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Highly Efficient and Selective Synthesis of (*E*)-α,β-Unsaturated Ketones by Crossed Condensation of Ketones and Aldehydes Catalyzed by an Air-Stable Cationic Organobismuth Perfluorooctanesulfonate

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Abstract: An air-stable cationic organobismuth perfluorooctanesulfonate possessing both acidic and basic characters was synthesized, and showed high catalytic activity, diastereoselectivity, stability, and reusability in the one-pot synthesis of (*E*)-α,β-unsaturated ketones through highly selective crossed condensation of ketones and aldehydes in water.

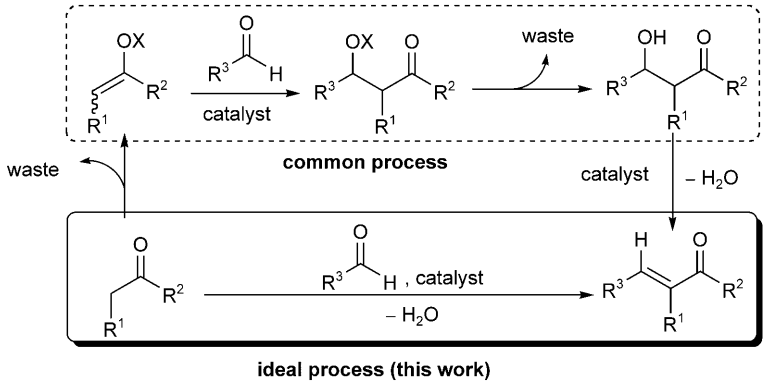
Keywords: crossed condensation; diastereoselectivity; organobismuth compounds; perfluorooctanesulfonates; (*E*)-α,β-unsaturated ketones

Introduction

It is known that bismuth is a stable heavy element that is free of toxicity.[1] The utilization of bismuth compounds in the field of catalysis and organic synthesis has been studied intensively in recent years.[1,2] Simple bismuth Lewis acids such as bismuth halides and triflates are highly efficient catalysts in a number of reactions.[2] The use of designed cationic organobismuth compounds in catalysis, however, is rarely reported partly due to the instability of the Bi–C bond.[3] We have been working on the synthesis of bismuth compounds and their applications in organic synthesis.[4] Very recently, we reported an organobismuth perchlorate that shows high catalytic efficiency in the direct diastereoselective Mannich reaction.[4d] Herein we report the excellent catalytic activity of another novel related air-stable cationic organobismuth-(III) compound for the stereoselective synthesis of (*E*)-α,β-unsaturated ketones in water.

α,β-Unsaturated carbonyl compounds are widely used as substrates for a number of reactions such as hydrogenation,[5] epoxidation,[6] peroxidation,[7] cycloaddition,[8] and conjugate addition.[9] Besides organic synthesis, the compounds can be applied in biochemistry as well.[10] The aldol condensation reaction of carbonyl compounds is the most common process for the synthesis of α,β-unsaturated carbonyl compounds (Scheme 1).[11] The Claisen–Schmidt condensation, a crossed aldol condensation of an aromatic aldehyde and an aliphatic ketone or aldehyde under basic conditions, is the traditionally used process. In this reaction, a relatively strong base (such as metal hydroxide or metal alkoxide) is employed, and selective monocondensation is often difficult due to side reactions such as bis-condensation and aliphatic aldehyde dimerization. Application of the method is further limited because substrates with base-sensitive functional groups are not suitable. A better approach is by means of the Mukaiyama-aldol reaction followed by subsequent dehydration catalyzed by a Lewis acid.[12] Recently, Yanagisawa et al. reported the one-pot selective synthesis of α,β-unsaturated ketones from alkenyl trichloroacetates and aldehydes; in this approach, ketones have to be converted to alkenyl trichloroacetates before the condensation reaction.[13]

The catalytic direct crossed condensation of ketones and aldehydes would be an ideal process for the



Scheme 1. A comparison between a common process and an ideal process for the selective synthesis of α,β-unsaturated ketones.

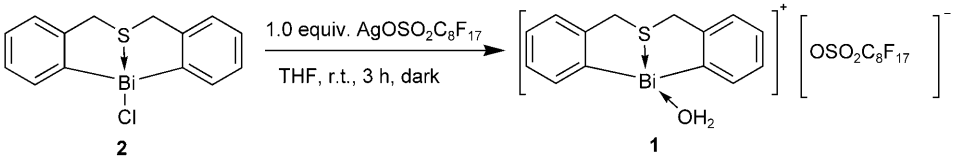
synthesis of α,β-unsaturated carbonyl compounds, because there is no need to prepare reactive intermediates (e.g., silyl enol ethers) and only H_2O is generated as a side-product (Scheme 1). Such a process is significantly "energy efficient" and "atom economic" since multistep transformations and separation of product (from by-products) are not necessary. Recently, the use of organocatalysts for direct crossed condensation reactions was reported, whereby a high catalyst loading is necessary (20 mol%).[14] In this paper, we describe an alternative, highly efficient catalyst system using the organobismuth compound $[S(CH_2C_6H_4)_2Bi(OH_2)]^+ [OSO_2C_8F_{17}]^-$ (**1**) and a primary amine.

