated H_2 activation in ethereal solvent is by the FLP (Fmes)$_2$BH/DABCO [Fmes = 2,4,6-tris(trifluoromethyl)phenyl, DABCO = diazobicyclo[2.2.2]-octane];[19] here the Lewis acidity remains unquenched because the steric bulk around the B centre in (Fmes)$_2$BH prevents Et$_2$O binding. In contrast, both **1** and B(C$_6$F$_5$)$_3$ coordinate Et$_2$O; **1**·OEt$_2$ is observable in Et$_2$O solution as shown in the ^{11}B NMR spectrum (δ 19.0 ppm), a shift indicative of four-coordinate boron. However, whilst B(C$_6$F$_5$)$_3$ forms a strong adduct that quenches FLP activity,[20] **1**·OEt$_2$ must dissociate sufficiently at ambient temperature to allow participation of **1** in H_2 heterolysis. This is analogous to the behaviour exhibited by the 2,6-dimethylpyridine/B(C$_6$F$_5$)$_3$ FLP, which cleaves H_2 only upon dissociation of the weakly-bound classical adduct.[21]

An unambiguous structural assignment of **2** by NMR spectroscopy was hampered by the insolubility of the compound in most non-donor media; only using 1,2-difluorobenzene at 80 °C (a solvent with a high dielectric constant reported to dissolve poorly soluble ionic salts)[22] was a ^{1}H NMR spectrum obtained that correctly reproduced the **1** : TMP ratio in **2**. Despite this, we were unable to observe any resonances in either the ^{1}H or ^{11}B NMR spectra which could be assigned to the B(μ-H)B unit in **2**. This property is reminiscent of the related [(C$_6$F$_5$)$_3$B(μ-H)B-(C$_6$F$_5$)$_3$] anion; here low temperature ^{1}H and ^{19}F NMR (<183 K) provided the only means of identification, with ^{11}B NMR unable to distinguish a B(μ-H)B environment.[23] IR spectroscopy of **2** and its deutero analogue, obtained from D_2 and TMP : **1** (1 : 2), also failed to unambiguously reveal a B–H(D) stretch.

On the other hand, dissolution occurred readily in pyridine-d$_5$ to give readily assignable ^{1}H (Fig. 3), ^{19}F and ^{11}B NMR spectra, which corresponded to the species [**1**·pyridine-d$_5$], [TMPH]$^+$, and the borohydride anion [**1**-H]$^-$ (1 : 1 : 1 ratio). The latter was cleanly resolved by a diagnostic terminal B*H* (1 : 1 : 1 : 1 quartet) in the ^{1}H NMR (δ = 4.53 ppm, $^1J_{11\text{-BH}}$ = 84 Hz), accompanied by an intense doublet in the ^{11}B NMR spectrum (δ = −7.2 ppm, $^1J_{11\text{-BH}}$ = 84 Hz). This confirms the composition of **2**, and reveals the behaviour of the anion in donor media as both a source of terminal borohydride [**1**-H]$^-$, and a labile equivalent of the Lewis acid **1**.

Conclusions

The facile synthesis of tris[3,5-bis(trifluoromethyl)phenyl] borane (**1**) has been achieved on a multi-gram scale. Gutmann–Beckett measurements indicate BArF$_{18}$ to be a stronger Lewis acid than the ubiquitous B(C$_6$F$_5$)$_3$, yet it appears to bind the oxygen donors H_2O and Et$_2$O more reversibly under comparable conditions. BArF$_{18}$ forms an FLP in the presence of TMP which reacts rapidly with H_2 to form the anion [μ-H(BArF$_{18}$)$_2$]$^-$ and has been crystallographically characterised. This is the first example of a bridging borohydride resultant from FLP-mediated H_2 heterolysis. Interestingly this reaction also proceeds in Et$_2$O, which is believed to be an example of a system operating on the classical/frustrated Lewis pair borderline. Current research is focusing on the use of different Lewis base partners whilst exploring catalytic hydrogenation chemistry of these FLP/H_2 protocols.

