C–H Activation

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Enantiodivergent Desymmetrization in the Rhodium(III)-Catalyzed Annulation of Sulfoximines with Diazo Compounds

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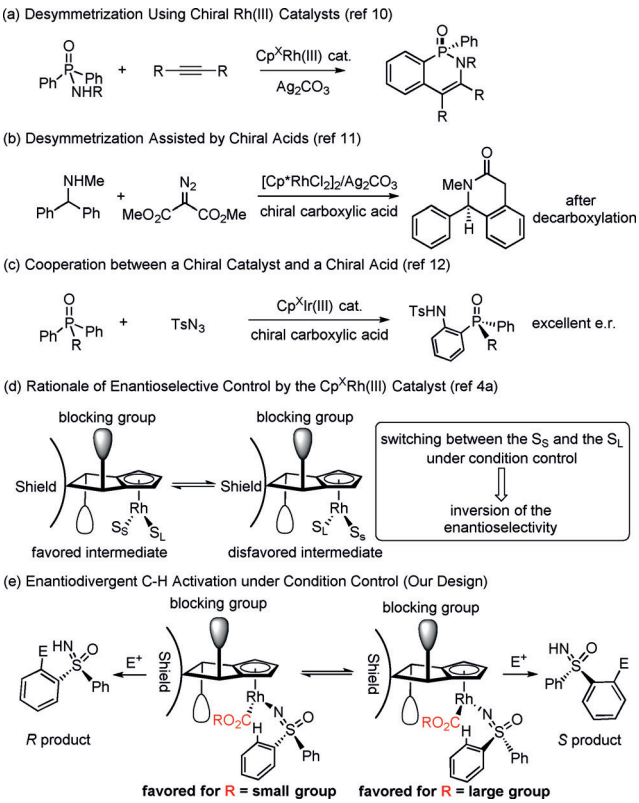
Abstract: *Rh^{III}- and Ir^{III}-catalyzed asymmetric C–H functionalization reactions of arenes have relied on the employment of chiral Rh^{III}/Ir^{III} cyclopentadienyl catalysts, the introduction of chiral carboxylic acids to achiral Cp^*RhX_2 catalysts, and the integration of both strategies. Despite considerable progress, each reaction only provided a specific configuration of the enantioenriched product when using a particular chiral catalyst. Reported in this work is the enantiodivergent coupling of sulfoximines with various diazo compounds by Rh^{III}-catalyzed desymmetrizing annulation. The enantiodivergence was enabled by a judicious choice of achiral carboxylic acids, and the enantioselectivity correlates with the steric bias of the carboxylic acid and the sulfoximine.*

Over the past decades, metal-catalyzed arene C–H activation has been established as a step- and atom-economic strategy to access various value-added products.[1] Cyclopentadienyl complexes of M^{III} (M = Co, Rh, and Ir) have stood out as highly efficient catalysts for the C–H functionalization of diverse arenes.[2] While most of these catalytic processes have been conducted using commercially available Cp^*MX_2-type catalysts, metal catalysts bearing other cyclopentadienyl ligand serve well in regulating the selectivity of the C–H functionalization.[2k,3] The groups of Cramer and You have made significant contributions towards the development of Rh and Ir catalysts stabilized by C_2-symmetric cyclopentadienyl ligands,[4] which enabled the enantioselective C–H activation of arenes and their functionalization with unsaturated coupling partners. Ward, Rovis, and Hyster took a different approach by using an achiral rhodium complex conjugated to a biotin tag.[5] Recently, Antonchick, Waldmann, and co-workers developed an enantioselective cycloaddition of imino esters to fulvenes for the synthesis of chiral cyclopentadienyl ligands and the corresponding Rh^{III} catalysts.[6] Very recently, Perekalin and co-workers applied a reduction/nucleophilic addition approach to rhodium fulvene complexes to access planar-chiral Cp^XRh^{III} catalysts.[7] In these asymmetric catalytic systems, the stereodetermining process is the C–H activation (in desymmetrization), the migratory insertion process,[4a,b,8] or the reductive elimination.[9]

