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Ullmann coupling reaction of 1,3-bistriflate esters of calix[4]arenes: facile syntheses of monoaminocalix[4]arenes and 4,4′:6,6′-diepithiobis(phenoxathiine)

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Abstract—Treatment of 1,3-bistriflate esters of thiacalix- (**6a**) and calix[4]arenes **6b** with benzylamine in the presence of CuI and K_3PO_4 results in the displacement of a TfO moiety with a benzylamino group, which provides an easy access to monoaminothiacalix[4]arene **4a** and its methylene-bridged counterpart **4b**. On the other hand, the reaction of **6a** in the absence of benzylamine leads to intramolecular dietherification, giving 4,4′:6,6′-diepithiobis(phenoxathiine) **7a**.

Calix[4]arenes are one of the most important molecular scaffolds in supramolecular chemistry.[1] A variety of sophisticated molecular hosts have been prepared by introducing substituents into the calixarene skeleton via the etherification or esterification of the hydroxy groups and/or the electrophilic substitution on the aromatic nuclei. However, the replacement of the hydroxy groups with other functions by cleaving the aryl-oxygen bonds is quite difficult particularly in the case of calixarenes with a small ring size because of the steric hindrance arisen from the sterically crowded cyclic structure, beside the poor nucleofugacity of the hydroxy group and the resonance-stabilized double-bond character of the aryl-oxygen linkage.[2] Although the C–O bond cleavage reactions of aryl triflates or other esters by using palladium or nickel catalysts, such as the Suzuki–Miyaura[3] and Migita–Kosugi–Stille coupling reactions,[4] are one of the most reliable ways for the displacement of the phenolic hydroxy group, such reactions have been applied in vain to calix[4]arenes,[5] with an exception of the recent report by Georghiou and co-workers, in which the Sonogashira coupling reaction of 1,3-bistriflate ester **6b** successfully afforded 1,3-dialkynylcalix[4]arenes.[6] We have been engaged in the development of novel functions of thiacalixarenes (e.g., **1a**), which have epithio linkages instead of the methylene bridges in the conventional calixarenes.[7] Recently, we succeeded in the synthesis of tetraaminothiacalix[4]arene **2** via a chelation-assisted nucleophilic aromatic substitution (S_NAr) reaction of the *rtct* stereoisomer[8] of tetra-*O*-methylsulfinylcalix[4]arene **3** with lithium benzylamide, followed by the debenzylation of the resulting tetra(benzylamino)sulfinylcalix[4]arene and the successive reduction of the sulfinyl functions.[9] In the solvent extraction experiment, while thiacalixarene **1a** extracted a variety of soft to intermediate metal ions, tetraaminothiacalixarene **2** selectively extracted the softest metal ions, gold and palladium,[10] owing to the softer nature of the amino nitrogen than the hydroxy oxygen to bind metal ions. This observation brought about further interest in the complexation ability of partially aminated thiacalixarenes toward metal ions. In this regard, we have found that mono- (**4a**) and 1,3-diaminothiacalixarenes **5a** can be prepared by applying the S_NAr protocol to another stereoisomer (*rctt*) of **3**.[11] As for the methylene-bridged counterparts, Biali and co-workers reported a method for the preparation of monoaminocalixarene **4b** via the oxidation of **1b** to a spirodienone derivative, followed by the imination of the carbonyl group with hydrazine and the subsequent rearomatization of the resulting Schiff base with Pd/C.[2c] Shinkai and co-workers succeeded in the preparation

Keywords: Ullmann coupling reaction; Aminocalixarenes; Intramolecularly-bridged calixarene.
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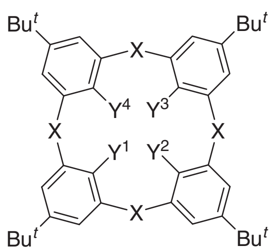
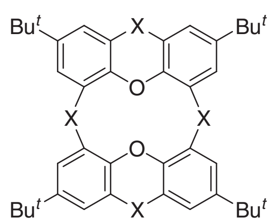
of 1,3-diaminocalixarene **5b** by the reaction of 1,3-bis(diethylphosphate) ester of **1b** with potassium amide in liquid ammonia using HMPA as a cosolvent.[2b] However, these methods require many steps and suffer from low yields. Therefore, the development of an alternative method for introducing amino substituents to the lower rim (narrow rim) is highly desirable. Herein, we wish to report a novel synthetic route to monoaminothiacalix[4]arene **4a**, as well as its methylene-bridged counterpart **4b**, by using an Ullmann-type amination[12] of 1,3-bistriflate esters **6** with benzylamine as a key step. Also reported is an Ullmann-type intramolecular etherification of **6a**, which provides an easy access to phenoxathiine-type thiacalixarene **7a**.



