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Synthesis, Structural Characterization, and Catalytic Activity of IPrNi(styrene)$_2$ in the Amination of Aryl Tosylates

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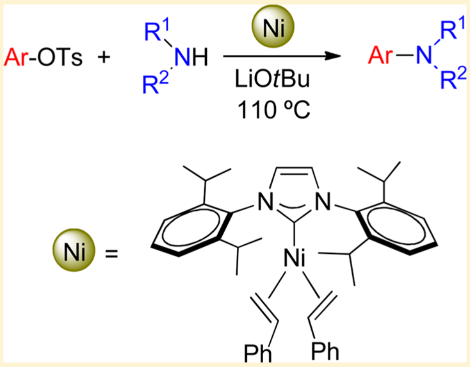
Ⓢ *Supporting Information*

ABSTRACT: A novel bis-styrene IPrNi^0 derivative has been synthesized from the reaction of Ni(COD)$_2$ and free 1,3-bis(2,6-diisopropylphenyl)imidazolidene (IPr) ligand in the presence of styrene. The complex has been characterized by spectroscopic data as well as by X-ray crystallography. Its catalytic performance in the amination reaction of aryl tosylates is also reported. The catalytic reactions proceed in a very selective manner, affording moderate to high yields of cross-coupling products in short reaction times at 110 °C.



The extraordinary success of the cross-coupling methodology for the formation of carbon−carbon and carbon−heteroatom bonds is closely linked to the development of catalytic systems based on palladium.[1] The fundamental properties of Pd such as its size, its strong preference for 0 and +2 oxidation states, and its electronegativity account for the versatility and selectivity of this metal in cross-coupling reactions.[2] However, Pd(0) complexes shows rather low reactivity toward organic chlorides and phenol-based electrophiles, which are more economical and available coupling partners in comparison to iodides, bromides, or triflates.[3] Electron-rich and sterically demanding donor ligands such as alkylphosphines[4] or N-heterocyclic carbenes[5] are required in order to improve the reactivity of Pd-based catalysts toward those less reactive electrophiles. Moreover, nickel is a more nucleophilic metal in comparison to Pd due to its smaller size,[3b] in such a way that Ni(0) has exhibited a high reactivity toward aryl chlorides even in the absence of any ligand.[6] Outstanding examples of nickel-mediated cross-coupling processes involving rarely used phenol-based electrophiles have recently appeared in the literature. Thus, ethers,[7] carboxylates,[8] carbamates,[9] sulfates and sulfamates,[10] and also phenolic salts[11] have been employed as substrates in different C−C coupling reactions catalyzed by Ni(II) systems bearing phosphine ligands. However, the use of electron-rich phosphine ligands in the Ni-catalyzed amination of phenol-derived electrophiles produced low yields of coupling products.[12] In these C−N bond formation processes, N-heterocyclic carbene ligands (NHCs) display a much better performance.

The catalytic activity of NHC−nickel complexes in cross-coupling chemistry has been less explored in comparison to that of palladium.[13] Among the examples described in the literature, those focused on the catalytic role of the NHC−Ni^0 species formed in situ or from a well-defined NHC−Ni^0 precursor are scarce and have been mostly reported in the context of carbon−heteroatom bond-forming reactions.[12,14] It is worth noting that NHC−Ni^0 species have shown remarkable activity in the activation of carbon−halide bonds, particularly organic chlorides and fluorides used as electrophiles in Kumada and Suzuki couplings.[15]

We are interested in the development of catalytic systems based on structurally well defined NHC−Ni complexes for cross-coupling reactions. Very recently, we have described[16] the first examples of room-temperature nickel-catalyzed Buchwald−Hartwig aminations of aryl and heteroaromatic chlorides mediated by IPrNi(allyl)Cl.[17] This NHC−Ni^{II} catalytic precursor had to be reduced in the presence of the base NaO^{t}Bu to generate the active IPrNi^0 species.[18] We thought of eliminating the reduction step to form the monoligated NHC−

