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Brief Communication

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Sequential Addition Reaction of Sulfanylmethyllithiums and Grignard Reagents to Thioformamides Leading to the Formation of 2-Phenyl-2-sulfanylethyl Tertiary Amines

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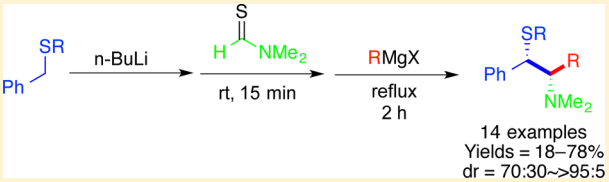
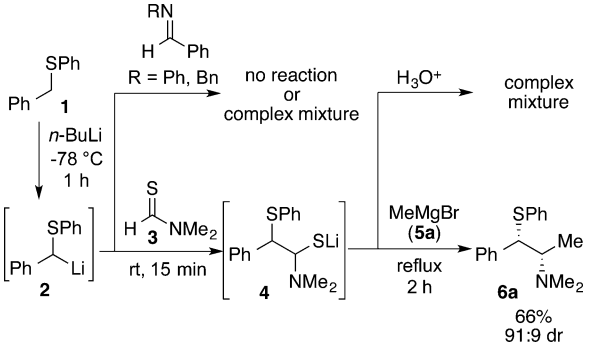
Supporting Information

ABSTRACT: The reaction of sulfanylmethyllithiums generated from benzylsulfanes and *n*-BuLi with *N*,*N*-dimethylthioformamide followed by the addition of Grignard reagents gave 2-phenyl-2-sulfanyl tertiary amines in moderate to good yields. A range of Grignard reagents involving primary alkyl, aryl, vinyl, and alkynyl Grignard reagents were used. Two carbon−carbon bond-forming reactions were achieved through a one-pot reaction. The reaction showed good to high diastereoselectivity, particularly with alkynyl Grignard reagents.



Phenethylamine skeletons are important motifs appearing in biologically active compounds.[1] Derivatives that include oxygen-containing functional groups such as ephedrines have shown a variety of biological activities.[2] Increasing attention has been paid to the introduction of sulfur-containing functional groups to phenethylamine skeletons,[3] since these functional groups are also expected to strongly affect the biological properties of the resulting compounds. Additionally, the properties of the sulfur atom can be applied to the design of new metal ligands.[4] For the synthesis of those skeletons, the Michael addition reaction of thiols to nitroalkenes[5] and ring-opening of aziridines with thiols[3d,e,6] have been developed. As alternative but versatile methods, we then envisioned the use of readily available benzyl sulfanes as a starting material. In fact, phenyl sulfanylmethyllithium **2**[7] generated from benzyl phenyl sulfane (**1**) was used in an attempt to add to imines derived from benzaldehyde (Scheme 1). However, the reaction either did not proceed or gave complex mixtures that included the starting materials under various reaction conditions. In contrast, reactions with amides[8] and thioamides[9] as synthetic equivalents of imines leading to amines have recently been developed. In this context, we found that the sequential reaction of organolithium and Grignard reagents to thioformamides gave tertiary amines.[10] In this sequence, the combination of a thioformamide and Grignard reagent can be regarded as an iminium salt derived from an aldehyde. We herein report the sequential addition reaction of sulfanylmethyllithiums and Grignard reagents to *N*,*N*-dimethylthioformamide leading to the formation of rare 2-phenyl-2-sulfanyl tertiary amines with good to high diastereoselectivity.