With regard to desymmetrization, Cramer and Sun reported an oxidative [4+2] annulation between phosphinamides and alkynes[10] where the desymmetrization was enabled by a chiral Cp^XRh^{III} catalyst (Scheme 1a). In principle, the desymmetrizing C–H activation of an arene may be realized by using an achiral Rh^{III} catalyst and a chiral carboxylic acid where the chiral carboxylic acid renders the Rh^{III} center chiral in a CMD mechanism. Indeed, this scenario was elegantly realized by the group of Lin, Yishino, and Matsunaga (Scheme 1b).[11] On the other hand, Cramer and co-workers realized a desymmetrizing amidation of phosphine oxides by making use of the cooperative effect of a chiral catalyst and a chiral acid (Scheme 1c).[12] In all of these systems, each reaction only led to a specific configuration of the enantioenriched product when a fixed chiral



Scheme 1. Desymmetrization of arenes with Rh^{III} and Ir^{III} catalysts.

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catalyst/chiral additive was used, which will limit the synthetic applications.

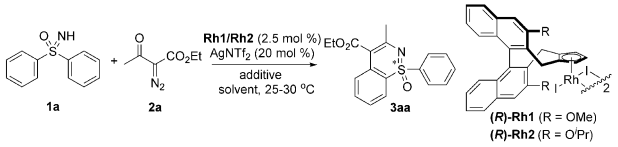
The effectiveness of the Cramer-type Cp^XRh^{III} chiral catalysts has been ascribed to their unique structure, which orients the incoming substrates/additives.[4a] In a typical perspective view of the metal intermediate (Scheme 1 d), the left section is shielded by an *R*-configured binaphthyl backbone, and the top front and the bottom back sections are blocked by the 2- and 2′-substituents, respectively, which orients the large substrate (S_L) distal to the bottom blocking group. We reasoned that in desymmetrizing C–H activation, the steric bulk of the carboxylic acid should have a direct impact on the stereochemical outcome. By increasing the steric hindrance of the acid, the ligated arene may be switched from S_L to S_S, which in turn inverts the enantioselectivity as C–H activation is the stereochemistry-determining step in this process (Scheme 1 e). We herein report an enantiodivergent annulation of sulfoximine and diazo compounds[13] by Rh^{III}-catalyzed desymmetrizing C–H activation where the enantiodivergence was enabled by a judicious choice of the carboxylic acid additive (Scheme 1 e).

We initiated our investigation by optimizing the coupling of the sulfoximine **1a** and ethyl diazo acetylacetate using **Rh1** as the chiral catalyst (Table 1). The coupling was sluggish in the absence of any acid additive. The reaction proceeded smoothly with AcOH as the additive to give the desired product in excellent yield with 95.5:4.5 e.r. (entry 1). The stereoselectivity only slightly varied when un- or monosubstituted benzoic acid was used (entries 2–4). Pleasingly, an optimal e.r. of 98:2 was recorded when 2-methoxybenzoic acid was introduced (conditions A, entry 5). Indeed, the e.r. generally decreased or was even inverted when a sterically hindered benzoic acid was applied, as in the case of various 2,6-disubstituted benzoic acids (entries 8–22). Although the electronic effect of the acid is also convoluted, there is no direct correlation of this effect with the enantioselectivity of the reaction. An optimal inversion of enantioselectivity (7:93) was realized when 2,6-dimethoxybenzoic acid was applied in the less polar solvent TCE (entry 19, conditions B). This outcome is in line with our rationale, and the weak ionizing ability of the TCE solvent disfavors dissociation of the carboxylic acid group. It should be noted that the switch in selectivity was dominated by the acid additive rather than the solvent because conducting this reaction with 2,6-dimethoxybenzoic in MeOH still gave an e.r. of 12.5:87.5 (entries 6 and 20). The effect of the Rh^{III} catalyst was also briefly examined. The reaction with **Rh2** under conditions A only afforded moderate enantioselectivity (entry 7). In contrast, the reaction efficiency and the enantioselectivity were essentially unaffected when **Rh1** was replaced with **Rh2** under conditions B (entry 21). Despite the small set of Rh^{III} catalysts, the inversion in enantioselectivity using different benzoic acids was quite remarkable.