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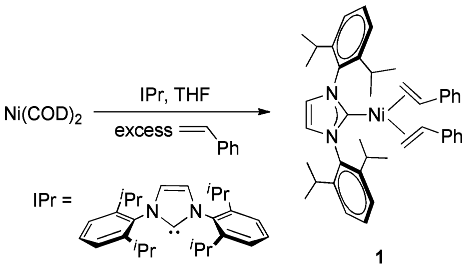
Ni^0 by preparing an easy to handle NHC−Ni^0 precursor. In this paper, we disclose the synthesis and the structural characterization of IPrNi(styrene)$_2$, a novel NHC-stabilized Ni(0) complex. The catalytic activity of this compound has been tested in the amination of aryl tosylates with cyclic secondary amines and anilines, a reaction for which only one example on the use of a nickel-based catalytic system has been reported so far.[19]

■ RESULTS AND DISCUSSION

Synthesis and Characterization of the Complex IPrNi(styrene)$_2$ (1). We have prepared complex **1** in high yields (90%) following a procedure similar to that reported by Cavell and co-workers for the preparation of IMesNi(DMFU)$_2$ (DMFU = dimethyl fumarate).[20] Thus, the addition of 1 equiv of the IPr carbene (generated beforehand by deprotonation of the imidazolium salt) in THF to a mixture of Ni(COD)$_2$ and styrene (1:8 ratio) dissolved in the same solvent led to the formation of IPrNi(styrene)$_2$ (eq 1). This compound was isolated as an orange crystalline material and is stable in the solid state, under a nitrogen atmosphere, for an unlimited period of time.



(1)

Complex **1** was fully characterized by NMR spectroscopy and X-ray crystallography. In contrast to the fluxional behavior observed in solution for the Pd analogue IPrPd(styrene)$_2$, due to olefin exchange processes,[21] the ^1H NMR spectrum of **1** shows sharp resonances at room temperature. Thus, the methine C*H* protons of the four ^{i}Pr groups appear as two distinct sets of resonances centered at δ 2.59 (heptet, *J* = 6.8 Hz, 2H) and 3.10 (heptet, *J* = 6.5 Hz, 2H). The olefinic protons of the two coordinated styrene molecules resonate at 2.38 (d, *J* = 9.6 Hz, 2H), 2.46 (d, *J* = 12.4 Hz, 2H), and 2.97 ppm (dd, *J* = 9.6 Hz, *J* = 12.4 Hz, 2H), notably at higher field than in free styrene (5.00, 5.59, and 6.55 ppm in C_6D_6). The same behavior is observed for the olefinic carbons in the $^{13}C\{^1H\}$ NMR spectrum of **1** (72.3 and 49.2 ppm for coordinated styrenes vs 135.5 and 112.0 ppm for the free olefin[20]). These data clearly support the existence of a strong metal back-donation of electron density into the π^* orbitals of the alkenes. The C_2 symmetry of **1** has been confirmed by a single-crystal X-ray analysis. The unit cell contains three independent molecules; one of them is shown in Figure 1 as an ORTEP diagram together with a list of selected bond distances and angles. As expected, the complex is isostructural with the palladium analogue IPrPd(styrene)$_2$.[21] The C=C bond distances of the two styrene ligands, C28A−C29A = 1.395(5) Å and C36A−C37A = 1.399(5) Å, are longer than those in free styrene (1.346(20) Å).[22] The NHC−Ni bond length (Ni−C1A = 1.955(3) Å) is similar to those found for other mono-NHC−Ni^0 complexes.[23] As observed for IPrPd(styrene)$_2$,[21] the two styrene molecules are coordinated to the nickel center in almost a quasi-planar fashion, as inferred from the dihedral angle between the coordination planes of the two styrenes (Ni1A−C28A−C29A and Ni1A−C36A−C37A) of 16.07(0.16)°.