	X	Y^1	Y^2	Y^3	Y^4
1a	S	OH	OH	OH	OH
1b	CH_2	OH	OH	OH	OH
2	S	NH_2	NH_2	NH_2	NH_2
3	SO	OMe	OMe	OMe	OMe
4a	S	NH_2	OH	OH	OH
4b	CH_2	NH_2	OH	OH	OH
5a	S	NH_2	OH	NH_2	OH
5b	CH_2	NH_2	OH	NH_2	OH
6a	S	OTf	OH	OTf	OH
6b	CH_2	OTf	OH	OTf	OH



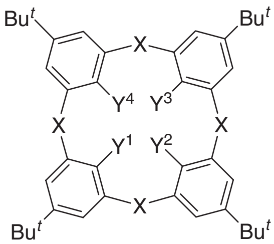
7a X=S
7b X=CH_2

Prerequisite 1,3-bistriflate **6a** was obtained in 85% yield by the treatment of thiacalix[4]arene **1a** with 3.0 mol equiv of trifluoroacetic anhydride in the presence of pyridine in dichloromethane at room temperature.[13] The amination of **6a** was first examined by using 2.4 mol equiv of benzylamine and an excess of CuI in refluxing toluene, varying a base (Table 1).[14] While Hunig's base, 1,4-diazabicyclo[2.2.2]octane (DABCO) and imidazole did not afford any products in meaningful yields under the conditions, K_3PO_4 gave monoamine **8a** together with bis(phenoxathiine) **7a**, 1,2-bistriflate **10a** and a certain number of other byproducts, exhausting substrate **6a** (entry 1). One reason for the complexity of the reaction products is that the Tf moieties of **6a** intra- and intermolecularly migrate under the basic conditions.[15] A carbonate, Cs_2CO_3, was also effective, giving **8a** in 22% yield (entry 2). Lowering the reaction temperature to 80 °C caused prolongation of the reaction time but improved the yield of **8a** to 32% at the expense of bis(phenoxathiine) **7a** and 1,2-bistriflate **10a** (entry 3). Therefore, the reaction conditions employed in entry 3 were adopted as the standard thereafter. When the reaction was carried out either in THF at reflux or in DMF or DMSO at 80 °C, monotriflate **9** and reduced product **12** formed predominantly (entries 4–6). Reducing the amounts of the reagents somewhat increased the yield of **8a** (entry 7). The reaction of methylene-bridged calix[4]arene **6b** was somewhat sluggish but gave monoamine **8b** in a good yield (entries 8 and 9). It should be noted that the treatment of monotriflate **9**, 1,2-bistriflate **10a**,[15] and dimethyl ether (**11**) of 1,3-bistriflate **6a** with benzylamine under the standard conditions resulted in no reaction. On the other hand, bis(phenoxathiine) **7a** was obtained as a main product in 68% yield by the reaction of bistriflate **6a** conducted at reflux in the absence of benzylamine,[16] while the same treatment of **6b** did not improve the yield of bis(xanthene) **7b** (3%). Also attempted were the reactions of **6a** with lithium amide, acetamide, and *p*-toluenesulfonamide with the intention of developing an easier access to free amine **4a** without the need of debenzylation (vide infra) but they did not afford any aminated products under the standard conditions.

