

M(acac)_n Covalently Anchored onto Amine Functionalized Silica: Highly Efficient and Recyclable Heterogeneous Catalysts for the Acetylation of Amines, Phenols and Alcohols Under Solvent-Free Conditions

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Abstract: In the present work, we have developed an efficient catalytic procedure for the chemo-selective acetylation of various substrates like amines, phenols and alcohols into their corresponding acetylated products using acetyl chloride in the presence of catalytic amount of metal acetylacetonates covalently anchored onto amine functionalized silica under solvent-free conditions. The catalysts were characterized by FT-IR, TGA and AAS analysis. The most active catalysts, SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂ were further characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). The catalysts were found to be stable and recycled several times without significant loss of activity. Easy preparation/heterogeneous nature of catalyst, solvent-free mild reaction conditions, higher yields and versatility towards various substrates make this method a facile tool for acetylation of various functional groups.

Keywords: Silica functionalized M(acac)_n, SiO₂-Co(acac)₂, SiO₂-Cu(acac)₂, acetylation of amines, phenols and alcohols, recyclable heterogeneous catalysts, solvent-free conditions.

1. INTRODUCTION

Selective protection of alcohols, phenols and amines is one of the most desirable transformations since it provides an efficient and inexpensive means of protecting hydroxy and amino groups in a multistep synthetic process [1]. These transformations are usually performed with acetic anhydride and/or acetyl chloride in the presence of stoichiometric amounts of either basic or acidic catalysts. A variety of procedures using homogeneous or heterogeneous catalysts [2-20] have been reported for this transformation. Although these procedures provide an improvement, yet many of these catalysts or activators need long reaction times, drastic reaction conditions or tedious work-up, and the catalysts are moisture sensitive or expensive.

In order to overcome above problems, development of green procedures using heterogeneous catalysts under solvent-free conditions has aroused great interest in recent years [21] since organic reactions run under solvent-free conditions have added advantages of formation of cleaner products and avoidance of toxic or volatile solvents. Heterogeneous catalytic materials play a very important role in the selective protection of functional groups, thus leads to economically advantageous, environmentally friendly and also improved process conditions for large scale synthesis [22-26]. In recent years, the development of covalently anchored heterogeneous catalysts has become a major area of research. These catalysts offer advantages over non-covalent analogues such as increased stability in harsh reaction conditions due to stronger bonding forces between

support and catalyst. The immobilized catalysts are stable and leach proof, since covalent bonds are formed between the solid support and metal complex [27-29]. With a stronger attachment, there is less aggregation and loss of single site nature. From a practical viewpoint, the development of simple, inexpensive, widely applicable and environmentally benign catalysts/procedures is still an active area of research.

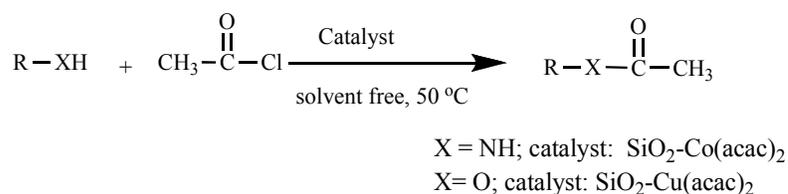
In the continuation of our studies on the applications of supported metal acetylacetonates [30, 31] as heterogeneous catalysts in organic transformations, we wish to report a mild and efficient method for the acetylation of amines, phenols and alcohols under solvent-free conditions (Scheme 1). The ultimate goal of this effort is to develop catalysts that impart selectivities, reactivity, and atom economy needed for cost-effective approaches to a variety of critical chemical transformations. Supported metal acetylacetonate complexes may not only serve as an overview of the fast growing field of transition-metal catalysis but also provide inspirations for the future discovery of more efficient and practical catalysts to help to tackle the economical and ecological challenges in the twenty-first century. We believe that the present protocol could be an important addition to the existing methodologies.