With optimized reaction conditions in hand, we next examined the scope and generality of this coupling system (Scheme 2). A broad scope of sulfoximines bearing various electron-donating (^{t}Bu and OMe), -withdrawing (ester, CN, and CF_3), and halogen (F, Cl, and Br) substituted were coupled with diazo reagent **2a** in generally good to excellent yields under conditions A. The reaction also tolerated *ortho*-Me and -F substituents (**3la**, **3ma**). Aside from the C–H activation of benzene rings, a thiophene ring was also activated (**3pa**). In most cases, the e.r. was greater than 95:5. X-ray crystal structure analysis of **3ea** allowed for the determination of the absolute configuration of the products.[14]

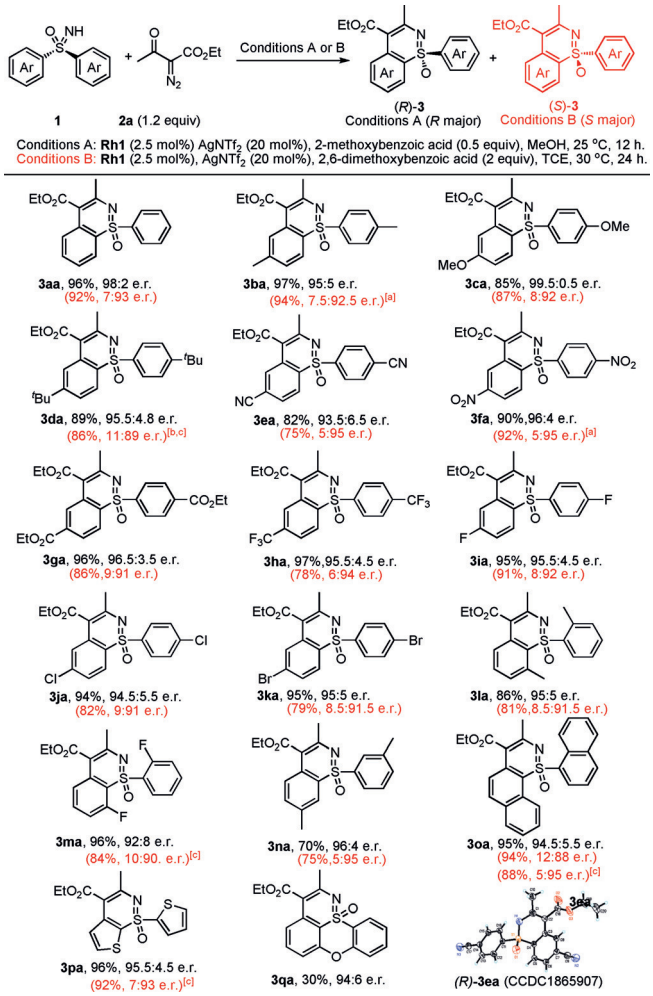
The diazo substrate was successfully extended to other substitutions and other classes (Scheme 3). Slightly lower enantioselectivities were observed when the ethyl ester was changed to a bulky ester group (**3ac**–**3ae**, typically 94.5:5.5 e.r.). Moreover, closely comparable e.r. values were also reached in the reactions of other ethyl diazo acylacetates and in those of α-diazo 1,3-diketones (**3af**–**3aj**). Extension of the diazo reagent to α-diazo arenesulfonyl ketones also proved successful, and good to excellent e.r. values were achieved regardless of the electronic effect of the *para*-substituted arenesulfonyl groups (**3ak**–**3ap**). The couplings of different sulfoximines and α-diazo keto esters generally proceeded with good to excellent enantioselectivities, with the e.r. ranging from 4.5:95.5 to 12:88. The enantioselectivity

Table 1: Optimization studies.[a]