Results and Discussion

Shown in Scheme 2 is the synthetic route for the organobismuth compound **1**. Treatment of $S(CH_2C_6H_4)_2BiCl$ (**2**)[15] with $AgOSO_2C_8F_{17}$[16] in THF afforded the organobismuth perfluorooctanesulfonate **1** quantitatively. ^1H NMR and elemental analyses show that the sample freshly obtained after recrystallization contains one water molecule. We found that compound **1** is air-stable; it remained under ambient environment as dry colorless crystals or white powder for more than one year. The crystal structure of **1** was confirmed by X-ray analysis. An ORTEP representation of **1**, and selected bond lengths and angles are shown in Figure 1. It is clear that the organobismuth component in compound **1** is a cation. The oxygen atom of the coordinating water occupies a vacant site of the cationic bismuth center, making the coordination geometry an equatorially distorted, vacant trigonal bipyramid with the sulfur and the oxygen atoms in the apical positions and the two carbon atoms in the equatorial positions. The Bi–S(1) distance [2.704 (2) Å] is shorter than that (2.845 Å) of precursor **2**,[15b] clearly showing the stronger sulfur-to-bismuth coordination in **1**. The Bi–O(1) distance [2.445 (7) Å] is longer than that of covalent Bi–O bonds (e.g., Bi–O bond distances of monomeric diorganobismuth alkoxides range 2.15–2.20 Å),[4b,17] indicating that the weakly coordinated water molecule can be replaced by another substrate.

The thermal behaviour of compound **1** was investigated by TG-DSC in an N_2 atmosphere (Figure 2). The TG-DSC curves show three stages of weight loss. The endothermic step below 150 °C can be assigned to the removal of H_2O molecules. The material is stable up to about 250 °C. The weight loss of an exothermic nature at 250 °C is plausibly due to the oxidation of organic entities. It is estimated from the TG analysis result that the empirical formula of the complex can be written as $[S(CH_2C_6H_4)_2Bi(OH_2)]^+ [C_8F_{17}SO_3]^-$ (**1**).

We employed the Hammett indicator method to determine the acidity and basicity of **1**, and found that it has relatively weak acidity with strength of $3.3 < H_o \leq 4.8$ and weak basicity with a strength of $7.2 \leq H_- < 8.9$.[16] With the accessible bismuth center acting as a Lewis acid site and the uncoordinated



Scheme 2. Synthesis of cationic organobismuth compound **1**.

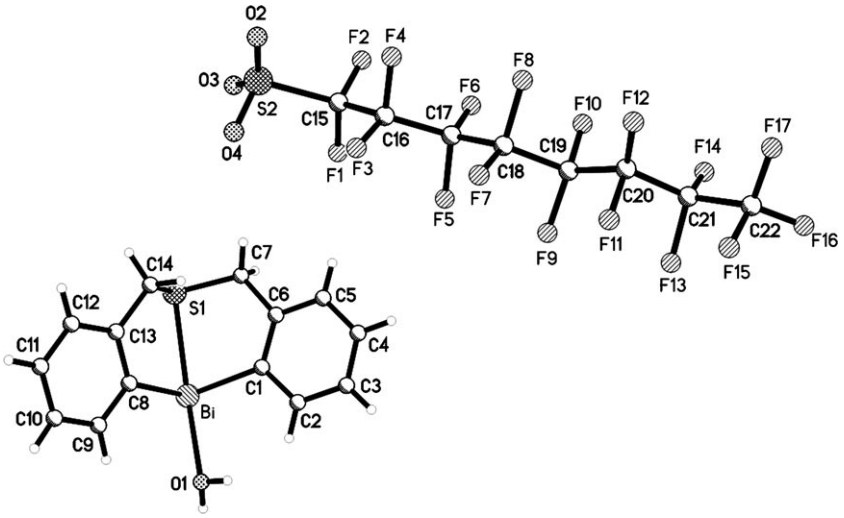


Figure 1. ORTEP view (50% probability level) of **1**. Selected bond lengths (Å) and angles (deg): Bi–C(1), 2.240(8); Bi–C(8), 2.236(8); Bi–O(1), 2.445(7); Bi–S(1), 2.704(2); S(1)–C(7), 1.787(10); S(1)–C(14), 1.795(10); C(1)–Bi–C(8), 100.6(3); C(8)–Bi–O(1), 84.7(3); C(1)–Bi–O(1), 89.4(3); C(8)–Bi–S(1), 77.3(3); O(1)–Bi–S(1), 155.42(19); C(7)–S(1)–C(14), 100.9(5).

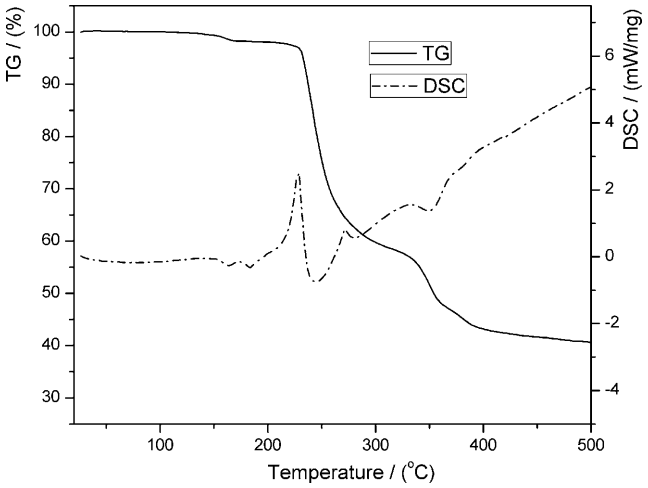


Figure 2. TG-DSC curves of compound **1**.

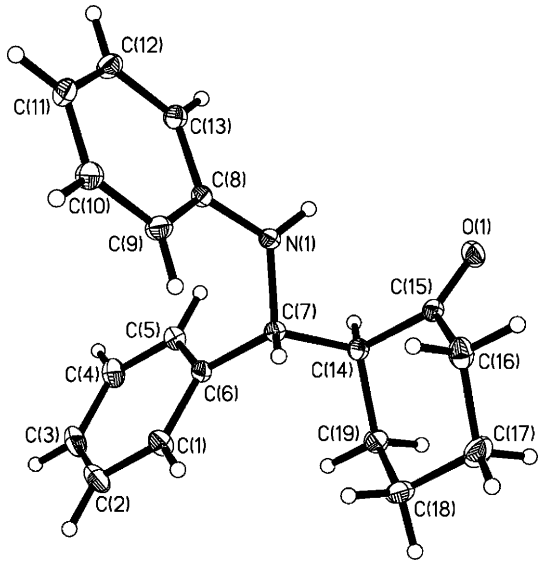


Figure 3. ORTEP view of crystal structure of (*S**)-2-[(*R**)-phenyl(phenylamino)methyl]cyclohexanone.