Amination of Aryl Tosylates with (IPr)Ni(styrene)$_2$. Among aromatic sulfonates, aryl tosylates represent an interesting group of starting materials, since they are stable toward hydrolysis and can be easily obtained from phenols and inexpensive tosyl chlorides, but these substrates are less prone to undergo oxidative addition reactions in comparison to aryl triflates.[3c,24] However, highly efficient nickel-based protocols have been designed for C−C coupling reactions involving aryl tosylates as coupling partners.[25] Regarding the use of aryl tosylates in C−N bond forming reactions catalyzed by nickel complexes, we are only aware of two examples. Bolm et al. first described[26] the use of Ni(COD)$_2$/BINAP as a catalyst for the coupling of aryl tosylates with sulfoximines as nucleophiles. Later, Gao and Yang[19] successfully achieved the cross-coupling of aryl tosylates with cyclic secondary amines and anilines in very short reaction times (15−30 min), using a phosphine−Ni^{II}−σ-aryl complex in combination with the IPr ligand. On the basis of this previous work, we decided to test the catalytic activity of our IPrNi^0 complex in a model amination reaction

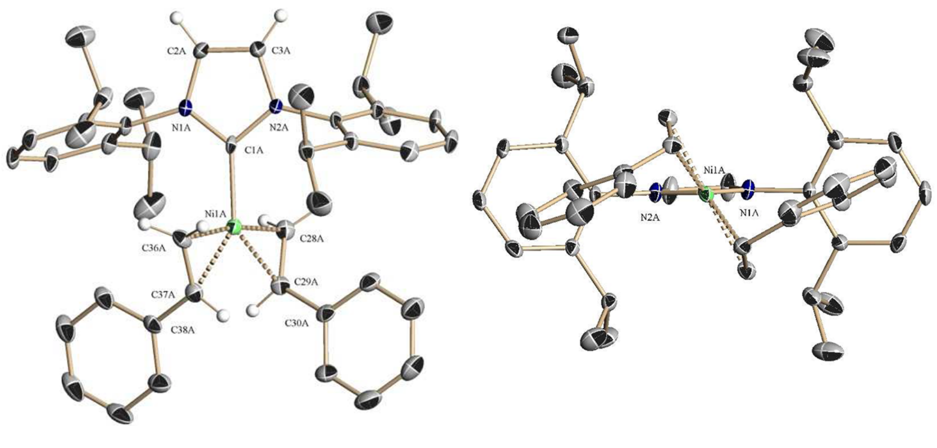
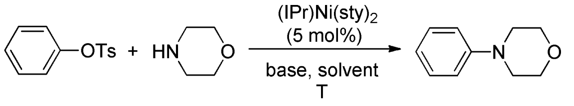


Figure 1. Molecular structure of **1**. Most of the hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg) for **1**: Ni−C1A = 1.897(4), C28A−C29A = 1.395(5), C36A−C37A = 1.399(5), Ni−28A = 1.987(4), Ni−C29A = 2.020(4), Ni−C36A = 1.987(4), Ni−C37A = 2.026(4); C1A−Ni−C28A = 94.64(16), C1A−Ni−C36A = 95.76(16), C1A−Ni−C29A = 134.63(17), C1A−Ni−C37A = 136.19(16), N1A−C1A−N2A = 101.6(3).

between phenyl tosylate and morpholine. The results of these catalytic tests are displayed in Table 1. Using 5 mol % of IPrNi(0) complex and NaO^{t}Bu as the base, the reaction conducted at 80 °C for 17 h produced a modest 44% isolated yield of the product along with the undesired formation of phenol (34% yield), due to the competitive cleavage of the S−O bond of phenyl tosylate (entry 1). A screening of base was carried out with the aim of decreasing this undesired product. With Cs_2CO_3 no phenol was detected (by ^1H NMR) but the conversion was low (entry 2). However, when LiO^{t}Bu was employed, the reaction afforded selectively the coupling product in quantitative yield (entry 3). As shown in entries 4 and 5, dioxane was the most appropriate solvent for this transformation. Notably, when the temperature was raised to 110 °C, the amination reaction was accomplished in 15 min (entry 6). It was of interest to compare the catalytic behavior of IPrNi(allyl)Cl complex with that of the IPrNi(styrene)$_2$ derivative in this cross-coupling process. Thus, using the best conditions (110 °C, 15 min) the IPrNi^{II} precatalyst afforded only 40% of the amination product (entry 7), suggesting that the reduction of the IPrNi^{II} complex is not fully completed in such a short reaction time.

