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Article

1,3-Dipolar Addition of Methyl *α*-Diazoacetoacetate to Enamines: A New Synthetic Route to 5-Amino-4,5-dihydrofurans

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The reaction of methyl *α*-diazoacetoacetate with enamines catalyzed by dirhodium and copper complexes underwent formal 1,3-dipolar addition to give 5-amino-4,5-dihydrofurans in moderate yields. The reaction was suggested to proceed via a nucleophilic addition of enamines to metal-carbenes and a subsequent intramolecular cyclization of the resulting zwitterionic intermediates.

Keywords dihydrofuran, enamine, 1,3-dipolar addition, diazoacetoacetate, catalysis

Introduction

Furans and dihydrofurans have received much attention because they are frequently found in many natural products arising from plants and marine organisms.[1] They are also used as synthetic intermediates of natural products with a variety of biological activities.[2] In past decades a number of synthetic methods of dihydrofurans have been reported.[3-6] Among them 1,3-dipolar cycloaddition of diazo ketones to electron-rich olefins is highly efficient for the preparation of many dihydrofurans due to the straightforward and facile feature of this methodology. Wenkert *et al.*[7] reported that the reaction of *α*-diazodicarbonyl compounds with enol ether catalyzed by copper catalysts gave dihydrofurans in low yield. Pirrung and Lee[8] found that the addition of cyclic diazoketones to vinyl ethers and other heterocyclic aromatic compounds provided dihydrofurans in moderate to good yields. This methodology has been used to prepare pseudosemiglabrin, furanocoumarins and other many biologically active compounds.[9] Davies *et al.*[10] developed an asymmetric synthesis of dihydrofurans by the rhodium-catalyzed reaction of chiral vinyldiazoacetates with vinyl ethers. On the other hand, enamines are also electron-rich olefins and easily prepared from ketones and aldehydes. The catalytic reaction of diazoacetates and diazomethanes with enamines has been studied.[11] The reactions could provide *α*-diazo-*β*-aminoesters or aminocyclopropanes as the major products depending on the used catalysts and structure of diazo compounds. However, to the best of our knowledge, the 1,3-dipolar addition of *α*-diazodicarbonyl compounds with enamines has not been reported. Recently we initiated a comprehensive study of the reactions of enamines with diazo compounds. We have found that the reaction of aryldiazoacetates with enamines catalyzed by dirhodium or copper catalysts gave *γ*-ketoesters in good yields.[12] In this paper we report the reaction of methyl *α*-diazoacetoacetate (**1**) with enamines, which provides a new synthetic route to 5-amino-4,5-dihydrofurans in moderate yields.

Results and discussion

The enamines **2a**—**2c**, prepared from acetophenone and cyclic secondary amines, were examined in the reaction with methyl *α*-diazoacetoacetate (**1**) using dirhodium tetraacetate as the catalyst in refluxing dichloroethane. The reaction of enamine **2a** with **1** took place to provide methyl 2-methyl-5-morpholino-5-phenyl-4,5-dihydrofuran-3-carboxylate (**3a**) in 34% yield. Change of reaction solvent from dichloroethane to fluorobenzene improved the yield to 39%. The structure of **3a** was confirmed by NMR, HRMS and X-ray diffraction analysis (Figure 1). The property of cyclic secondary amines was found to have profound effect on this transformation. The enamines **2b** and **2c** prepared from pyrrolidine and piperidine respectively, were found to afford rather complex reaction mixture, from which none of dihydrofurans could be separated. These results are summarized in Table 1.