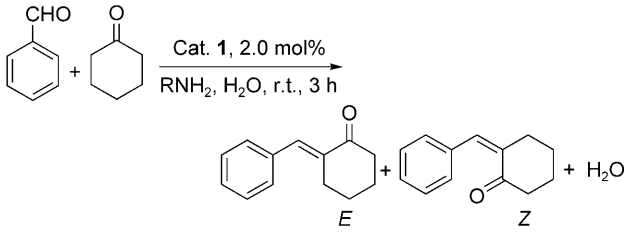
lone-pair electrons of sulfur as a Lewis base, it is expected that **1** can act as a bifunctional Lewis acid/base catalyst.[18]

We first investigated the catalytic performance of **1** towards the direct three-component Mannich reaction of benzaldehyde, cyclohexanone and aniline in water, and observed the formation of Mannich adducts {(*S**)-2-[(*R**)-phenyl(phenylamino)methyl]cyclohexanone} with high diastereoselectivity (*anti*/*syn* > 99/1) (Figure 3).[4d] However, when propylamine was used instead of aniline, a completely different product, the (*E*)-α,β-unsaturated ketone, was obtained. Since this process was efficient under mild conditions, we further evaluated the catalytic performance of **1** towards the synthesis of α,β-unsaturated ketones.

Table 1 shows the structural effect of amines on this reaction. Primary amines with *n*-alkyl groups are highly active (Table 1, entries 1–4, 85–95%), with the bulkier primary amines showing lower efficiency (Table 1, entries 5 and 6). In the cases of secondary and tertiary amines (Table 1, entries 7 and 8) or in the absence of amine (Table 1, entry 9), there is no detectable reactivity whatsoever. It is clear that the presence of a primary amine is indispensable for the occurrence of the reaction.

The reaction occurs smoothly in CH_2Cl_2 and MeOH, but rather slowly in THF, Et_2O, and hexane

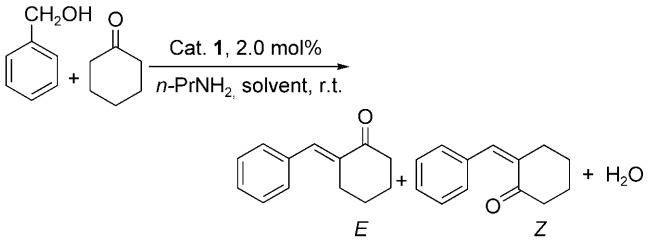
Table 1. Synthesis of α,β-unsaturated ketones using various aliphatic amines.[a]



Entry	RNH_2	Yield [%][b]	*E*/*Z*[c]
1	$EtNH_2$	88	>99/1
2	*n*-$PrNH_2$	95	>99/1
3	*n*-$BuNH_2$	93	>99/1
4	*n*-$HexNH_2$	85	>99/1
5	$CyNH_2$	71	>99/1
6	*t*-$BuNH_2$	21	>99/1
7	Et_2NH	NR[d]	–
8	Et_3N	NR[d]	–
9	No amine	NR[d]	–

[a] PhCHO, 1.0 mmol; aliphatic amine, 1.0 mmol; cyclohexanone, 1.2 mmol; **1**, 0.02 mmol; H_2O, 2.0 mL; room temperature, 3 h.
[b] Isolated yield.
[c] Determined by ^1H NMR.
[d] No reaction.

Table 2. Synthesis of α,β-unsaturated ketones in various solvents.[a]



Entry	Solvent	Time [h]	Yield [%][b]	*E*/*Z*[c]
1	*n*-Hexane	12	67	>99/1
2	CH_2Cl_2	6	85	>99/1
3	Et_2O	8	78	>99/1
4	CH_3CN	7	85	>99/1
5	THF	8	76	>99/1
6	CH_3OH	6	93	>99/1
7	H_2O	3	95	>99/1

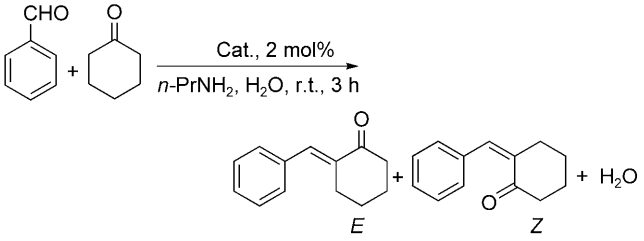
[a] PhCHO, 1.0 mmol; *n*-$PrNH_2$, 1.0 mmol; cyclohexanone, 1.2 mmol; **1**, 0.02 mmol; solvent, 2.0 mL; room temperature.
[b] Isolated yield.
[c] Determined by ^1H NMR.

(Table 2). Especially, the efficiency is high when water is used as a solvent (yield, 95%, *E*/*Z* > 99/1). It is apparent that the *E*-selectivity is independent of the employed solvents.

To show the uniqueness of **1**, we compared the catalytic activity of **1** with those of $S(CH_2C_6H_4)_2BiCl$ (**2**), the cationic organobismuth compounds [*t*-$BuN(CH_2C_6H_4)_2Bi]^+[B(C_6F_5)_4]^-$ (**3**),[3] $[S(CH_2C_6H_4)_2Bi(OH_2)]^+[ClO_4]^-$ (**4**),[4d] $Bi(OSO_2CF_3)_3$ (**5**), $Bu_2Sn(OMe)_2$ (**6**),[13a] DIMCARB (*N*,*N*-dimethylammonium *N*′′,*N*′′-dimethylcarbamate) (**7**),[19] NaOH (**8**), NaOMe (**9**), and $C_8F_{17}SO_3H$ (**10**). As shown in Table 3, catalyst **1** is superior to the other nine catalysts in terms of product yield and stereoselectivity.