2. MATERIALS AND METHODS

2.1. General Remarks

The chemicals used were either prepared in our laboratories or purchased from Aldrich Chemical Company or Merck. The spectral data of the products were compared with those obtained from Aldrich, unless otherwise specified by a reference. The ¹H NMR data were recorded in CDCl₃ or DMSO-*d*₆ on Bruker DPX 200 spectrometer and FTIR spectra on Perkin-Elmer FTIR spectrophotometer. The mass spectral data were recorded on Bruker Esquires 3000 (ESI). SEM images were recorded using Jeol make T-300 Scanning

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Scheme 1. SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂ catalyzed acetylation of amines, alcohols and phenols at 50 °C under solvent-free conditions.

Electron Microscope and Transmission Electron Micrographs (TEM) were recorded on H7500 Hitachi. The amount of metal in catalysts was determined by AAS analysis and thermal analysis was carried out on Linsesis STA PT-1000 make thermal analyzer. All yields refer to the isolated yields.

2.2. General Procedure for the SiO₂-Co(acac)₂ Catalyzed Acetylation of Amines Under Solvent-Free Conditions

To a mixture of amine (1 mmol) and acetyl chloride (1 mmol) in a round bottom flask (25 mL), SiO₂-Co(acac)₂ (0.1 g, 2.4 mol% Co) was added and the reaction mixture was stirred at 50 °C under solvent-free conditions for an appropriate time (Table 1). After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and filtered. The residue was washed with hot ethyl acetate (30 mL), followed by distilled water (150 mL). The organic layer was washed with water and dried over anhydrous Na₂SO₄. Finally, the product was obtained after crystallization with EtOAc: pet ether.

2.3. General Procedure for the SiO₂-Cu(acac)₂ Catalyzed Acetylation of Phenols and Alcohols Under Solvent-Free Conditions

A mixture of phenol or alcohol (1 mmol), acetyl chloride (1 mmol) and SiO₂-Cu(acac)₂ (0.1 g, 1.7 mol% Cu) was

taken in a round bottom flask (25 mL) and stirred at 50 °C under solvent-free conditions for an appropriate time (Table 2). After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with ethyl acetate and filtered. The residue was washed with hot ethyl acetate (30 mL), followed by distilled water (150 mL). The organic layer was washed with water and dried over anhydrous Na₂SO₄. Finally, the product was obtained after crystallization with EtOAc: pet ether.

The structures of the products were confirmed by IR, ¹H NMR, mass spectral data and comparison with authentic samples obtained commercially or prepared according to the literature methods.

3. RESULTS AND DISCUSSION

3.1. Catalyst Preparation and Characterization

Silica functionalized metal acetylacetonates were prepared following the earlier reported procedure [30].

All the six heterogeneous catalysts were characterized by FTIR, TGA and AAS analysis [30]. The FTIR spectra of silica and AMPS exhibited strong bands, which are characteristic of the support matrix. The bands in the range of 3765-3308 cm⁻¹ were assigned to surface -OH groups and two strong bands at about 1103 and 799 cm⁻¹ were assigned to ν_{as}(Si-O-Si) and ν_s(Si-O-Si), respectively. After surface

Table 1. SiO₂-Co(acac)₂ Catalyzed Acetylation of Amines at 50 °C Under Solvent-Free Conditions^a

Entry	Substrate	Time (min)	Yield (%) ^b	m.p./lit. m.p (°C)
1	Aniline	5	94	110-114/113-115 [33]
2	2-Toluidine	30	91	109-111/112 [34]
3	3-Toluidine	30	90	65-66/66 [33]
4	4-Toluidine	10	91	152-153/154 [33]
5	2-Nitroaniline	30	95	92-94/94 [33]
6	3-Nitroaniline	60	90	154-155/155 [33]
7	4-Nitroaniline	20	91	214-215/216 [33]
8	2-Anisidine	10	88	88-87/88 [33]
9	4-Anisidine	15	89	129-130/130 [33]
10	2-Chloroaniline	15	90	87-88/88 [33]
11	4-Chloroaniline	5	91	178-180/179 [33]
12	Diethylamine	30	85	184-186/182-186(bp) [35]
13	2-Amino-4-phenylthiazole	10	90	207-209/208-209 [33]
14	2-Aminobenzene thiol	15	91	132-134/135 [33]

^aReaction conditions: Amine (1 mmol), acetyl chloride (1 mmol), SiO₂-Co(acac)₂ (0.1 g, 2.4 mol% Co) at 50 °C under solvent-free conditions.