Table 1. Optimization Studies for IPrNi(0)-Catalyzed Amination of Aryl Tosylates.[a]

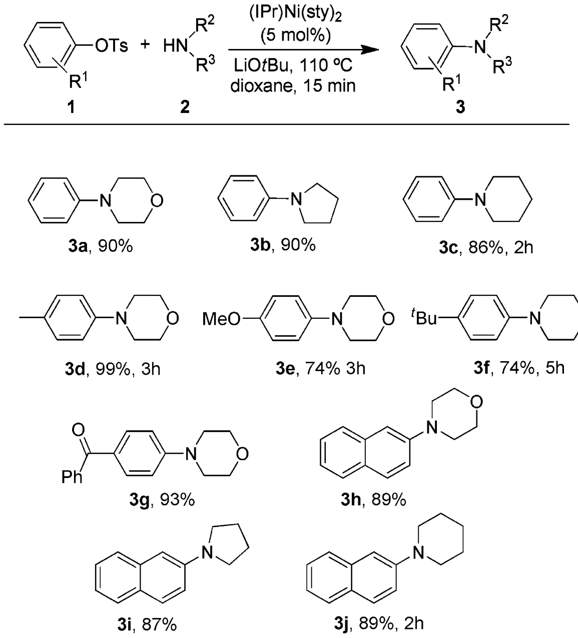


entry	base	solvent	temp (°C)	time	yield (%)[b]
1	NaO^{t}Bu	dioxane	80	17 h	44[c]
2	Cs_2CO_3	dioxane	80	17 h	14
3	LiO^{t}Bu	dioxane	80	17 h	94
4	LiO^{t}Bu	toluene	80	17 h	87
5	LiO^{t}Bu	DMF	80	17 h	nr[d]
6	LiO^{t}Bu	dioxane	110	15 min	90[e]
7	LiO^{t}Bu	dioxane	110	15 min	40[f]

[a] Reaction conditions: aryl tosylate (1 mmol), morpholine (1.5 mmol), base (1.5 mmol), Ni complex (5 mol %), solvent (1 mL). [b] Isolated yield; average of two different experiments. [c] 34% yield of phenol was also isolated. [d] No reaction. [e] 100% conversion by ^1H NMR. [f] Reaction carried out using IPrNi(allyl)Cl (5 mol %) as the catalyst; unreactive tosylate accounted for the overall mass balance.

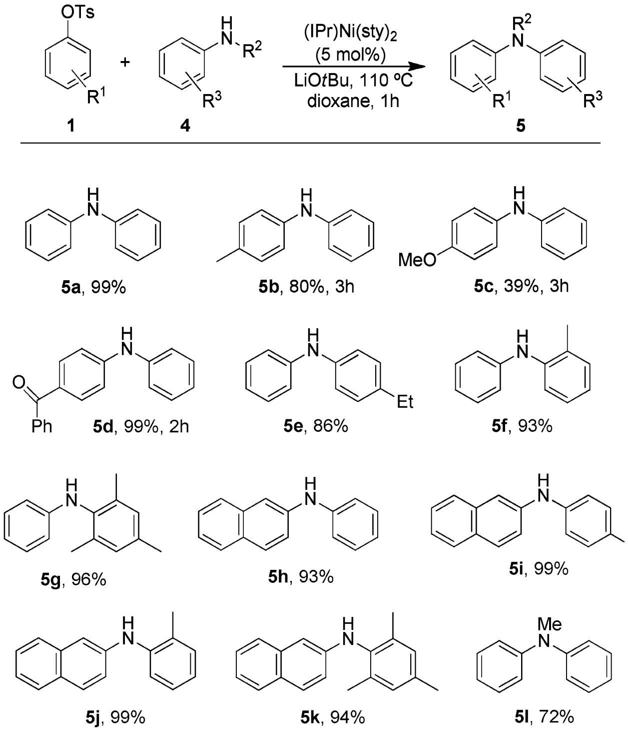
Under the optimized conditions developed in Table 1, several cyclic secondary amines were coupled efficiently with an array of aryl tosylates within 15 min to 5 h, without the formation of the corresponding phenol byproduct (Scheme 1). Both electron-neutral and electron-poor aryl tosylates reacted in high yields in shorter reaction times, whereas electron-rich substrates required prolonged heating to furnish good yields of coupling products (**3d−f**). Of note, with the methodology described by Gao and Yang,[19] deactivated aryl tosylates containing electron donating groups such as *p*-methoxy and *p*-*tert*-butyl failed to give the amination reaction.