Various aromatic aldehydes with electron-donating and electron-withdrawing groups as well as enolizable aliphatic aldehydes were employed to test the versatility of the catalytic system (Table 4). In all cases of benzaldehydes, the desired products were obtained in high yields. One can also see that the aldehydes with an electron-withdrawing group on the phenyl ring exhibit higher activity than the aldehydes with an electron-donating group (Table 4, entries 2–5). The reaction of cinnamaldehyde can occur at 0 °C (Table 4, entry 6), while the *E*-selectivity for cinnamaldehyde is the lowest. It is worth noting that the reaction of enolizable aliphatic aldehydes selectively produces (*E*)-α,β-unsaturated ketones in quantitative yields without

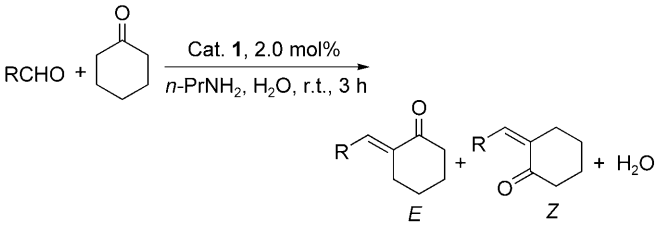
Table 3. Synthesis of α,β-unsaturated ketones over different catalysts.[a]



Entry	Cat.	Yield [%][b]	*E*/*Z*[c]
1	$[S(CH_2C_6H_4)_2Bi(OH_2)]^+[OSO_2C_8F_{17}]^-$ (**1**)	95	>99/1
2	$S(CH_2C_6H_4)_2BiCl$ (**2**)	55	43/57
3	$[t\text{-}BuN(CH_2C_6H_4)_2Bi]^+[B(C_6F_5)_4]^-$ (**3**)	92	64/36
4	$[S(CH_2C_6H_4)_2Bi(OH_2)]^+[ClO_4]^-$ (**4**)	93	93/7
5	$Bi(OSO_2CF_3)_3$ (**5**)	87	86/14
6	$Bu_2Sn(OMe)_2$ (**6**)	34	78/22
7	DIMCARB (**7**)	20	79/21
8[d]	NaOH (**8**)	10	81/19
9[d]	NaOMe (**9**)	14	82/18
10	$C_8F_{17}SO_3H$ (**10**)	6.4[e]	–

[a] PhCHO, 1.0 mmol; *n*-$PrNH_2$, 1.0 mmol; cyclohexanone, 1.2 mmol; Cat., 0.02 mmol; H_2O, 2.0 mL; room temperature, 3 h.
[b] Isolated yield.
[c] Determined by ^1H NMR.
[d] Side product is 2-[hydroxy(phenyl)methyl]cyclohexanone.
[e] GC yield.

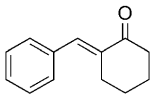
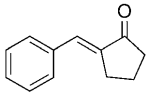
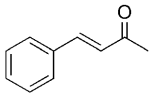
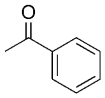
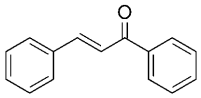
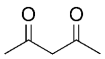
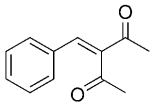
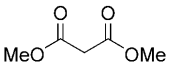
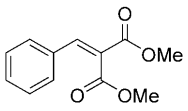
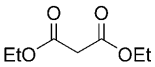
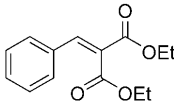
Table 4. Synthesis of α,β-unsaturated ketones using various aldehydes.[a]



Entry	RCHO	Yield [%][b]	*E*/*Z*[c]
1	PhCHO	95	>99/1
2	*p*-$CH_3C_6H_4CHO$	90	97/3
3	*p*-$CH_3OC_6H_4CHO$	88	97/3
4	*p*-ClC_6H_4CHO	96	98/2
5	*p*-$CF_3C_6H_4CHO$	99	99/1
6 [d]	(*E*)-Ph-CH=CHCHO	83	93/7
7	$PhCH_2CH_2CHO$	97	99/1
8	$nC_7H_{15}CHO$	99	99/1

[a] RCHO, 1.0 mmol; *n*-$PrNH_2$, 1.0 mmol; cyclohexanone, 1.2 mmol; **1**, 0.02 mmol; H_2O, 2.0 mL; room temperature, 3 h.
[b] Isolated yield.
[c] Determined by ^1H NMR.
[d] 0 °C.

Table 5. Synthesis of α,β-unsaturated ketones using various ketones and malonates.[a]

Entry	Ketone	Product (*E*)	Yield [%][b]	*E*/*Z*[c]
1			95	>99/1
2			97	>99/1
3[d]			96	>99/1
4[e]			84	>99/1
5			96	–
6			95	–
7			94	–

[a] PhCHO, 1.0 mmol; *n*-$PrNH_2$, 1.0 mmol; ketone, 1.2 mmol; **1**, 0.02 mmol; H_2O, 2.0 mL; room temperature, 3 h.
[b] Isolated yield.
[c] Determined by ^1H NMR.
[d] 0 °C to room temperature.
[e] 24 h.

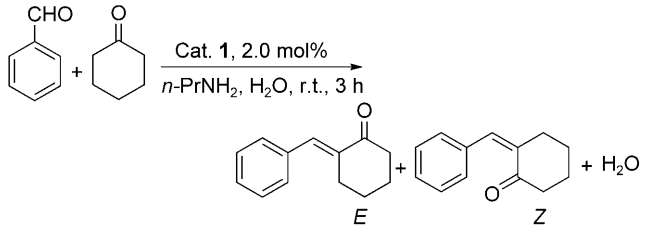
the formation of aldehyde self-condensation products or any other side-products (Table 4, entries 7 and 8).