^bIsolated yields.

Table 2. SiO₂-Cu(acac)₂ Catalyzed Acetylation of Phenols and Alcohols at 50 °C Under Solvent-Free Conditions^a

Entry	Substrate	Time (min)	Yield (%) ^b	m.p./lit. m.p (°C)
1	2-Nitrophenol	45	90	39-40/41 [33]
2	4-Nitrophenol	35	95	79-80/83 [33]
3	4-Chlorophenol	55	87	259/260 (bp) [36]
4	1-Naphthol	40	88	43-44/43-46 [33]
5	2-Naphthol	45	89	68-69/69-70 [33]
6	Resorcinol	30	92	144-146/146 (bp) [33]
7	Benzylalcohol	10	93	77-78/78 (bp) [35]
8	4-Chlorobenzylalcohol	10	92	79-81/78-81(bp) [37]
9	<i>n</i> -Butanol	25	94	124/124-126 (bp) [35]
10	<i>n</i> -Propanol	20	85	100-102/102 (bp) [35]
11	Isopropanol	15	84	89-90/85-91 (bp) [35]

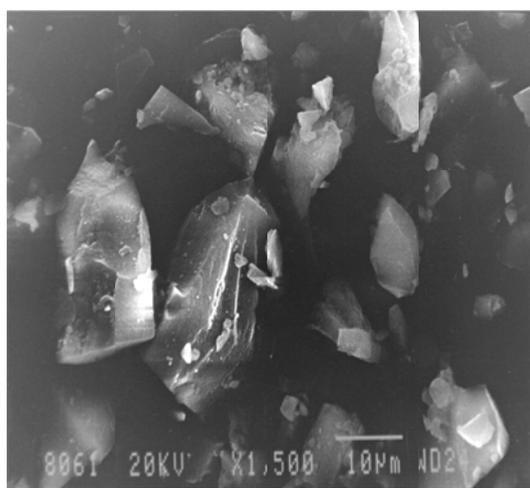
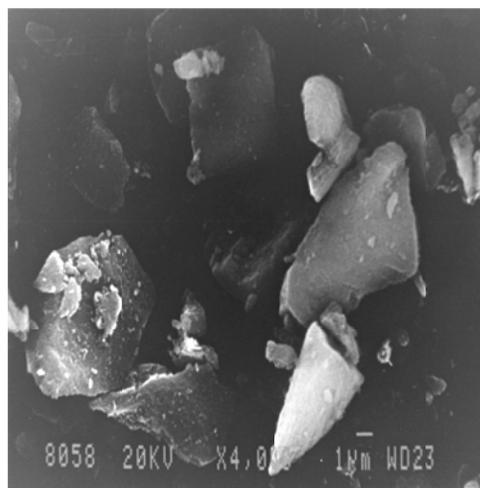
^aReaction conditions: Phenol or alcohol (1 mmol), acetyl chloride (1 mmol), SiO₂-Cu(acac)₂ (0.1 g, 1.7 mol% Cu) at 50 °C under solvent-free conditions.

^bIsolated yields.

modification, 3-aminopropylsilica (AMPS) displayed characteristic -CH₂ stretching bands at 2933 and 2974 cm⁻¹. After complexation, the -CH₂ stretching band got shifted to 2925 cm⁻¹ and the characteristic band due to C=N bond appeared at 1637 cm⁻¹ in the case of [SiO₂-Co(acac)₂] and 1633 cm⁻¹ for [SiO₂-Cu(acac)₂]. The amount of the metal supported onto AMPS was determined by Atomic Absorption Spectrometry (AAS). SiO₂-Co(acac)₂ contained 0.0145 g of cobalt and SiO₂-Cu(acac)₂ contained 0.011 g of copper, per g of the catalyst. The stability of the catalysts was determined by Thermo Gravimetric Analysis (TGA). The TGA was recorded by heating the sample at the rate of 10 °C min⁻¹. The TGA curve of SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂ showed an initial weight loss up to 120 °C, which was attributed to loss of the residual solvent and water trapped onto the surface of silica. Further, decomposition of organic functionalities starts from 260 to 450 °C. The major weight loss at high temperature is characteristic of chemisorbed material and confirms that the aminopropyl

group is chemically bound onto the surface of silica. Thus, the catalysts are stable up to 260 °C and it is safe to carry out the reaction at 50 °C under heterogeneous conditions.