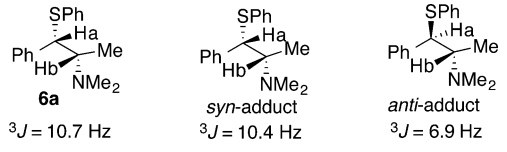
Scheme 1. Generation and Reaction of Phenyl Sulfanylmethyllithium 2



Initially, *N*,*N*-dimethylthioformamide (**3**) was added to **2**, aqueous workup gave a complex mixture, and the starting **3** was not recovered at all, which indicated that **2** reacted with **3** to possibly generate the adduct **4** (Scheme 1). Methylmagnesium bromide (**5a**) was then added to the reaction mixture of **2** and **3** to give the desired product **6a** in 66% yield with a diastereoselectivity of 91:9. The substitution reaction at the carbon atom having a dimethylamino group in **4** with **5a** proceeded.

The stereochemistry of the product **6a** was determined by comparison of the ^3J coupling constants between Ha and Hb, as shown in Chart 1. The ^3J coupling constant reported for the *syn*-adduct was 10.4 Hz, and that for the *anti*-adduct was 6.9

Chart 1. ^3J Coupling Constants of 6a and Those of Reported Results



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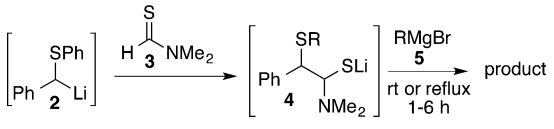
Hz.[11] On the basis of these values, product **6a** was determined to be the *syn*-adduct.

A range of Grignard reagents were used in the sequential addition reaction (Table 1). The reaction of primary alkyl

Table 1. Addition Reaction of Lithium 2 and Grignard Reagents 5 to Thioformamide 3[a]



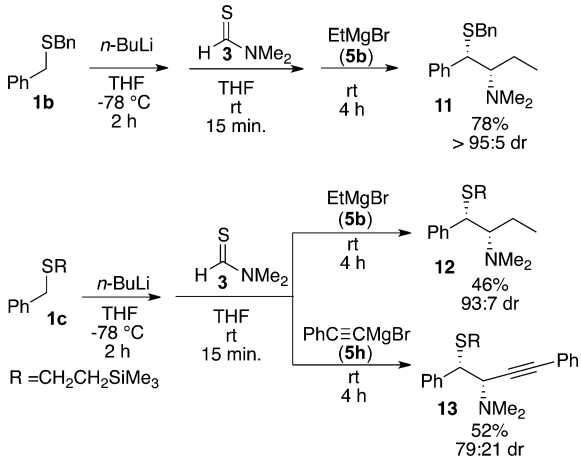
entry	RMgBr	product	yield (%)	dr
1	EtMgBr **5b**	**6b**	66	95:5
2	MgBr **5c**	**7**	64	81:19
3	MgBr **5d**	**8**	77	77:23
4	4-MeC$_6$H$_4$MgBr **5e**	**9a**	21	70:30
5	4-MeOC$_6$H$_4$MgBr **5f**	**9b**	25	78:22
6	4-FC$_6$H$_4$MgBr **5g**	**9c**	18	71:29
7	PhC≡CMgBr **5h**	**10a**	66	92:8
8	*n*-BuC≡MgBr **5i**	**10b**	66	>95:5
9	TMSC≡MgBr **5j**	**10c**	56	>95:5
10	C≡CMgBr **5k**	**10d**	56	88:12

[a]The reaction was carried out with **1** (0.5 mmol), *n*-BuLi (1.05 equiv), **3** (1.2 equiv), and Grignard reagent (1.5 equiv) in THF.

Grignard reagents proceeded smoothly to give **6b** (entry 1), whereas the reaction of secondary and tertiary Grignard reagents gave the desired products in only low yields. Allylic and vinyl Grignard reagents participated in the reaction to give the corresponding products **7** and **8** in good yields. In contrast, the use of aromatic Grignard reagents gave the products **9** in low yields with lower diastereoselectivity. In these cases, products[12] in which 2 equiv of Grignard reagent **5e**–**g** was added to the carbon atom of **3a** were also obtained as byproducts. This implied that the reaction between **2** and **3** leading to **4** is a reversible process and aromatic Grignard reagents preferably react with the starting **3**. The reaction of alkynyl Grignard reagents **5h**–**j** at room temperature took place, giving the corresponding products **10a**–**c** in low yields, while the reaction under reflux in THF led to **10a**–**c** with high efficiency. Notably, higher diastereoselectivity was observed for the reaction with alkynyl Grignard reagents **5h**–**j**.