Table 5 summarizes the results of the reaction between benzaldehyde and various ketones or malonates. Both the cyclic and acyclic ketones selectively produce (*E*)-α,β-unsaturated ketones in high yields (Table 5, entries 1–4); the active methylene compounds are efficient substrates as well. Using the adopted method, we obtained almost quantitative yields of the desired products when pentane-2,4-dione, dimethyl and diethyl malonates were used (Table 5, entries 5–7).

To test the reusability of **1**, the catalyst was subject to cycles of benzaldehyde, propylamine or cyclohexanone reaction (Table 6). We observed that within a test of 7 cycles, there was almost no change in product yield (94–95%) and stereoselectivity (*E*/*Z*>99/1). Moreover, we have analyzed the structural integrity of the recycled catalyst by NMR techniques and found that the structure of the recycled catalyst is consistent with that of the freshly prepared catalyst. In other words, the catalyst is very stable and suitable for reuse.

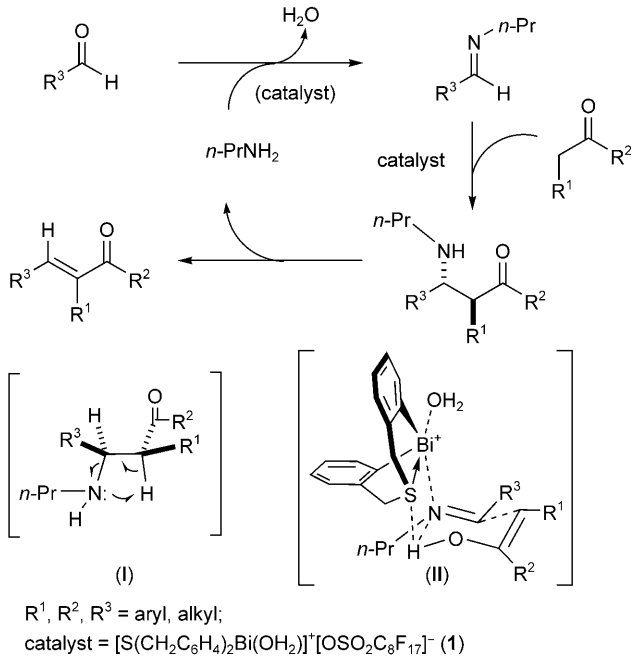
The fact that the reaction only proceeds with primary amines suggests that the formation of imine (its presence in the reaction mixture was confirmed) is essential. We envisaged that the amine is regenerated in the final step, and only a catalytic amount of amine would be enough. Indeed we found that the reaction can efficiently proceed with only 10 mol% of amine (Scheme 3). Although further study is necessary to clarify the reaction mechanism, the results mentioned so far suggest that the reaction probably takes place through a Mannich-type mechanism as shown in Scheme 4. The formation of imines from an aldehyde and an amine can proceed without a catalyst, while compound **1** probably has a positive effect on the imine formation. It is worth noting that the *E*/*Z*-selectivity of the current reaction very well corresponds to the *anti*/*syn*-selectivity of the Mannich reaction using $PhNH_2$ instead of *n*-$PrNH_2$, which we recently reported (for **1**, >99:1 *vs.* >99:1; for **2**, 43:57 *vs.* 57:43; for **3**, 64:36 *vs.* 64:36; for **4**, 93:7 *vs.* 95:5; for **5**, 86:14 *vs.* 86:14).[4d] This result strongly suggests that the change of amines does not affect the diastereoselectivity of the Mannich adducts, and that the final product is formed through stereospecific *syn*-elimination from the intermediate Mannich adduct, as shown in (**I**).

Table 6. The reusability of catalyst **1** in the synthesis of α,β-unsaturated ketones.[a]



Cycle	Yield of recovered Cat. [%]	Yield of product [%][b]	*E*/*Z*[c]
1	99	95	>99/1
2	96	95	>99/1
3	97	94	>99/1
4	96	95	>99/1
5	95	94	>99/1
6	94	95	>99/1
7	92	94	>99/1

[a] PhCHO, 1.0 mmol; *n*-$PrNH_2$, 1.0 mmol; cyclohexanone, 1.2 mmol; Cat., 0.02 mmol; H_2O 2.0 mL; room temperature, 3 h.
[b] Isolated yield.
[c] Determined by ^1H NMR.



Scheme 4. A plausible catalytic cycle for the crossed-condensation reaction of ketones and aldehydes catalyzed by **1** in the presence of *n*-$PrNH_2$.

The structures of the cationic parts of catalysts **1** (and **4**) and **3** are relatively similar. However, the stereoselectivity of the reaction was very different. This result would suggest the importance of the sulfur atom in **1**. As mentioned above, the sulfur atom in **1** can act as a weak Lewis base, and the high stereoselectivity may be explained if the addition reaction step proceeds through a transition state like (**II**) in which both the Lewis acid and the Lewis base parts of **1** act simultaneously to gather two reacting substrates in a chair-type cyclohexane arrangement with less steric repulsion.