In addition to this, the most active catalysts were further characterized by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The microstructure and morphology was studied using SEM (Fig. 1) which showed uniform surface morphology. The SEM images of SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂ showed a very slight roughening of the top surface of the catalyst which may possibly be due to the interaction of Co(acac)₂ and Cu(acac)₂ with the surface of the support material. The TEM images (Fig. 2) provided the distribution of cobalt and copper onto the surface of aminofunctionalized silica. No bulk aggregation of the metal occurred indicating that cobalt and copper are dispersed evenly onto the surface of support material. Furthermore, in the TEM images the black colour spots could be attributed to the presence of grafted Co and

**SiO₂-Co(acac)₂****SiO₂-Cu(acac)₂****Fig. (1).** SEM images of SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂.

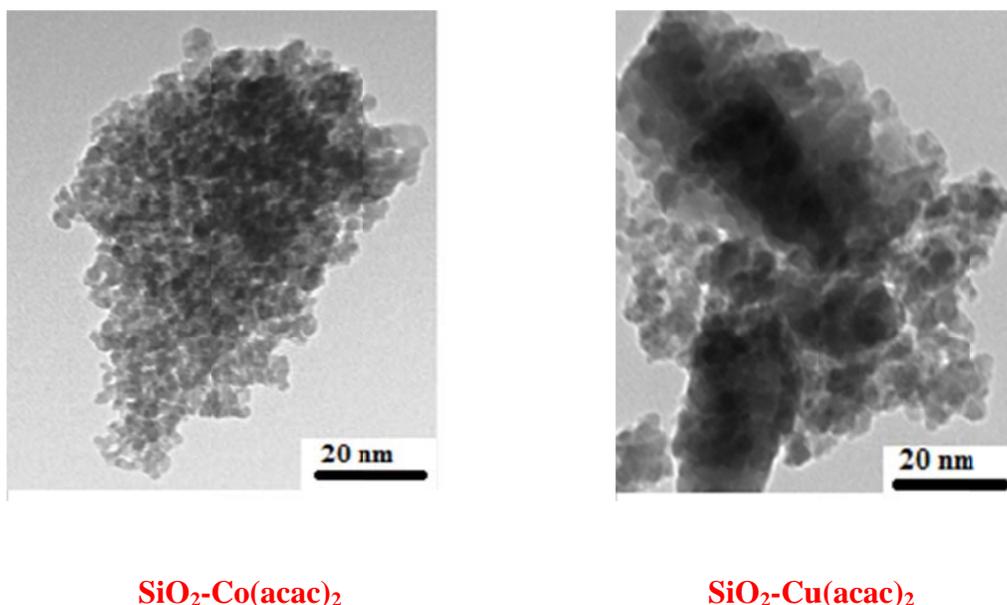


Fig. (2). TEM micrographs of SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂.

Cu-sites formed due to the coordination of AMPS with Co(II) and Cu(II) at the surface.

3.2. Catalyst Testing for the Acetylation of Amines, Phenols and Alcohols Under Solvent-Free Conditions

Initially, to select the most appropriate heterogeneous metal acetylacetonate catalyst, the acetylation of the test substrates was carried out using different silica functionalized metal acetylacetonates [SiO₂-M(acac)_n (M= Co, Cu, Mn, Pd and Ru, n= 2 or 3, 2.4 mol% metal)] at 50 °C under solvent-free conditions (Table 3). The screening of various catalysts allowed us to select SiO₂-Co(acac)₂ as the most effective catalyst for acetylation of amines and in case of phenols and alcohols, SiO₂-Cu(acac)₂ was found to be the best among rest of the catalysts (Table 3, entries 1 and 5).