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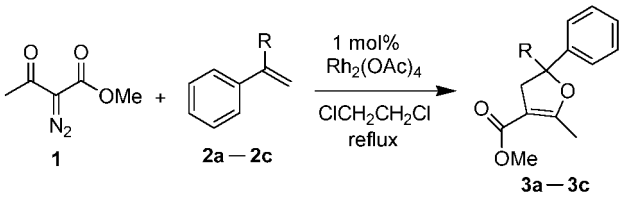
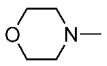
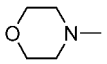
Table 1 Reaction of **1** with enamines **2a—2c** catalyzed by dirhodium tetraacetate[a]



Entry	R	Enamine	Time/h	Yield[b]/%
1		**2a**	2	34
2		**2a**	2	39[c]
3		**2b**	4	~0
4		**2c**	5	~0

[a] The reactions were carried out with **1** (1 mmol) and **2a—2c** (1.5 mmol) in refluxing 1,2-dichloroethane. [b] Isolated yield after column chromatography. [c] The reaction was carried out in refluxing fluorobenzene.

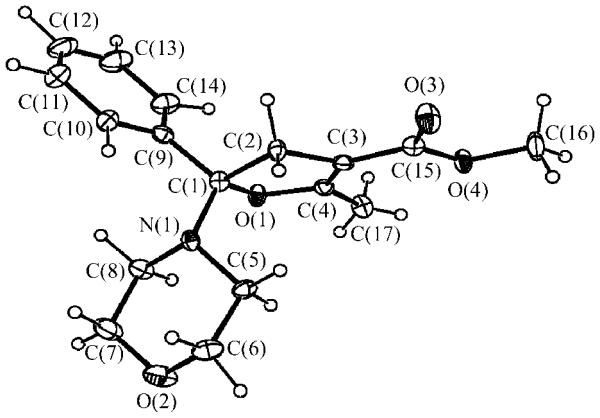
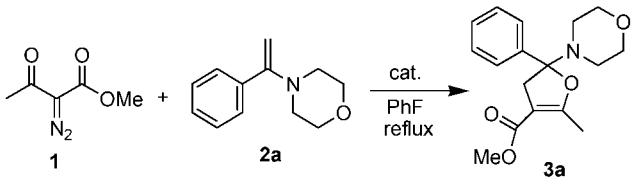


Figure 1 ORTEP drawing of **3a**.

Although $Rh_2(OAc)_4$ was thought as a superior catalyst for the decomposition of diazo compounds and consequent transformations,[13] copper(I) and copper(II) salts were also efficient catalysts for many transformations with diazo compounds. A variety of copper salts were examined in the reaction of enamine **2a** with methyl α-diazoacetoacetate (**1**) and the results are summarized in Table 2. In general both copper(I) and copper(II) salts worked in the reaction. The $Cu(hfacac)_2$ provided best catalytic activity and chemical yield.

A number of enamines **2a—2g** were also studied in the reaction with methyl α-diazoacetoacetate (**1**) using $Cu(hfacac)_2$ as the catalyst and fluorobenzene as the solvent. The results are summarized in Table 3.

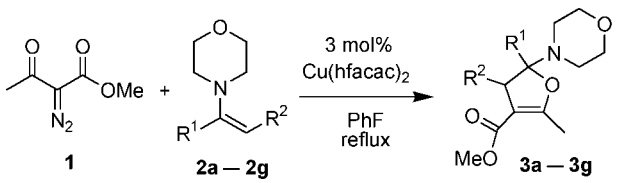
Table 2 Reaction of **1** and enamine **2a** catalyzed by dirhodium and copper complexes[a]

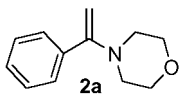
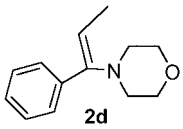
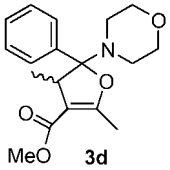
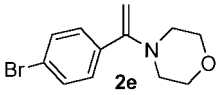
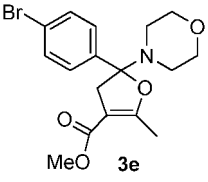


Entry	Catalyst	Mol/%	Time/h	Yield[b]/%
1	None	N.A.[c]	24	0
2	$Rh_2(OAc)_4$	1	2	39
3	$Cu(OTf)_2$[d]	3	16	20
4	$Cu(hfacac)_2$[e]	3	1	46
5	CuI	3	6	42
6	$Cu(acac)_2$	3	2	45
7	$CuPF_6$	3	2	30