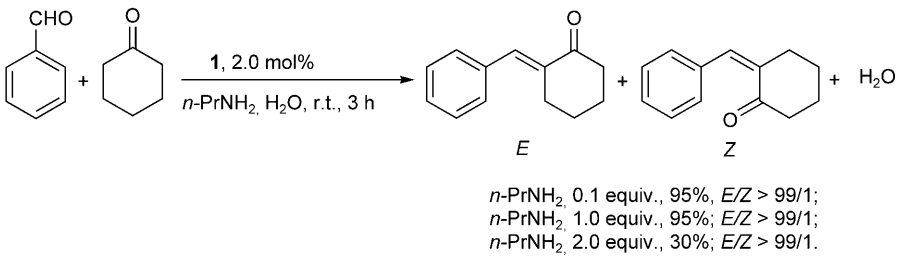
Conclusions

In conclusion, we have synthesized and characterized an organobismuth perfluorooctanesulfonate **1**, which is air-stable and exhibits both acidic and basic characteristics. The compound shows high catalytic activity, stereoselectivity, stability, and reusability for the synthesis of (*E*)-α,β-unsaturated ketones by the direct crossed condensation of aldehydes and ketones. We found that the new procedure works effectively with aromatic as well as enolizable aliphatic aldehydes. It is expected that the compound **1** will find broad applications in organic synthesis.

Experimental Section

General

All chemicals were purchased from Aldrich. Co., Ltd. as well as other chemical providers and used as received unless otherwise indicated. $[S(CH_2C_6H_4)_2BiCl]$ (**2**), the precursor of $[S(CH_2C_6H_4)_2Bi(OH_2)]^+[C_8F_{17}SO_3]^-$ (**1**), was prepared according to the procedure described in the literature.[15] The catalytic reactions were carried out under air in water. The NMR spectra were recorded at 25 °C over an INOVA-400 M



Scheme 3. Effect of the amount of *n*-$PrNH_2$ on product yield.

(Varian) instrument calibrated using tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed with a VARIO EL III (Elementar). The single-crystal X-ray diffraction analysis on **1** was performed in Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences with a SMART-APEX instrument. The TG-DSC analysis was performed on a NETZSCH-STA-449C (operation conditions: N_2, 5 °C/min heating rate). Melting points were determined with an XT-4 micro melting point apparatus (Beijing Tech Instrument Co., Ltd.). The acidity was measured by the Hammett indicator method.[16] The employed indicators included crystal violet ($pK_a=0.8$), dimethyl yellow ($pK_a=3.3$), methyl red ($pK_a=4.8$), neutral red ($pK_a=6.8$), bromothymol blue ($pK_a=7.2$), and thymol blue ($pK_a=8.9$). Acid/base strength was expressed by the Hammett acidity function (H_0) and the Hammett basicity function (H_-), respectively, which was scaled by the pK_a value of the indicators.

Preparation of $[S(CH_2C_6H_4)_2Bi(OH_2)]^+ [C_8F_{17}SO_3]^-$ (1)

To a solution of $S(CH_2C_6H_4)_2BiCl$ (0.456 g, 1.0 mmol) in THF (20 mL), a solution of $AgOSO_2C_8F_{17}$[16a] (0.607 g, 1.0 mmol) in THF (10 mL) was added. After the mixture had been stirred in the dark at room temperature for 3 h, it was subject to filtration under air. The filtrate was then mixed with hexane (1.0 mL), and after 24 h, colorless crystals formed; yield: 927 mg (99%); mp 188–189 °C. Crystals suitable for X-ray diffraction analysis were obtained by recrystallization of **1** from THF/hexane solution. ^{1}H NMR (400 MHz, acetone-d_6, 25 °C, TMS): $\delta=8.29$ (d, 2H, $^3J_{H,H}=7.6$ Hz, ArH), 7.86 (d, 2H, $^3J_{H,H}=8.0$ Hz, ArH), 7.58 (t, 2H, $^3J_{H,H}=6.8$, 7.2 Hz, ArH), 7.46 (t, 2H, $^3J_{H,H}=6.8$, 7.2 Hz, ArH), 5.15 (d, 2H, $^2J_{H,H}=15.6$ Hz, $ArCH_2$), 4.85 (d, 2H, $^2J_{H,H}=16.4$ Hz, $ArCH_2$), 2.99 (s, 2H, H_2O); ^{13}C NMR (100 MHz, acetone-d_6, 25 °C, TMS): $\delta=45.53$, 128.72, 130.98, 132.64 (2C), 138.19, 153.62, 206.06 ($C_8F_{17}SO_3$); ^{19}F NMR (376 MHz, acetone-d_6, 25 °C): $\delta=-121.18$ (b, 2F, $^3J_{F,F}=15.79$ Hz, -CF_2-), −117.72 (s, 2F, -CF_2-), −116.88 [s, 4F, -$(CF_2)_2$-], −116.56 (s, 2F, -CF_2-), −115.32 (s, 2F, -CF_2-), −109.15 (t, 2F, $^3J_{F,F}=14.29$ Hz, -CF_2-), −76.04 (t, 3F, $^3J_{F,F}=10.90$ Hz, CF_3-); elemental analysis calcd. (%) for $C_{22}H_{14}BiF_{17}O_4S_2$: C 28.16, H 1.50, S 6.83; found: C 28.19, H 1.49, S 6.82.

Crystal data for **1**: $C_{22}H_{14}BiF_{17}O_4S_2$; $M=938.43$; monoclinic; space group $P2_1/c$; $a=24.7673$ (17) Å, $b=11.7803$ (8) Å, $c=10.0588$ (7) Å; $\beta=97.8420(10)$ deg; $V=2907.4$ (3) Å^3; $T=293(2)$ K; $Z=4$; reflections collected/unique, 15666/5693, $R_{int}=0.089$; final R indices [$I>2\sigma(I)$], $R_1=0.0518$, $wR_2=0.1352$; R indices (all data), $R_1=0.0693$, $wR_2=0.1287$. GOF = 0.940. CCDC 733233 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Typical Procedure for the Synthesis of (*E*)-α,β-Unsaturated Ketones in Water Catalyzed by Catalyst 1