For the generation of sulfanylmethyllithiums, dibenzylsulfane **1b** and benzylsilylethylsulfane **1b** were also used as starting materials (Scheme 2). Although the sequential addition reaction proceeded, the substituents on the sulfur atom influenced the diastereoselectivity.

Scheme 2. Sequential Reaction of Thioformamide 3 with Phenyl Sulfanylmethyllithiums Generated from Benzyl Sulfanes 1 and Grignard Reagents 5b



CONCLUSION

We demonstrated the sequential addition reaction of phenylsulfanyllithiums and Grignard reagents to N,N-dimethylthioformamide to give 2-sulfanyl tertiary amines as products. A range of Grignard reagents could be used in the present reaction, and the reaction showed good to high diastereoselectivity.

EXPERIMENTAL SECTION

General Remarks. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$. Chemical shifts of protons are reported in δ values referenced to tetramethylsilane as an internal standard in $CDCl_3$, and the following abbreviations were used: s: singlet, d: doublet, t: triplet, m: multiplet. The HRMS spectra were recorded on a double-focusing mass spectrometer (EI). Column chromatography was performed on silica gel 60 N (spherical neutral) 100–210 μm. Flash column chromatography was performed on silica gel 60 N (spherical neutral) 40–50 μm. All manipulations were carried out under an argon atmosphere.

Preparation of 2-Phenyl-2-sulfanyl Tertiary Amines. *Typical Procedure for the Preparation of N,N-Dimethyl-1-phenyl-1-(phenylsulfanyl)propan-2-amine (**6a**).* To a solution of benzylphenylsulfane (**1**) (0.5 mmol, 0.1001 g) in THF (2.0 mL) was added *n*-BuLi (1.05 equiv) at −78 °C, and the mixture was stirred for 1 h. To the resulting solution was added a solution of *N*,*N*-dimethylthioformamide (**3**) (1.2 equiv, 0.051 mL) in THF (1.5 mL), and the mixture was stirred for 15 min at room temperature. To this was added methylmagnesium bromide (**5a**) (1.5 equiv), and this mixture was stirred at reflux for 2 h. The resulting mixture was poured into a saturated aqueous solution of NH_4Cl and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated in

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vacuo. The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc/Et_3N = 10:1:0.01) to give the amine **6a** (0.089 g, 66%, dr = 91:9) as a pale yellow oil.

*N,N-Dimethyl-1-phenyl-1-(phenylsulfanyl)propan-2-amine (**6a**):*[11] pale yellow oil, 66% yield (0.089 g); ^{1}H NMR ($CDCl_3$) δ 0.75 (d, J = 6.3 Hz, 3H), 2.37 (s, 6H), 3.07−3.14 (dq, J = 6.3 and 10.7 Hz, 1H), 4.17 (d, J = 10.7 Hz, 1H), 7.02−7.49 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 8.9, 40.4, 59.5, 63.7, 126.8, 127.1, 128.2, 128.4, 129.0, 133.3, 135.7, 141.1.

*N,N-Dimethyl-1-phenyl-1-(phenylsulfanyl)butan-2-amine (**6b**):* pale yellow solid, 66% yield (0.094 g) as a diastereomeric mixture (dr = 95:5); mp 48.8−50.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.65 (t, J = 7.6 Hz, 3H), 1.22−1.32 (m, 1H), 1.49−1.60 (m, 1H), 2.46 (s, 6H), 2.87−2.92 (m, 1H), 4.28 (d, J = 9.8 Hz, 1H), 7.04−7.22 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 13.3, 20.9, 40.7, 58.8, 69.9, 126.5, 126.8, 128.0, 128.2, 129.1, 132.9, 135.8, 141.1; MS (EI) m/z 285 (M^+); HRMS (EI) calcd for $C_{18}H_{23}NS$ (M^+) 285.1551, found 285.1561.