Table 1. Amination of 1,3-bistriflates **6**

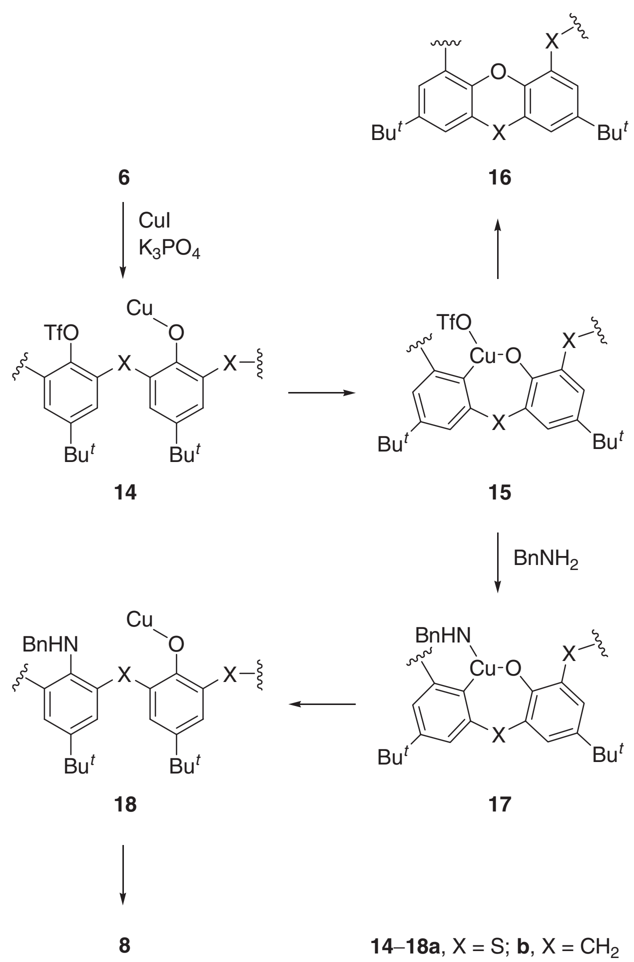
Entry	Substrate	$BnNH_2$ (mol equiv)	CuI (mol equiv)	Base (mol equiv)	Solvent	Temperature [time (h)]	Yield[a] (%)		
							8	**7**	**10**
1	**6a**	2.4	6.0	K_3PO_4 (4.0)	Toluene	Reflux (6)	24	11	35
2	**6a**	2.4	6.0	Cs_2CO_3 (4.0)	Toluene	Reflux (6)	22	23	4
3	**6a**	2.4	6.0	K_3PO_4 (4.0)	Toluene	80 °C (15)	32	3	6
4[b]	**6a**	2.4	6.0	K_3PO_4 (4.0)	THF	Reflux (1)	8	9	8
5[c]	**6a**	2.4	6.0	K_3PO_4 (4.0)	DMF	80 °C (1)	12	3	2
6[d]	**6a**	2.4	6.0	K_3PO_4 (4.0)	DMSO	80 °C (1)	8	6	4
7	**6a**	1.2	2.2	K_3PO_4 (2.0)	Toluene	80 °C (15)	43	4	16
8[e]	**6b**	1.2	2.2	K_3PO_4 (2.0)	Toluene	80 °C (36)	60	1	—
9	**6b**	2.0	4.0	K_3PO_4 (4.0)	Toluene	80 °C (18)	73	—	—

[a] Isolated yield.
[b] Compounds **9** (24%) and **12** (24%) were also isolated.
[c] Compounds **9** (14%) and **12** (28%) were also isolated.
[d] Compounds **9** (21%) and **12** (40%) were also isolated.
[e] Compound **13** (8%) was also isolated.



	X	Y^1	Y^2	Y^3	Y^4
8a	S	NHBn	OH	OTf	OH
8b	CH_2	NHBn	OH	OTf	OH
9	S	OTf	OH	OH	OH
10a	S	OTf	OTf	OH	OH
10b	CH_2	OTf	OTf	OH	OH
11	S	OTf	OMe	OTf	OMe
12	S	H	OH	OTf	OH
13	CH_2	OTf	OTf	OTf	OH