To a 25-mL round-bottomed flask were added catalyst **1** (18 mg, 0.02 mmol), PhCHO (106 mg, 1.0 mmol), *n*-$PrNH_2$ (59 mg, 1.0 mmol), cyclohexanone (117 mg, 1.2 mmol) and H_2O (2.0 mL). Then the mixture was stirred for 3 h as monitored by TLC analysis until PhCHO as well as the intermediate imine obtained from PhCHO and *n*-$PrNH_2$ were consumed completely. Then the mixture was extracted with Et_2O (10 mL × 3), and the combined organic layer was evaporated under vacuum. The resulting residue was subject to column chromatography on silica gel (200–300 meshes) (petroleum ether/ethyl acetate = 5/1, v/v); yield: 177 mg (95% based on PhCHO). All the products were characterized by comparison of ^{1}H and ^{13}C NMR spectral data as reported.[20]

(*E*)-2-Benzylidenecyclohexanone (Table 4, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=1.77$–1.78 (m, 2H, CH_2), 1.92–1.94 (m, 2H, CH_2), 2.54 (t, $^3J_{H,H}=6.8$ Hz, 2H, CH_2), 2.84–2.85 (m, 2H), 7.32–7.35 (m, 1H, ArH), 7.36–7.40 (m, 4H, ArH), 7.50 (t, $^4J_{H,H}=2.4$ Hz, 1H, ArCH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta=23.40$, 23.87, 28.92, 40.33, 128.31, 128.50, 130.27, 135.56, 136.66, 201.78.

(*E*)-2-(4-Methylbenzylidene)cyclohexanone (Table 4, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$, 25°, TMS): $\delta=1.75$–1.78 (m, 2H, CH_2), 1.91–1.94 (m, 2H, CH_2), 2.37 (s, 3H, CH_3), 2.51–2.55 (t, $^3J_{H,H}=6.8$ Hz, 2H, CH_2), 2.82–2.86 (m, 2H, CH_2), 7.18–7.20 (d, $^3J_{H,H}=8.0$ Hz, 2H, ArH), 7.30–7.33 (d, $^3J_{H,H}=8.4$ Hz, 2H, ArH), 7.49 (1H, s, ArCH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta=21.38$, 23.36, 23.89, 29.00, 40.28, 129.11, 130.45, 132.82, 135.83, 138.81, 159.98, 202.11.

(*E*)-2-(4-Methoxybenzylidene)cyclohexanone (Table 4, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=1.65$–1.73 (m, 2H, CH_2), 1.79–1.87 (m, 2H, CH_2), 2.44 (t, $^3J_{H,H}=6.7$ Hz, 2H, CH_2), 2.76 (m, 2H, CH_2), 3.75 (s, 3H, -OCH_3), 6.83 (d, $^3J_{H,H}=8.8$ Hz, 2H, ArH), 7.31 (d, $^3J_{H,H}=8.8$ Hz, 2H, ArH), 7.41 (t, $^4J_{H,H}=2.1$ Hz, 1H, Ar-CH=C); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta=23.20$, 23.92, 28.68, 40.31, 55.46, 114.09, 128.9, 132.40, 134.51, 136.64, 160.11, 201.92.

(*E*)-2-(4-Chlorobenzylidene)cyclohexanone (Table 4, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=1.61$–1.69 (m, 2H, CH_2), 1.77–1.85 (m, 2H, CH_2); 2.42 (t, $^3J_{H,H}=6.8$ Hz, 2H, CH_2), 2.68 (m, 2H, CH_2), 7.19–7.25 (m, 4H, ArH), 7.32 (t, $^4J_{H,H}=2.2$ Hz, 1H, Ar-CH=C); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta=23.23$, 23.74, 28.85, 40.20, 128.53, 131.47, 134.02, 134.34, 137.07, 201.08.

(*E*)-2-[4-(Trifluoromethyl)benzylidene]cyclohexanone (Table 4, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=1.80$ (t, $^3J_{H,H}=6.8$ Hz, 2H, CH_2), 1.96 (t, $^3J_{H,H}=9.6$ Hz, 2H, CH_2), 2.56 (t, $^3J_{H,H}=6.8$ Hz, 2H, CH_2), 2.82 (t, 2H, $^3J_{H,H}=6.4$ Hz, CH_2), 7.52 (d, $^3J_{H,H}=8.0$ Hz, 2H, ArH), 7.64 (d, $^3J_{H,H}=8.0$ Hz, 2H, ArH), 7.88 (s, 1H, ArCH=); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta=23.30$, 23.87, 28.93, 40.32, 124.09, 129.11, 130.45, 132.92, 135.73, 138.82, 161.13, 200.98.

(*E*)-2-[(*E*)-3-Phenylallylidene]cyclohexanone (Table 4, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=1.77$–1.91 (m, 4H, CH_2), 2.48 (t, 2H, $^3J_{H,H}=6.8$ Hz), 2.74 (t, $^3J_{H,H}=6.0$ Hz, 2H, CH_2), 6.90–7.04 (m, 2H, ArH), 7.24–7.48 (m, 6H, ArH and olefinic-H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta=23.20$, 23.52, 27.12, 40.19, 123.24, 127.32, 128.88, 129.09, 135.12, 135.63, 136.77, 141.05, 200.92.

(*E*)-2-(3-Phenylpropylidene)cyclohexanone (Table 4, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=1.68$–1.62 (m, 2H, CH_2), 1.84–1.77 (m, 2H, CH_2), 2.44–2.36 (m,

6H, -CH_2-CH_2Ph, CH_2), 2.75 (t, $^3J_{H,H}$=8.0 Hz, 2H, CH_2), 6.65 (t, $^3J_{H,H}$=2.8 Hz, 1H, CH=C), 7.21–7.16 (m, 3H, ArH), 7.28 (t, $^3J_{H,H}$=7.2 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=23.51, 23.64, 26.82, 29.90, 34.83, 40.29, 126.26, 128.61, 137.04, 138.13, 138.06, 141.47, 201.42.