*N,N-Dimethyl-1-phenyl-1-(phenylsulfanyl)pent-4-en-2-amine (**7**):* pale yellow oil, major isomer: 52% yield (0.077 g); minor isomer: 12% yield (0.176 g). Major isomer: ^{1}H NMR ($CDCl_3$) δ 2.03−2.10 (m, 1H), 2.26−2.33 (m, 1H), 2.46 (s, 6H), 3.09−3.14 (m, 1H), 4.31 (d, J = 9.8 Hz, 1H), 4.78−4.83 (m, 2H), 5.45−5.56 (m, 1H), 7.03−7.24 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 32.1, 41.0, 58.3, 68.4, 115.9, 126.7, 127.0, 128.0, 128.3, 129.2, 133.0, 135.4, 137.2, 140.4; MS (EI) m/z 297 (M^+); HRMS (EI) calcd for $C_{19}H_{23}NS$ (M^+) 297.1551, found 297.1533.

*N,N,4-Trimethyl-1-phenyl-1-(phenylsulfanyl)pent-3-en-2-amine (**8**):* colorless solid, major isomer: 57% yield (0.089 g); minor isomer: 20% (0.031 g). Major isomer: mp 65.1−69.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3H), 1.54 (s, 3H), 2.33 (s, 6H), 3.63 (d, J = 10.3 Hz, 1H), 4.28 (d, J = 10.3 Hz, 1H), 4.98 (t, J = 10.3 Hz, 1H), 7.03−7.25 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 18.0, 25.8, 40.6, 57.2, 65.9, 118.1, 126.2, 126.5, 127.5, 128.2, 128.6, 129.0, 132.2, 135.7, 137.6, 140.4; MS (EI) m/z 311 (M^+); HRMS (EI) calcd for $C_{20}H_{25}NS$ (M^+) 311.1708, found 311.1695.

*N,N-Dimethyl-2-phenyl-2-(phenylsulfanyl)-1-(p-tolyl)ethan-1-amine (**9a**):* pale yellow oil, 21% yield (0.036 g) as a diastereomeric mixture (dr = 70:30). Major isomer: ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 3H), 2.30 (s, 6H), 4.06 (d, J = 11.2 Hz, 1H), 4.83 (d, J = 11.2 Hz, 1H), 6.88−7.19 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 21.3, 41.2, 56.4, 73.2, 126.7, 127.1, 127.8, 128.5, 129.2, 129.6, 130.6, 133.0, 133.8, 135.3, 136.9, 140.2; MS (EI) m/z 347 (M^+); HRMS (EI) calcd for $C_{23}H_{25}NS$ (M^+) 347.1708, found 347.1691.

*1-(4-Methoxyphenyl)-N,N-dimethyl-2-phenyl-2-(phenylsulfanyl)-ethan-1-amine (**9b**):* pale yellow oil, 25% (0.045 g) as a diastereomeric mixture (dr = 78:22). Major isomer: ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 6H), 3.72 (s, 3H), 4.07 (d, J = 11.1 Hz, 1H), 4.82 (d, J = 11.1 Hz, 1H), 6.72 (d, J = 8.7 Hz, 2H), 6.91−7.20 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 40.8, 55.0, 56.2, 72.7, 112.8, 125.6, 126.5, 126.9, 127.7, 128.3, 129.0, 130.5, 133.5, 135.0, 139.9, 158.6; MS (EI) m/z 363 (M^+); HRMS (EI)calcd for $C_{23}H_{25}NOS$ (M^+) 363.1657, found 363.1687.