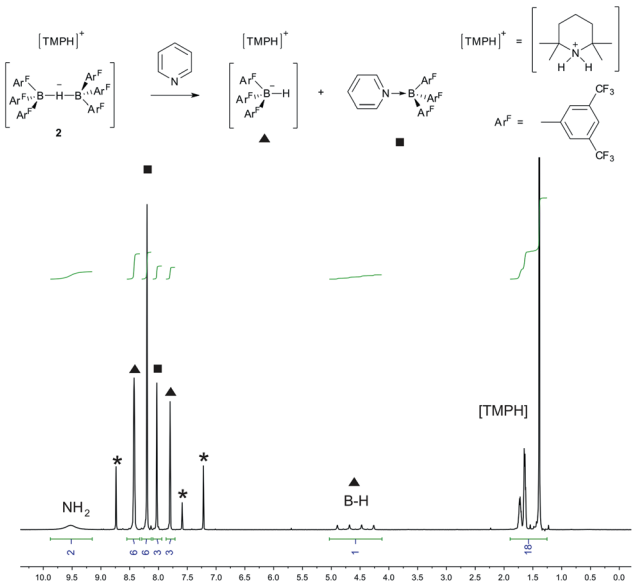


Fig. 3 ^{1}H NMR spectrum of **2** (pyridine-d$_5$). Solvent peaks denoted by *, ▲ and ■ denote **1**·pyridine-d$_5$ and [**1**-H]$^-$ respectively.

Acknowledgements

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Notes and references

‡Data for compound **1**: ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 8.24 (s, 3H, *para-H*), δ 8.02 (s, 6H, *ortho-H*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 101 MHz): δ 142.8 (s, br, *ipso-C*), δ 138.3 (s, *ortho-C*), δ 132.2 (q, $^2J_{CF}$ = 33.5 Hz, *meta-C*), δ 127.0 (s, *para-C*), δ 123.7 (q, $^1J_{CF}$ = 272.9 Hz, *C*F$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 376 MHz): δ −63.4 (s, *C*F$_3$). ^{11}B NMR (CD$_2$Cl$_2$, 128 MHz): δ 68.1 (s, br). HRMS (EI, *m*/*z*): for BC$_{24}$F$_{18}$H$_9$ Calcd: 650.0510. Found: 650.0510. IR (KBr, cm^{-1}): 1615 (m), 1607 (m), 1385 (m), 1283 (s), 1227 (m), 1169 (s), 1127 (s), 909 (m), 844 (w), 720 (m), 708 (w), 683 (m), 657 (m). Anal. Calcd for C$_{24}$H$_9$BF$_{18}$: C 44.34; H 1.40; N 0.00. Found: C 44.22; H 1.29; N 0.00.

Data for **2**: ^{1}H NMR (C$_6$H$_4$F$_2$, 400 MHz, 353 K): δ 7.84 (s, 6H, *para-H*), δ 7.73 (s, 12H, *ortho-H*), δ 4.00 (br, 2H, N*H*2), 1.57 (m, 2H, C*H*$_2$), 1.46 (m, 4H, C*H*$_2$), 1.23 (s, 12H, C*H*$_3$). IR (KBr, cm^{-1}): 3274 (m), 3234 (m), 3095 (m), 3034 (m), 2983 (m), 1616 (m), 1577 (w), 1459 (w),

1365 (s), 1279 (s), 1165 (s), 1126 (s), 900 (s), 841 (m), 710 (s), 682 (s), 649 (s). Anal. Calcd for $C_{57}H_{39}B_2F_{36}N$: C 47.43; H 2.72; N 0.97. Found: C 47.34; H 2.63; N 1.02.

Crystal data for **2**·Et_2O: $(C_{48}H_{19}B_2F_{36})(C_9H_{20}N)\cdot C_4H_{10}O$, M = 1517.63, triclinic, $P\bar{1}$ (no. 2), a = 12.0325(5), b = 15.7928(8), c = 17.3620(9) Å, α = 90.233(4), β = 92.367(4), γ = 100.933(4)°, V = 3236.4(3) Å^3, Z = 2, D_c = 1.557 g cm^{-3}, μ(Mo-Kα) = 0.164 mm^{-1}, T = 173 K, colourless tablets, Oxford Diffraction Xcalibur 3 diffractometer; 13 209 independent measured reflections (R_{int} = 0.0305), F^2 refinement, R_1(obs) = 0.0822, wR_2(all) = 0.2509, 7684 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 57°], 1009 parameters.

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