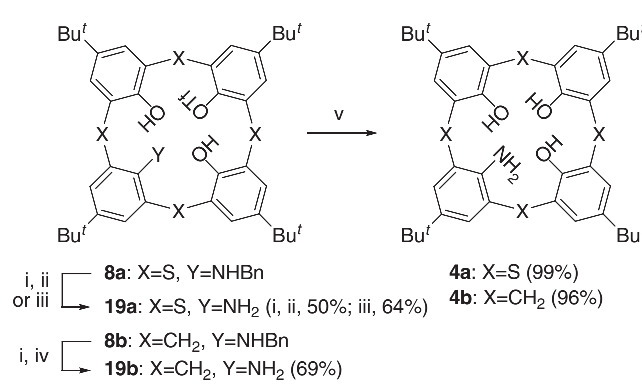
Based on these observations, a feasible reaction mechanism is depicted in Scheme 1. A phenoxy oxygen of bistriflate **6** ligates to a copper ion to form copper complex **14**, which facilitates the oxidative addition of an adjacent aryl–OTf bond to the metal center. This coincides with the fact that hydroxy-protected 1,3-bistriflate **11** underwent neither the amination nor the intramolecular cyclization (vide supra). Resulting metalacycle **15** may reductively eliminate phenoxathiine or xanthene **16**; metalacycle **15a** having epithio linkages exhibited a higher tendency to eliminate cyclic compound **16** than methylene-bridged analog **15b**. Although the reason is not clear at present, the larger ring size of the thiacalixarene macrocycle than that of the conventional calixarene may reduce a steric strain caused by the ring closure.[17] Another reaction path of **15** is the ligand exchange with benzylamine to form another metalacycle **17**, which is followed by the reductive elimination of the aminated product from metal center (**18**). In the presence of benzylamine, this reaction path is more favorable than the cyclization to predominantly afford amine **8** after aqueous workup. This agrees with the observation that lowering the reaction temperature improved the yield of amine **8a** at the expense of bis(phenoxathiine) **7a** (vide supra). Therefore, it may be concluded that the formation of copper complex **14** enables otherwise difficult oxidative addition of the Ar–OTf bond of calix class compounds. However, it is apparent that the presence of an adjacent hydroxy group to the TfO moiety is important but not sufficient to cleave the Ar–OTf bond, considering the fact that monotriflate **9**, as well as 1,2-bistriflate **10a**, underwent neither the amination nor the intramolecular cyclization (vide supra). In addition, it should be noted that monoamines **8** did not undergo further amination in spite of possessing of the hydroxy groups adjacent to the TfO moiety. It is easily conceivable that the two adjacent hydroxy groups or hydroxy and amino groups of these compounds will ligate to a copper ion to form a stable chelated complex. However such a complex will not be active enough to further the reaction because the metal center resides too apart from the aryl–OTf bond to insert into the covalent bond.



Scheme 1.

Compounds **8** were debenzylated to give free amines **19** according to our previously reported procedure,[9] that is, the initial bromination of benzylamine **8**, followed by spontaneous dehydrobromination to the corresponding imine and subsequent acidic hydrolysis (Scheme 2). Alternatively, deprotection of **8a** could be achieved by refluxing the compound with conc. HCl in THF with somewhat improved yield. Alkaline hydrolysis of the resulting amino esters **19** gave desired monoamines **4a** and **4b** in total yields of 23% and 47%, respectively, staring from commercially available compounds **1**. The yields of the monoamines have greatly improved as compared with those achieved by the reported procedures.[2c,11]

It has been reported that the thermal dediazoniation of a diazonium salt of monoaminocalix[5]arene afforded a



Scheme 2. Reagents and conditions: (i) NBS, BPO, benzene, reflux; (ii) 2 M HCl, $CHCl_3$, room temp; (iii) concd HCl, THF, reflux; (iv) 6 M HCl, $CHCl_3$, reflux; (v) 2 M NaOH, THF–EtOH (1:1), reflux.

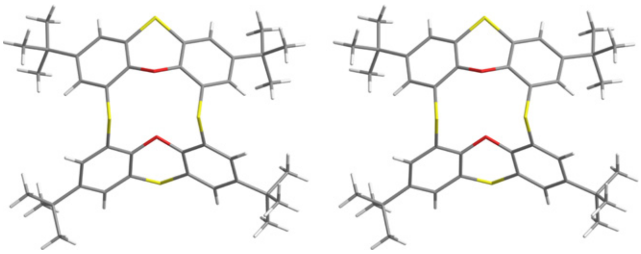


Figure 1. Stereoview of the X-ray structure of bis(phenoxathiine) **7a**.