*1-(4-Fluorophenyl)-N,N-dimethyl-2-phenyl-2-(phenylsulfanyl)-ethan-1-amine (**9c**):* pale yellow solid, 18% (0.032 g) as a diastereomeric mixture (dr = 71:29). Major isomer: mp 86.1−90.0 °C; H NMR ($CDCl_3$) δ 2.31 (s, 6H), 4.08 (d, J = 11.4 Hz, 1H), 4.78 (d, J = 11.4 Hz, 1H), 6.87 (m, 2H), 6.97 (m, 7H), 7.08 (m, 3H), 7.18 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 40.9, 56.2, 72.7, 114.5, 126.7, 127.0, 127.7, 128.3, 128.9, 130.8, 133.6, 134.7, 139.5, 160.6, 163.1; ^{19}F NMR ($CDCl_3$) δ −115.06; MS (EI) m/z 351 (M^+); HRMS (EI) calcd for $C_{22}H_{22}FNS$ (M^+) 351.1457, found 351.1469.

*N,N-Dimethyl-1,4-diphenyl-1-(phenylsulfanyl)but-3-yn-2-amine (**10a**):* pale yellow solid, major isomer: 61% yield (0.109 g); minor isomer: 5% yield (0.09 g). Major isomer: mp 88.9−93.2 °C; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 6H), 3.97 (d, J = 10.9 Hz, 1H), 4.41 (d, J = 10.9 Hz, 1H), 7.09−7.33 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 41.7, 57.1, 63.7, 84.0, 88.4, 123.1, 127.1, 127.5, 128.1, 128.2, 128.6, 129.3, 131.8, 133.2, 134.7, 139.9; MS (EI) m/z 357 (M^+); HRMS (EI) calcd for $C_{24}H_{23}NS$ (M^+) 357.1551, found 357.1561.

*N,N-Dimethyl-1-phenyl-1-(phenylsulfanyl)oct-3-yn-2-amine (**10b**):* pale yellow solid, 66% yield (0.111 g) as a diastereomeric mixture (dr = >95:5). Major isomer: mp 64.4−69.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 7.3 Hz, 3H), 1.21 (m, 2H), 1.30 (m, 2H), 2.06 (m, 2H), 2.35 (s, 6H), 3.75 (d, J = 11.0 Hz, 1H), 4.27 (d, J = 11.0 Hz, 1H), 7.06−7.24 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 13.6, 18.4, 21.9, 31.1, 41.6, 57.4, 63.2, 74.0, 88.6, 127.1, 127.3, 128.1, 128.5, 129.3, 133.3, 134.9, 140.2; MS (EI) m/z 337 (M^+); HRMS (EI) calcd for $C_{22}H_{27}NS$ (M^+) 337.1864, found 337.1886.

*N,N-Dimethyl-1-phenyl-1-(phenylsulfanyl)-4-(trimethylsilyl)but-3-yn-2-amine (**10c**):* colorless solid, 56% yield (0.099 g) as a diastereomeric mixture (dr = >95:5). Major isomer: mp 88.6−94.7 °C; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9H), 2.34 (s, 6H), 3.70 (d, J = 10.8 Hz, 1H), 4.28 (d, J = 10.8 Hz, 1H), 7.05−7.28 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 0.3, 41.7, 57.0, 64.0, 93.2, 100.1, 127.2, 127.6, 128.2, 128.7, 129.5, 133.1, 134.9, 139.9; MS (EI) m/z 353 (M^+); HRMS (EI) calcd for $C_{21}H_{27}NSSi$ (M^+) 353.1633, found 353.1609.