While optimizing the different acetylating agents, acetyl chloride was found to be superior over acetic anhydride or acetic acid for the acetylation of amines, phenols and alcohols. The results are presented in Table 4. Varala has reported the acetylation of phenols and alcohols with acetic anhydride while acetyl chloride was used for amines [32].

Acetylation with acetic anhydride or acetic acid did not give good results with our catalytic system (Table 4) which clearly demonstrates that the acetylation is dependent on the nature of the catalyst.

To study the applicability of this method, wide range of anilines containing various electron-donating (Table 1, entries 2, 3, 4, 8, 9) and electron-withdrawing groups (Table 1, entries 5, 6, 7, 10, 11), and aliphatic amine (Table 1, entry 12) were taken and excellent results were obtained in each case affording the corresponding acetylated products in good yields. Furthermore, heteroaromatic amines and thiols (Table 1, entries 13, 14) were also converted to corresponding products in excellent yields. Phenolic compounds containing electron-withdrawing groups (Table 2, entries 1, 2, 3) also undergoes acetylation under the selected conditions. In general, acetylation of phenols proceeded relatively slower as compared to amines whereas the alcohols were selectively converted to corresponding acetates in quantitative yields (Table 2). Among the various hydroxy compounds studied, benzylic alcohols were found to be most active, giving the

Table 3. Comparison of Catalytic Activities of Different Covalently Anchored Metal Acetylacetonate Complexes for Acetylation of Amines, Phenols and Alcohols Under Solvent-Free Conditions

Entry	Catalyst	Amines		Phenols		Alcohols	
		Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
1	SiO ₂ -Co(acac) ₂	0.5	95	3	92	1	90
2	SiO ₂ -Mn(acac) ₃	2	94	1	93	1	93
3	SiO ₂ -Co(acac) ₃	1	92	3.5	93	1.5	90
4	SiO ₂ -Pd(acac) ₂	0.8	93	1	94	2	90
5	SiO ₂ -Cu(acac) ₂	3	90	0.58	95	0.42	94
6	SiO ₂ -Ru(acac) ₃	1	94	1.5	94	1.5	92

Reaction conditions: Substrate [2-nitroaniline or 4-nitrophenol or *n*-butanol] (1 mmol), acetyl chloride (1 mmol), SiO₂-M(acac)_n (2.4 mol% M) where M= Cu, Ru, Pd, Co, Mn; n=2 or 3 at 50 °C under solvent-free conditions.

Table 4. Effect of Different Acylating Agents in SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂ Catalyzed Acetylation of Amines, Phenols and Alcohols Under Solvent-Free Conditions

Entry	Substrate	Acylating Agent ^a	Time (h)	Yield (%) ^b
1	2-Nitroaniline	A	0.5	95
		B	4	10
		C	4	Traces
2	4-Nitrophenol	A	0.58	95
		B	4	10
		C	4	5
3	<i>n</i> -Butanol	A	0.42	94
		B	4	5
		C	4	15

Reaction conditions: Substrate (1 mmol), acylating agent (1 mmol), catalyst (0.1 g [SiO₂-Co(acac)₂ for entry 1, SiO₂-Cu(acac)₂ for entries 2, 3]) at 50 °C under solvent-free conditions.

^aA = CH₃COCl; B = CH₃COOH; C = (CH₃CO)₂O.

^bIsolated yields [A: entries 1-3], column chromatography yields [B: entry 1; B, C: entries 2 and 3].

corresponding acetylated products within a very short reaction time (Table 2, entries 7, 8).