(*E*)-2-Octylidenecyclohexanone (Table 4, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=0.88 (t, $^3J_{H,H}$=6.0 Hz, 3H, CH_3), 1.25–1.38 (m, 12H), 1.76–1.83 (m, 2H, CH_2), 2.36–2.42 (m, 4H, C=CH-CH_2, CH_2), 2.76 (t, $^3J_{H,H}$=8.4 Hz, 2H, CH_2), 6.55 (t, $^3J_{H,H}$=2.8 Hz, 1H, CH=C); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=14.02, 22.68, 23.33, 23.64, 25.17, 26.68, 27.82, 28.5, 29.14, 31.81, 40.02, 135.93, 139.67, 200.79.

(*E*)-2-Benzylidenecyclopentanone (Table 5, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=2.06 (t, $^3J_{H,H}$=7.6 Hz, 2H, CH_2), 2.44 (t, $^3J_{H,H}$=8.0 Hz, 2H, CH_2), 3.00 (t, $^3J_{H,H}$=7.2 Hz, 2H, CH_2), 7.30–7.48 (m, 4H, ArCH and ArCH=C), 7.56–7.59 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=20.20, 29.36, 37.79, 128.73, 128.36, 130.55, 132.42, 135.57, 136.12, 208.24.

(*E*)-4-Phenylbut-3-en-2-one (Table 5, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=2.35 (s, 3H, CH_3), 6.70 (d, $^3J_{H,H}$=16.9 Hz, 1H, =CH-C=O), 7.39–7.35 (m, 3H, ArH), 7.54–7.47 (m, 3H, ArH and Ar-CH=C); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=26.81, 128.70, 129.46, 130.62, 132.48, 139.31, 142.75, 197.72.

(*E*)-Chalcone (Table 5, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °, TMS): δ=7.40 (d, $^3J_{H,H}$=6.8 Hz, 3H, ArH), 7.52 (t, $^3J_{H,H}$=16.0 Hz, 1H, -CH-C=O), 7.55–7.60 (m, 2H, ArH), 7.63–7.65 (m, 2H, ArH, ArH), 7.79 (d, $^1J_{H,H}$=16.0 Hz, 1H, ArCH=C), 8.02 (d, ^3J=7.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=122.09, 128.45, 128.49, 128.60, 128.94, 130.51, 132.75, 134.90, 138.22, 144.73, 190.42.

3-Benzylidenepentane-2,4-dione (Table 5, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=2.24 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 7.36 (m, 5H, ArH), 7.44 (s, 1H, ArCH=C); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=26.22, 31.33, 128.71, 129.39, 130.41, 132.68, 139.62, 142.51, 196.47, 205.31.

Dimethyl 2-benzylidenemalonate (Table 5, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=3.84 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 7.38–7.40 (m, 3H, ArH), 7.45 (t, 2H, $^3J_{H,H}$=5.0 Hz, ArH), 7.77 (s, 1H, ArCH=C); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=60.92, 60.97, 126.32, 128.77, 129.41, 130.47, 132.89, 142.12, 164.12, 166.69.

Diethyl 2-benzylidenemalonate (Table 5, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=1.27–1.35 (m, 6H, 2CH_3), 4.30 (m, 4H, 2CH_2), 7.37–7.40 (m, 3H, ArH), 7.44–7.47(t, 2H, $^3J_{H,H}$=4.8 Hz, ArH), 7.74 (s, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=13.86, 14.12, 61.62, 61.67, 126.30, 128.75, 129.42, 130.49, 132.88, 142.11, 164.11, 166.66.

Typical Procedure for the Synthesis of (*E*)-α,β-Unsaturated Ketones Catalyzed by Recovered Catalyst 1

To a 100-mL round-bottomed flask were added catalyst **1** (0.18 g, 0.2 mmol), PhCHO (1.06 g, 10.0 mmol), *n*-$PrNH_2$ (0.59 g, 10.0 mmol), cyclohexanone (1.17 g, 12.0 mmol) and H_2O (20.0 mL). Then the mixture was stirred for 3 h monitored by TLC analysis until PhCHO as well as the intermediate (*E*)-*N*-benzylidenepropan-1-amine obtained from PhCHO and *n*-$PrNH_2$ were consumed completely. The mixture was extracted with CH_2Cl_2 and subject to evaporation under vacuum. Then the residue was suspended in diethyl ether, followed by filtration. After the filter cake of the catalyst had been washed twice with ethyl ether, it was used for catalyzing the next reaction cycle (Table 6). The combined filtrate was evaporated under vacuum, and the product was purified by column chromatography on silica gel (200–300 mesh) (petroleum ether/ethyl acetate = 5/1, v/v).

Crystal Data Refinements

Refinement of F^2 against all reflections: the weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt), etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on all data will be even larger. Hydrogen site location: inferred from neighbouring sites, H atoms treated by a mixture of independent and constrained refinement. Data collection: Bruker *SMART*; cell refinement: Bruker *SMART*; data reduction: Bruker *SHELXTL*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: Bruker *SHELXTL*; software used to prepare material for publication: Bruker *SHELXTL*.

Crystal data for (*S**)-2-[(*R**)-phenyl(propylamino)methyl]cyclohexanone: $C_{19}H_{21}NO$; M=279.37; monoclinic; space group $P2_1/n$; a=24.7673(17) Å, b=10.2965(7) Å, b=10.6213(7) Å, c=14.1700(10) Å; β=95.4070(10) deg; V=1542.77(18) Å^3; T=293(2) K; Z=4; reflections collected/unique, 3730/3235, R_{int}=0.016; final *R* indices [$I > 2\sigma(I)$], R_1=0.0470, wR_2=0.1330; *R* indices (all data), R_1=0.0537, wR_2=0.1420. GOF=0.940. CCDC 734040 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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