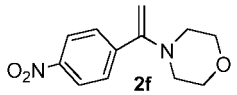
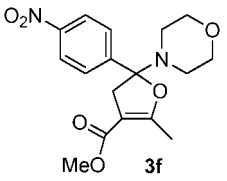
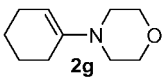
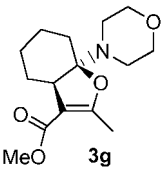
[a] The reactions were carried out with **1** (1 mmol) and **2a** (1.5 mmol) in refluxing fluorobenzene. [b] Isolated yield after column chromatography. [c] Not applicable. [d] $Cu(OTf)_2$=copper(II) bistrifluoromethanesulfonate. [e] $Cu(hfacac)_2$=bis-hexafluoroacetoacetonato copper(II).

Table 3 Reaction of **1** with enamines **2a—2g** catalyzed by $Cu(hfacac)_2$[a]



Entry	Enamine	Product	Time/h	Yield[b]/%
1			1	46
2			4	63[c]
3			2.5	57

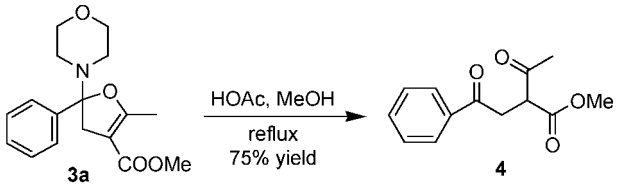
Continued

Entry	Enamine	Product	Time/h	Yield[b]/%
4	 **2f**	 **3f**	2	55
5	 **2g**	 **3g**	4	37

[a] The reactions were carried out with **1** (1 mmol), enamine (1.5 mmol) and $Cu(hfacac)_2$ (0.03 mmol) in refluxing fluorobenzene. [b] Isolated yield after column chromatography. [c] *Cis* or *trans* configuration of the product **3d** was not determined.

The reaction of **1** with 2-methyl substituted enamine **2d** provided better yields of dihydrofurans (Table 3, Entry 2). The introduction of electron withdrawing group such as bromo or nitro group also improved the chemical yields of dihydrofurans (Table 3, Entries 3 and 4). However the reaction with enamine **2g** derived from cyclohexanone gave lower yield of dihydrofuran (Table 3, Entry 5). Furthermore acid catalyzed hydrolysis of **3a** provided 1,4-diketone (**4**) in good yield (Scheme 1).

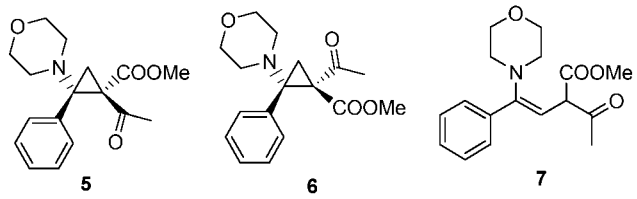
Scheme 1 Acid catalyzed hydrolysis of **3a**



3a **4**

Previous study provided controversial mechanism for the reaction of diazoketones with electron-rich olefins. The concerted 1,3-dipolar addition mechanism was supported by Huisgen *et al.*,[14] with the evidence that no cyclopropane intermediate was observed and isolated in the reaction. Moreover the cyclopropane products prepared from other route did not isomerize to five membered heterocycles.[15] Pirrung[16] suggested the cyclopropanation and subsequent ring opening pathway for the reaction of cyclic rhodium carbenoid with vinyl ethers. The complicated product distribution could be rationalized based on this suggestion. In the study of the reaction of α-diazodicarbonyl compounds with benzofurans, Alonso[17] suggested a stepwise mechanism through addition of olefins to metal-carbenes and formation of zwitterionic intermediates, which undergo further transformations to provide different products. Doyle[18] also proposed a similar stepwise mechanism to account for the 1,3-dipolar addition of diazoketones with vinyl ethers.