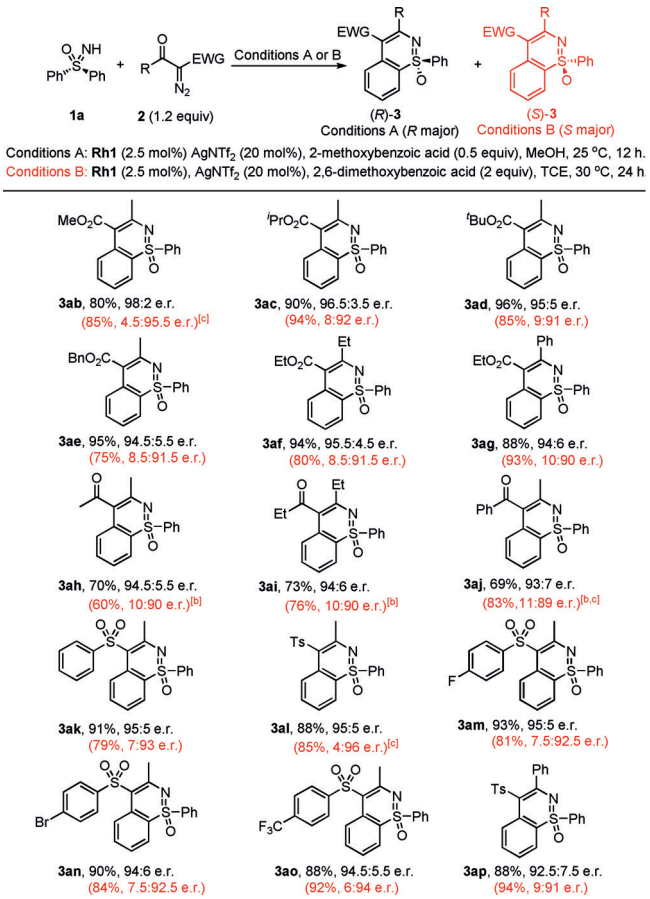


Entry	Rh	Additive (1.0 equiv)	Solvent	Yield[b] [%]	e.r.[c]
1[d]	**Rh1**	HOAc	MeOH	94	95.5:4.5
2[d]	**Rh1**	$PhCO_2H$	MeOH	88	94:6
3[d]	**Rh1**	2-$MeC_6H_4CO_2H$	MeOH	87	96.5:3.5
4[d]	**Rh1**	2-$NO_2C_6H_4CO_2H$	MeOH	86	95:5
5[d,f]	**Rh1**	2-$OMeC_6H_4CO_2H$	MeOH	95	98:2
6[d,f]	**Rh1**	2-$OMeC_6H_4CO_2H$	DCE	80	82.5:17.5
7[d,f]	**Rh2**	2-$OMeC_6H_4CO_2H$	MeOH	93	78:22
8[d]	**Rh1**	$MesCO_2H$	MeOH	68	39:61
9[e]	**Rh1**	$MesCO_2H$	DCM	85	22:78
10[e]	**Rh1**	2,4,6-$^i Pr_3C_6H_2CO_2H$	DCM	79	22.5:77.5
11[e]	**Rh1**	2,6-$Me_2C_6H_3CO_2H$	DCM	85	19:81
12[e]	**Rh1**	2,6-$F_2C_6H_3CO_2H$	DCM	85	54:46
13[e]	**Rh1**	2,6-$Cl_2C_6H_3CO_2H$	DCM	88	12:88
14[e]	**Rh1**	2,6-$Br_2C_6H_3CO_2H$	DCM	84	13:87
15[e]	**Rh1**	2,6-$I_2C_6H_3CO_2H$	DCM	79	18:82
16[e]	**Rh1**	2,6-$(CF_3)_2C_6H_3CO_2H$	DCM	79	15:85
17[e]	**Rh1**	2,6-$(NO_2)_2C_6H_3CO_2H$	DCM	72	7:93
18[e]	**Rh1**	2,6-$(OMe)_2C_6H_3CO_2H$	DCE	94	8:92
19[e,g]	**Rh1**	2,6-$(OMe)_2C_6H_3CO_2H$	TCE	92	7:93
20[e,g]	**Rh1**	2,6-$(OMe)_2C_6H_3CO_2H$	MeOH	92	12.5:87.5
21[e,g]	**Rh2**	2,6-$(OMe)_2C_6H_3CO_2H$	TCE	90	7:93
22[e,g,h]	**Rh1**	2,6-$(OMe)_2C_6H_3CO_2H$	TCE	63	7:93

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), Rh catalyst (2.5 mol%), $AgNTf_2$ (20 mol%), and an acid additive in the indicated solvent (2.0 mL) under N_2 atmosphere, 12 h. [b] Yield of isolated product after purification by column chromatography. [c] Determined by HPLC analysis on a chiral stationary phase. [d] At 25 °C. [e] At 30 °C. [f] With 0.5 equiv of acid. [g] With 2.0 equiv of acid. [h] With Ag_2SO_4 instead of $AgNTf_2$. The e.r. gives the *R*/*S* ratio. DCE = 1,2-dichloroethane, DCM = dichloromethane, NTf_2^- = bis(trifluoromethanesulfonyl)imide, TCE = 1,1,2,2-tetrachloroethane.