xanthene-type compound, xanthenocalix[5]arene, by an intramolecular cyclization between the in situ-generated phenyl cation and an adjacent hydroxy group.[18,19] Xanthenocalix[6]arene[20] and alkoxy group-incorporated xanthenocalix[5], [6], and [8]arenes[21] have also been prepared from spirodienone derivatives of the corresponding calix[*n*]arenes. As for the intramolecularly cyclized phenoxathiine-type thiacalixarene, however, bis(phenoxathiine) **7a** has only been obtained as a byproduct in the base-catalyzed rearrangement of 1,3-bistriflate **6a** to 1,2-counterpart **10a**.[15,22] To our pleasure, recrystallization of compound **7a** from 1,2-dichloroethane–acetonitrile gave single crystals suitable for X-ray crystallographic analysis (Fig. 1).[23] The X-ray structure shows that the two phenoxathiine moieties are folded oppositely to each other along their respective imaginary lines passing through the S and O atoms of the 1,4-oxathiine rings. The C–S–C and C–O–C bond angles and the folding angle between the two benzene planes are 97.51°, 116.17°, and 140.83° for one phenoxathiine moiety and 97.88°, 115.95°, and 140.09° for the other, which is in reasonable agreement with those reported for the parent compound (97.7°, 117.4°, and 147.8°, respectively).[24] The two S atoms connecting these phenoxathiine halves have ordinary bond angles (98.29° and 100.92°). Therefore, no strain is found in the tricyclic structure. On the other hand, the X-ray data for amine **8a** showed that it adopted a cone conformation but detailed analysis failed because of its severely disordered structure.

In conclusion, we have shown here a convenient method for the synthesis of monoaminothiacalix[4]arene **4a** and its methylene-bridged analog **4b** via an Ullmann-type amination. It has also been shown that bis(phenoxathiine) **7a** can be readily prepared by an Ullmann-type etherification of 1,3-bistriflate **6a**.

Acknowledgements

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13. Compound **6a**: mp 296–298 °C (decomp.); IR (KBr) 3460, 2966, 1427, 1211, 1138, 1065 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 [18H, s, $C(CH_3)_3\times 2$], 1.34 [18H, s, $C(CH_3)_3\times 2$], 6.12 (2H, s, $OH\times 2$), 7.16 (4H, s, ArH), 7.74 (4H, s, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.65, 31.39, 34.30, 34.45, 121.00, 128.81, 133.37, 134.86, 143.82, 147.69, 151.49, 155.41; FAB-MS *m*/*z* 984 (M^+). Anal. Calcd for $C_{42}H_{46}F_6O_8S_6$: C, 51.20; H, 4.71; S, 19.53. Found: C, 51.01; H, 4.71; S, 19.82.
14. *Typical procedure for the amination*: To a suspension of bistriflate **6a** (1.00 g, 1.02 mmol), CuI (425 mg, 2.23 mmol), and K_3PO_4 (433 mg, 2.04 mmol) in toluene (40 mL) was added benzylamine ($d = 0.983$ g mL^{-1}; 133 μL, 1.22 mmol) and the mixture was stirred at 80 °C for 15 h. After aqueous work-up, the crude mixture was recrystallized from dichloromethane–methanol to give monoamine **8a** (308 mg). The mother liquor was concentrated and chromatographed twice on silica gel with hexane–chloroform (1:1) and then hexane–ethyl acetate (6:1) to give an additional crop of **8a** (100 mg) for a total yield of 408 mg (43%), mp 241–243 °C (decomp.); IR (KBr) 3425, 3283, 2963, 1450, 1427, 1207, 1134 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 [9H, s, $C(CH_3)_3$], 1.13