The reaction of styrene with α-diazoacetoacetates was found to provide corresponding cyclopropane derivatives exclusively.[19] In the reaction of **1** with **2a**, amino cyclopropane **5** or **6** (Figure 2) was not detected in the crude reaction mixture. On the other hand, in the reaction of **2a** with methyl phenyldiazoacetate, the formation of a substituted enamine through a possible proton transfer step from a zwitterionic intermediate was observed.[12] However in the reaction of **1** with **2a**, none of similar proton transfer product **7** (Figure 2) was observed.

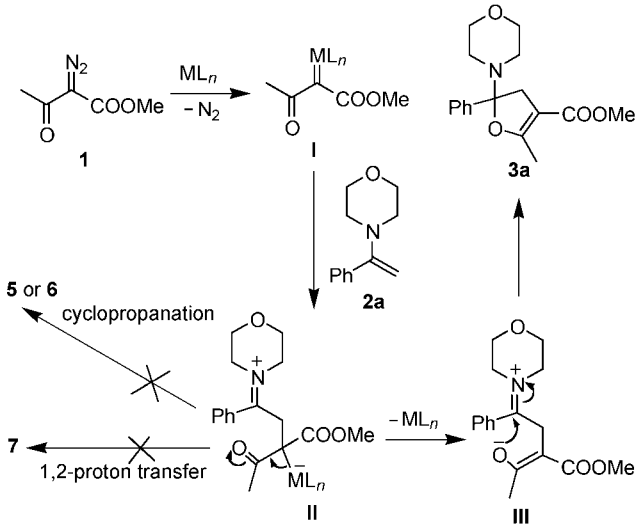


5 **6** **7**

Figure 2 Chemical structures of compounds **5**, **6** and **7**.

Our experiment results could be rationalized based on a stepwise mechanism (Scheme 2). The addition of the electron-rich enamine **2a** to the metal-carbene provided the intermediate **II**. After losing the metal catalyst and following an enolization process, the zwitterionic intermediate **III** was formed. **III** underwent an intramolecular cyclization to provide dihydrofuran **3a** as the final product. The formation of the cyclopropanation product **5** or **6** and 1,2-proton transfer product **7** from intermediate **II** could not compete with the enolization process to form intermediate **III**.

Scheme 2 Proposed reaction mechanism



Conclusion

In conclusion a new reaction of methyl α-diazoacetoacetate with enamines catalyzed by copper or dirhodium complexes has been found. The reaction provided 5-amino-4,5-dihydrofurans in moderate yields. The acid

The acid catalyzed hydrolysis of the resulting dihydrofuran could give 1,4-diketone in good yield. Further study of the scope of the reaction and application to the synthesis of natural products are under way.

Experimental

All reactions were carried out in oven-dried glassware using standard Schlenk technique under argon atmosphere. Hexane, benzene, toluene and tetrahydrofuran were distilled from sodium-benzophenone. 1,2-Dichloroethane and fluorobenzene were distilled over CaH_2. Other solvents were used as their commercial anhydrous grade. The flash column chromatography was carried out on Merck Silica gel (230—400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal (δ = 77.00). High-resolution mass spectra were obtained with a GCT-TOF instrument. Elemental analyses were performed on a Carlo-Erba EA1110 CNNO-S analyzer. Unless otherwise stated, all chemicals were purchased from Aldrich or Acros chemical company and used thus without further purification. Mesyl azide (MsN_3),[20] methyl α-diazoacetoacetate[21] and enamines[22] were prepared according to known procedures.

Preparation of methyl α-diazoacetoacetate (1)

To a solution of methyl acetoacetate (1.16 g, 10 mmol) and triethylamine (1.01 g, 20 mmol) in anhydrous THF (10 mL) under stirring at room temperature was added MsN_3 (1.33 g, 11 mmol). The resulting solution was kept stirring for 4 h. After water (10 mL) was added, the reaction mixture was extracted with ether (10 mL×3). The combined extract was concentrated under reduced pressure at 20 ℃ to give a yellow oil, which was purified by flash column chromatography over silica gel (petroleum ether∶ethyl acetate, 4∶1, *V*/*V*) to afford methyl α-diazoacetoacetate (**1**) as a yellow oil (1.39 g, 97.9% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.85 (s, 3H), 2.49 (s, 3H).