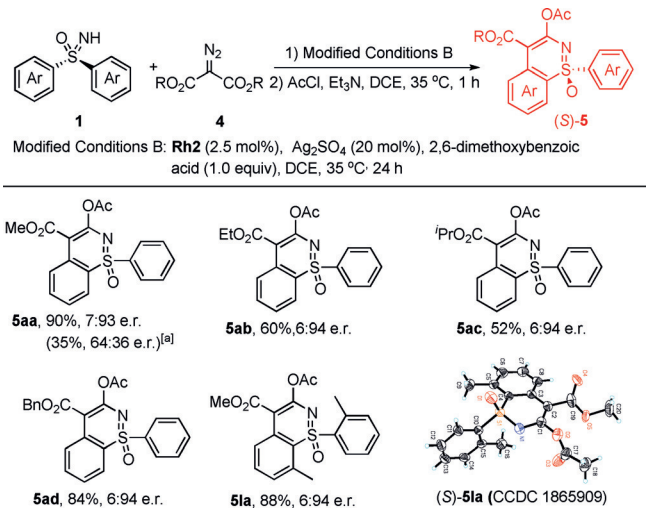
Scheme 2. Sulfoximine scope of the desymmetrization. [a] DCE instead of TCE. [b] MeOH instead of TCE. [c] **Rh2** instead of **Rh1**. The e.r. gives the *R*/*S* ratio.



Scheme 3. Diazo substrate scope of the desymmetrizing annulation. [a] DCE instead of TCE. [b] MeOH instead of TCE. [c] **Rh2** instead of **Rh1**. The e.r. gives the *R*/*S* ratio. Ts = tosyl.

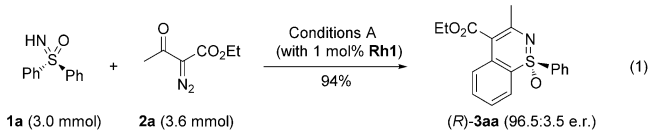
tended to be lower when sterically hindered sulfoximines were used (**3la**, **3ma**, **3oa**), possibly owing to the less pronounced steric bias between the 2,6-dimethoxybenzoate group and these sulfoximines. In certain cases, the **Rh2** catalyst outperformed the **Rh1** analogue, possibly owing to the enhanced steric effect of the O*i*Pr group (**3ab**, **3aj**, **3al**, **3da**, **3ma**, **3oa**, and **3pa**).

The high enantioselectivity was maintained over a broad range of other diazo compounds. Thus α-diazo 1,3-diketones and α-diazo arenesulfonyl ketones were also effective substrates (**3ah**–**3ap**), affording the annulation products in comparably high or even slightly higher enantioselectivity. In line with the slightly lower enantioselectivity for the α-diazo β-diketones under conditions A, the inverted selectivity was also attenuated under conditions B (**3ah**–**3aj**). This high *S* selectivity was maintained for the coupling of sulfoximines and α-diazo malonates under modified conditions B using **Rh2** as the catalyst (Scheme 4). With Ag_2SO_4 as an additive in DCE, the reaction proceeded to give a (metastable) phenol intermediate, acetylation of which afforded the ester product in consistently high enantioselectivity (typically 6:94 e.r.).