[9H, s, $C(CH_3)_3$], 1.30 [18H, s, $C(CH_3)_3 \times 2$], 4.42 (2H, s, CH_2Ph), 6.94 (2H, s, ArH), 7.32–7.47 (5H, m, ArH), 7.52 (2H, s, ArH), 7.66 (4H, s, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.42, 30.97, 31.41, 34.14, 34.20, 34.33, 57.52, 121.36, 121.43, 127.52, 128.61, 128.62, 129.41, 130.01, 132.32, 134.70, 134.90, 136.10, 138.05, 143.01, 146.92, 148.47, 149.40, 151.16, 156.32; FAB-MS *m/z* 941 (M^+). Anal. Calcd for $C_{48}H_{54}F_3NO_5S_5$: C, 61.18; H, 5.78; N, 1.49; S, 17.01. Found: C, 61.42; H, 5.77; N, 1.48; S, 16.80. A similar procedure gave compound **8b**. See Table 1 for the reaction conditions and the yield of **8b**, mp 120–122 °C; IR (KBr) 3584, 3526, 3329, 2955, 1462, 1396, 1362, 1207, 1138, 1072 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 [9H, s, $C(CH_3)_3$], 1.06 [9H, s, $C(CH_3)_3$], 1.27 [18H, s, $C(CH_3)_3 \times 2$], 3.45 (2H, d, $J = 13.9$ Hz, $ArCH_2Ar$), 3.48 (2H, d, $J = 13.9$ Hz, $ArCH_2Ar$), 3.94 (2H, d, $J = 13.9$ Hz, $ArCH_2Ar$), 4.13 (2H, s, CH_2Ph), 4.24 (2H, d, $J = 13.9$ Hz, $ArCH_2Ar$), 6.81 (2H, s, ArH), 6.93 (2H, s, ArH), 7.05 (2H, *d*, $J = 2.4$ Hz, ArH), 7.14 (2H, *d*, $J = 2.4$ Hz, ArH), 7.29–7.38 (5H, m, ArH); ^{13}C NMR (100 MHz; $CDCl_3$) δ 30.71, 31.04, 31.58, 32.75, 33.88, 34.00, 34.04, 34.78, 56.30, 125.29, 125.66, 125.74, 127.28, 127.33, 127.56, 127.68, 127.83, 128.68, 133.09, 134.60, 138.40, 138.89, 141.47, 142.52, 147.74, 150.21, 150.78; FAB-MS *m/z* 869(M^+). Anal. Calcd for $C_{52}H_{62}F_3NO_5S$: C, 71.78; H, 7.18; N, 1.61. Found: C, 71.68; H, 7.15; N, 1.48.

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16. *Synthesis of bis(phenoxathiine)* **7a**: To a suspension of CuI (234 mg, 1.23 mmol) and K_3PO_4 (181 mg, 0.853 mmol) in toluene (25 mL) was added dropwise a solution of bistriflate **6a** (203 mg, 0.206 mmol) in toluene (15 mL) over 30 min at room temperature and the mixture was heated at reflux for 1 h. After aqueous work-up, the crude product was chromatographed on silica gel with hexane–chloroform (1:1) as the eluent to give bis(phenoxathiine) **7a** (95.7 mg, 68%), mp 282–284 °C (decomp.); IR (KBr) 2963, 1427, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 [36H, s, $C(CH_3)_3 \times 4$], 7.11 (4H, d, $J = 2.3$ Hz, ArH), 7.59 (4H, d, $J = 2.3$ Hz, ArH), ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.17, 34.44, 122.18, 124.88, 124.89, 132.91, 147.97, 151.72; FAB-MS *m/z* 684 (M^+). Anal. Calcd for $C_{40}H_{44}O_2S_4$: C, 70.13; H, 6.47; S, 18.72. Found: C, 70.11; H, 6.51; S, 18.80.
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22. See also Ref. 2e.
23. Crystallographic data for **7a**: $C_{40}H_{44}O_2S_4$, $M = 684.99$, monoclinic, $a = 11.4917(12)$ Å, $b = 10.6563(9)$ Å, $c = 14.7500(14)$ Å, $\beta = 92.153(3)°$, $V = 1805.0(3)$ Å^3, $T = 100(2)$ K, space group $P2_1$, $Z = 2$, $D_{calc} = 1.260$ g/cm^3, μ(Mo-Kα) $= 0.297$ mm^{-1}, 13,402 reflections measured, 8105 independent reflection ($R_{int} = 0.0233$), 6772 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0384$, $wR_2 = 0.0739$ (observed), $R_1 = 0.0464$, $wR_2 = 0.0754$ (all data), GOF = 0.922. The details of the crystal data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 648696.
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