Preparation of *N*-(1-styryl)morpholine (2a)

To a solution of acetophenone (5 mL, 43 mmol) and morpholine (22.4 mL, 257 mmol) in anhydrous hexane (100 mL), was added $TiCl_4$ (2.6 mL, 23 mmol) over 10 min. The reaction mixture was stirred at room temperature for 24 h and filtered. The filtrate was evaporated under vacuum to give a yellow oil, which was distilled under reduced pressure (4.0 Pa, 85—90 ℃) to give *N*-(1-styryl)morpholine (**2a**) as a pale yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.56—7.26 (m, 5H), 4.33 (s, 1H), 4.20 (s, 1H), 3.77 (s, 4H), 2.85 (s, 4H).

Representative procedure of the reaction of methyl α-diazoacetoacetate with enamines

To a round-bottom flask equipped with a stirrer and an addition funnel under argon atmosphere, was charged *N*-(1-styryl)morpholine (**2a**) (284 mg, 1.5 mmol), $Cu(hfacac)_2$ (14.3 mg, 0.03 mmol) and fluorobenzene (3 mL). The reaction solution was heated in an oil-bath and kept refluxing. The addition funnel was charged with a solution of methyl α-diazoacetoacetate (**1**) (142 mg, 1 mmol) in fluorobenzene (3 mL), which was added dropwise to the reaction solution over 20 min. The reaction mixture was refluxed for additional 1 h. After the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography (petroleum ether∶ethyl acetate, 10∶1, *V*/*V*) over silica gel to give methyl 2-methyl-5-morpholino-5-phenyl-4,5-dihydrofuran-3-carboxylate (**3a**) as a light yellow solid (0.14 g, 46% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.31 (d, J=8.8 Hz, 2H), 7.36 (t, J_1=8.8, J_2=8.4 Hz, 2H), 7.28 (t, J_1=8.4, J_2=6.0 Hz, 1H), 3.67 (s, 3H), 3.66 (m, 4H), 3.28 (d, J=16.8 Hz, 1H), 2.97 (d, J=16.8 Hz, 1H), 2.78 (m, 2H), 2.45 (m, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.8, 166.6, 143.9, 129.0, 128.1, 125.9, 105.8, 100.5, 67.6, 51.3, 46.6, 41.9, 14.1. Anal. calcd for $C_{17}H_{21}NO_4$: C 67.31, H 6.98, N 4.62; found C 67.52, H 7.07, N 4.55. HRMS (EI^+) calcd for $C_{17}H_{21}NO_4$ 303.1471, found 303.1429.

Methyl 2,4-dimethyl-5-morphlino-5-phenyl-4,5-dihydrofuran-3-carboxylate (3d): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.45 (d, J=8.4 Hz, 2H), 7.36~7.26 (comp, 3H), 3.72 (s, 3H), 3.64 (m, 4H), 3.24 (q, J=6.8 Hz, 1H), 2.79 (m, 2H), 2.42 (m, 2H), 2.36 (s, 3H), 0.56 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.1, 166.5, 139.5, 128.4, 128.1, 127.7, 109.2, 107.5, 67.7, 51.3, 47.4, 43.8, 19.4, 14.2. Anal. cacld for $C_{18}H_{28}NO_4$: C 68.12, H 7.30, N 4.41; found C 68.25, H 7.51, N 4.26. HRMS (EI^+) cacld for $C_{18}H_{23}NO_4$ 317.1627, found 317.1436.