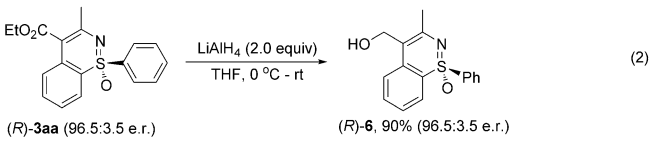


Scheme 4. Diazo malonates in the C–H activation/desymmetrization reaction. See the Supporting Information for detailed reaction conditions. [a] Reaction conditions: **1** (0.2 mmol), **4** (0.24 mmol), **Rh2** (2.5 mol%), Ag_2SO_4 (20 mol%), HOAc (2.0 equiv) in DCE at 35 °C for 30 h, followed by the acylation step. The e.r. gives the *R*/*S* ratio.

The synthetic applications of this system were briefly evaluated. (*R*)-**3aa** was synthesized on 3 mmol scale, even at a reduced loading (1 mol%) of the **Rh1** catalyst, in excellent yield and 96.5:3.5 e.r. [Eq. (1)]. Reduction of the ester group in **3aa** afforded alcohol **6** with no erosion of the enantiopurity [Eq. (2)].

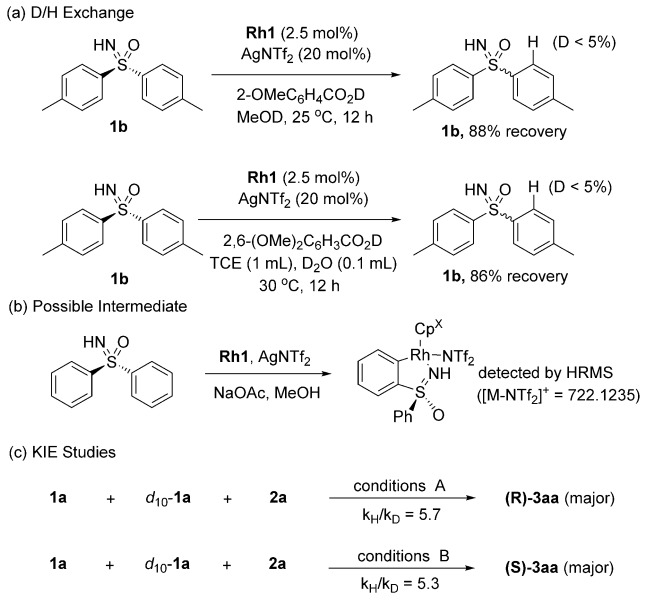


(1)



(2)

Several reactions were performed to explore the reaction mechanism. This system very likely follows a C–H activation pathway on the basis of the racemic coupling system reported by Bolm and Cheng.[13a] H/D exchange studies with arene **1b** under both conditions A and B also revealed < 5% D incorporation (Scheme 5a), which suggests that the C–H activation process is irreversible. Furthermore, HRMS analysis suggested the formation of a rhodacyclic species in the reaction of the **Rh1** catalyst and sulfoximine **1a** (Scheme 5b). To better understand the C–H activation process, kinetic isotope effects (KIEs) were also measured in intermolecular competition experiments, using **1a** and **1a**-d_{10} and diazo substrate **2a** under both conditions A and B (Scheme 5c). In both cases, a large KIE was obtained, indicating that the C–H bond cleavage is probably turnover-limiting. In addition, these comparable KIE values may also suggest that the mechanisms of the C–H activation processes are similar. The coupling system is proposed to follow acid-dependent enantioselective C–H activation, followed by carbene formation and migratory insertion of the Rh–aryl bond into the resulting carbene species, leading to alkylation. Subsequent nucleophilic condensation furnishes the [4+2] product.[13]



Scheme 5. Mechanistic analysis of the C–H activation step and KIE experiments.

In summary, we have realized an enantiodivergent [4+2] annulative coupling of sulfoximines and diazo compounds by Rh^{III}-catalyzed desymmetrizing C–H activation. The reaction proceeded in good to excellent enantioselectivity for a broad scope of sulfoximines, with several classes of diazo compounds being viable substrates. The enantioselectivity of the reaction seems to be correlated to the steric bias between the benzoic acid additive and the arene substrate. The inversion of enantioselectivity achieved by simply switching the achiral carboxylic acid additive is rare and may find important applications in the development of stereodivergent C–H activation systems.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: asymmetric C–H activation · desymmetrization · enantiodivergence · rhodium · sulfoximes

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[14] CCDC 1865907 and 1865909 (**3ea** and **5la**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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