In order to find out the role of SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂ as the heterogeneous catalysts, the reaction was carried out in case of entry 5 (Table 1) and entry 2 (Table 2)

in the presence of activated silica, 3-aminopropyl silica (AMPS) and without using any catalyst. The results are summarized in Table 5. It is clear that SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂ catalyzes the acetylation reaction. To study the deactivation and recyclability of the catalysts, a series of five consecutive runs were carried out with SiO₂-Co(acac)₂

Table 5. Effect of Catalyst in the Acetylation^a of Amines and Phenols Under Solvent-Free Conditions at 50 °C

Entry	Catalyst	Amines		Phenols	
		Time (h)	Yield (%) ^b	Time (h)	Yield (%) ^b
1	No catalyst	3	10	3	5
2	Activated SiO ₂	3	15	3	10
3	AMPS	3	20	3	15
4	SiO ₂ -Co(acac) ₂	0.5	95	3	88
5	SiO ₂ -Cu(acac) ₂	3	90	0.58	95

^aReaction conditions: Substrate [2-nitroaniline or 4-nitrophenol (1 mmol)], acetyl chloride (1 mmol), activated SiO₂ or AMPS or SiO₂-Co(acac)₂ or SiO₂-Cu(acac)₂ (0.1 g) at 50 °C under solvent-free conditions.

^bIsolated yields.

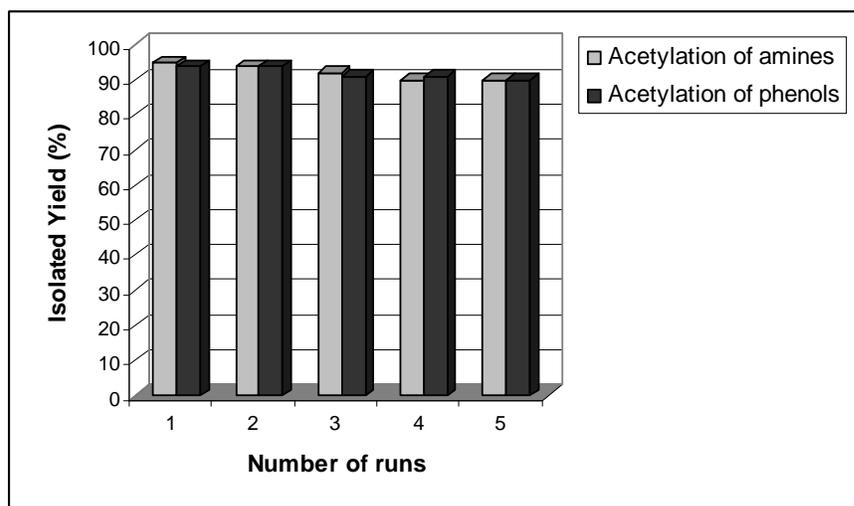


Fig. (3). Recyclability of SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂: Reaction conditions-Aniline (1 mmol), acetyl chloride (1 mmol), SiO₂-Co(acac)₂ (0.1 g, 2.4 mol% Co) at 50 °C under solvent-free conditions for 5 min (for acetylation of amines); Resorcinol (1 mmol), acetyl chloride (1 mmol), SiO₂-Cu(acac)₂ (0.1 g, 1.7 mol% Cu) at 50 °C under solvent-free conditions for 30 min (for acetylation of phenols).

and SiO₂-Cu(acac)₂ under the optimised conditions (Table 1, entry 1, Table 2, entry 6). The results are shown in Fig. (3), which indicated that, there is insignificant change in the activity of the catalyst up to 5th use. Further, there is no change in the amount of Co or Cu in SiO₂-M(acac)₂ after 5th use (as determined by AAS analysis).

4. CONCLUSION

In conclusion, we have developed a mild and efficient method for the acetylation of amines, phenols and alcohols using covalently anchored SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂ under solvent-free conditions. A variety of amines, phenols and alcohols were selectively and efficiently converted into corresponding products by treatment with acetyl chloride in the presence of catalytic amount of SiO₂-Co(acac)₂ and SiO₂-Cu(acac)₂. The use of silica functionalized metal acetylacetonates as highly efficient, easy to handle, non-toxic and reusable catalysts makes the present procedure eco-friendly and economically acceptable. Furthermore, the reaction conditions are fast, operationally simple, reasonably clean, high yielding and do not require excess reagents, which make this procedure a useful and attractive addition in the field of modern organic synthesis.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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