*4-(Cyclohex-1-en-1-yl)-N,N-dimethyl-1-phenyl-1-(phenylsulfanyl)but-3-yn-2-amine (**10d**):* colorless solid, 56% yield (0.101 g) as a diastereomeric mixture (dr = 88:12). Major isomer: mp 111.1−113.4 °C; ^{1}H NMR ($CDCl_3$) δ 1.54 (m, 4H), 1.92 (br, 2H), 2.00 (br, 2H), 2.37 (s, 6H), 3.85 (d, J = 11 Hz, 1H), 4.32 (d, J = 11 Hz, 1H), 5.89 (m, 1H), 7.07−7.28 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 21.8, 22.5, 25.8, 29.6, 41.8, 57.2, 63.8, 81.0, 90.4, 120.6, 127.1, 127.5, 128.2, 128.7, 129.4, 133.1, 134.6, 135.0, 140.1; MS (EI) m/z 361 (M^+); HRMS (EI) calcd for $C_{24}H_{27}NS$ (M^+) 361.1864, found 361.1840.

*1-(Benzylsulfanyl)-N,N-dimethyl-1-phenylbutan-2-amine (**11**):* pale yellow oil, 78% yield (0.117 g) as a diastereomeric mixture (dr = >95:5). Major isomer: ^{1}H NMR ($CDCl_3$) δ 0.51 (t, J = 7.5 Hz, 3H), 1.05−1.11 (m, 1H), 1.35−1.46 (m, 1H), 2.30 (s, 6H), 2.68−2.74 (m, 1H), 3.10 (d, J = 13.5 Hz, 1H), 3.28 (d, J = 13.0 Hz, 1H), 3.71 (d, J = 9.7 Hz, 1H), 7.11−7.35 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 13.6, 21.1, 35.2, 40.9, 54.3, 70.5, 126.9, 127.5, 128.5, 128.7, 129.3, 129.7, 139.0, 141.3; MS (EI) m/z 299 (M^+); HRMS (EI) calcd for $C_{19}H_{25}NS$ (M^+) 299.1708, found 299.1690.

*N,N-Dimethyl-1-phenyl-1-((2-(trimethylsilyl)ethyl)sulfanyl)butan-2-amine (**12**):* colorless oil, 46% yield (0.071 g) as a diastereomeric mixture (dr = 93:7). Major isomer: ^{1}H NMR($CDCl_3$) δ 0.00 (s, 9H), 0.73−0.81 (m, 1H), 0.77 (t, J = 7.5 Hz, 3H), 0.90−0.98 (m, 1H), 1.29−1.37 (m, 1H), 1.59−1.68 (m, 1H), 2.09−2.24 (m, 2H), 2.56 (s, 6H), 2.90−2.95 (m, 1H), 4.12 (d, J = 9.7 Hz, 1H), 7.34−7.53 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −1.6, 13.8, 17.3, 21.3, 41.0, 54.5, 70.4, 127.2, 128.6, 129.4, 141.7; MS (EI) m/z 309 (M^+); HRMS (EI) calcd for $C_{17}H_{31}NSSi$ (M^+) 309.1946, found 309.1926.

*N,N-Dimethyl-1,4-diphenyl-1-((2-(trimethylsilyl)ethyl)sulfanyl)-but-3-yn-2-amine (**13**):* yellow oil, 52% yield (0.099 g) as a diastereomeric mixture (dr = 80:20). Major isomer: ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H), 0.93−1.01 (m, 1H), 1.06−1.14 (m, 1H), 2.38−2.52 (m, 2H), 2.70 (s, 6H), 4.16 (d, J = 10.8 Hz, 1H), 4.42 (d, J = 10.8 Hz, 1H), 7.48−7.74 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −1.7, 17.2, 26.2, 41.7, 52.9, 64.3, 84.5, 88.1, 123.2, 127.7, 128.2, 128.3, 128.5, 129.2, 131.8, 140.2; MS (EI) m/z 381 (M^+); HRMS (EI) calcd for $C_{23}H_{31}NSSi$ (M^+) 381.1946, found 381.1947.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01857.

^{1}H NMR and ^{13}C NMR spectra for new products (PDF)

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Notes

The authors declare no competing financial interest.

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