Methyl 5-(4-bromophenyl)-2-methyl-5-morpholino-4,5-dihydrofuran-3-carboxylate (3e): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.49 (d, J=7.6 Hz, 2H), 7.31 (d, J=7.6 Hz, 2H), 3.71 (s, 3H), 3.66 (m, 4H), 3.27 (d, J=16.0 Hz, 1H), 2.92 (d, J=16.0 Hz, 1H), 2.76 (m, 2H), 2.42 (m, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.6, 166.3, 142.99, 132.1, 127.8, 122.1, 105.2, 100.5, 67.4, 51.3, 46.5, 41.7, 14.0; HRMS (EI^+) calcd for $C_{17}H_{20}BrNO_4$(81) 383.0555, found 383.0569; HRMS (EI^+) calcd for $C_{17}H_{20}BrNO_4$(79) 381.0576, found 381.0595.

Methyl 2-methyl-5-morpholino-5-(4-nitrophenyl)-4,5-dihydrofuran-3-carboxylate (3f): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.23 (d, J=8.8 Hz, 2H), 7.65 (d, J=8.8 Hz, 2H), 3.74 (s, 3H), 3.68 (m, 4H), 3.33 (d, J=16.4 Hz, 1H), 2.91 (d, J=16.4 Hz, 1H), 2.81 (m, 2H), 2.41 (m, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.4, 166.0, 150.96, 147.9, 127.1, 124.4, 104.8, 100.6, 67.3, 51.4, 46.5, 41.8, 14.0; HRMS (EI^+) calcd for $C_{17}H_{20}N_2O_6$ 348.1321, found 348.1317.

Methyl 2-methyl-7a-morpholino-3a,4,5,6,7a-hexahydrobenzofuran-3-carboxylate (3g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.76 (s, 3H), 3.69 (m, 4H), 3.09 (s, 1H), 2.77 (m, 2H), 2.65 (m, 2H), 2.22 (s, 3H), 1.90 (m, 1H), 1.74 (m, 3H), 1.58 (m, 1H), 1.46 (m, 3H), 1.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.4, 166.8, 104.99, 104.3, 67.5, 50.9, 45.3, 44.4, 27.0, 23.2, 16.6, 16.4, 14.2; HRMS (EI^+) calcd for $C_{15}H_{23}NO_4$ 281.1627, found 281.1590.

Preparation of methyl 2-acetyl-4-oxo-4-phenylbutanoate (4)

To a refluxing solution of **3a** (0.151 g, 0.5 mmol) in methanol (10 mL), was added HOAc (1.5 mL). The reaction mixture was refluxed for 1 h. After the solvent was evaporated under vacuum, the crude product was purified by flash column chromatography (petroleum ether∶ethyl acetate, 5∶1, *V*/*V*) over silica gel to give methyl 2-acetyl-4-oxo-4-phenylbutanoate (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J=7.2 Hz, 2H), 7.57 (t, J_1=7.6, J_2=6.4 Hz, 1H), 7.46 (t, J=7.2 Hz, 2H), 4.23 (dd, J_1=6.0, J_2=2.0 Hz, 1H), 3.76 (s, 3H), 3.70 (dd, J_1=10.0, J_1=9.2 Hz, 1H), 3.53 (dd, J_1=5.2, J_2=4.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 202.7, 197.8, 169.7, 136.2, 133.9, 128.99, 128.4, 53.9, 53.1, 37.8, 30.7; HRMS (EI^+) calcd for $C_{13}H_{14}O_4$ 234.0892, found 234.0916.

Crystallographic data of 3a

Crystallographic data of **3a** have been deposited in the Cambridge Crystallographic Data Center (CCDC No: 242663). Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (E-mail: linstead@ccdc.cam.ac.uk or eposit@ccdc.cam.ac.uk; Fax: +44 1223 336033). Data collection: Rigaku Mercury CCD area detector; radiation: Mo Kα wavelength: λ=7.1070 nm; crystal size: 0.20 mm×0.38 mm×0.34 mm; crystal system: orthorhombic; space group: *Pbca* (#61); unit cell: a=132.08(3) nm, b=91.67(2) nm, c=264.59(6) nm, α=89°, β=89°, γ=90°, V=3203700(13) nm^3, Z=8, μ=0.89 cm^{-1}.

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