Scheme 1. Amination Reactions of Aryl Tosylates with Secondary Cyclic Amines Catalyzed by 1[a]



[a] Reaction conditions: aryl tosylate (1 mmol), amine (1.5 mmol), LiO*t*Bu (1.5 mmol), Ni complex (5 mol %), dioxane (1 mL). [b] Isolated yield, average of two experiments.

Scheme 2. Amination Reactions of Aryl Tosylates with Anilines Catalyzed by 1[a]



[a] Reaction conditions: aryl tosylate (1 mmol), aniline (1.5 mmol), LiO^{t}Bu (1.5 mmol), Ni complex (5 mol %), dioxane (1 mL), $T = 100$ °C, $t = 10$ h. [b] Isolated yield, average of two experiments. [c] Reaction performed in 24 h.

To further extend the scope of application of the IPrNi^0 catalyst, the coupling of aryl tosylates with anilines was examined next. With this protocol, reactions were accomplished within 1 h in most cases, with isolated yields varying from 39 to 99%, as shown in Scheme 2. The reaction rate depended on the electronic nature of substituents on the electrophile in a way similar to that described for reactions with secondary cyclic amines (entries **5b**,**c**). Thus, electron-rich tosylates were less prone to undergo C−N coupling processes. Alkyl-substituted anilines were successfully converted, even when they were sterically hindered (**5e−g,i−k** in Scheme 2). We noted, however, that the use of sterically demanding 2,4,6-trimethylphenyl tosylate was not tolerated, presumably due to difficulties in the oxidative addition step. Finally, secondary *N*-methylaniline afforded a good yield of the diarylamine product (**5l**), indicating that the steric bulk on the N atom is well tolerated.

CONCLUSION

In summary, we have synthesized and structurally characterized a stable monoligated IPrNi^0 complex stabilized with olefinic ligands. In this compound the metal center is in a three-coordinate environment and no ligand exchange is observed in solution at room temperature. The complex has been used as a precursor for active IPrNi^0 species in the amination reactions of aryl tosylates with cyclic secondary amines and anilines. This methodology has provided the derived coupling products in moderate to excellent yields without the observation, in any case, of phenol byproducts.

EXPERIMENTAL SECTION

General Methods. All reactions and manipulations were carried out under an oxygen-free nitrogen atmosphere with standard Schlenk techniques. All substrates were purchased from Aldrich. Solvents were dried and degassed before use. [Ni(COD)$_2$],[27] 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPrHCl),[28] and aryl tosylates[29] were prepared according to the literature procedures. NMR spectra were recorded using Varian Mercury 400 MHz and Bruker Advance III 300 MHz spectrometers. ^{1}H NMR shifts were measured relative to deuterated solvent peaks but are reported relative to tetramethylsilane. Elemental analyses were performed by the Unidad de Análisis Elemental of the Universidad de Huelva.

Synthesis of (IPr)Ni(styrene)$_2$ (1).[30] 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride (IPrHCl; 1.0 g, 2.35 mmol) and sodium *tert*-butoxide (0.29 g, 2.59 mmol) were stirred in THF (20 mL) for 1 h inside a glovebox. The suspension containing the preformed carbene was filtered and added to a mixture of bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$; 0.64 g, 2.33 mmol) and styrene (2 mL, 18.80 mmol) in THF (20 mL) which was previously stirred for 10 min at room temperature. The resulting orange-red solution was stirred for 2 h and filtered through a Celite pad. The solvent was evaporated under vacuum and the solid residue dissolved in THF (5 mL). Addition of petroleum ether produced the precipitation of the nickel complex (IPr)Ni(styrene)$_2$ as an orange crystalline solid (1.28 g, 2.10 mmol, 90%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.5−7.2 (m, 12H, CH_{arom}), 6.39 (s, 2H, CH_{imid}), 6.12 (d, 4H, $J = 6.6$ Hz, CH_{arom}), 3.10 (heptet, 2H, $J = 6.8$ Hz, $CH(CH_3)_2$), 2.97 (dd, 2H, $J = 12.4$ Hz, $J = 9.6$ Hz, CH_{olef}), 2.59 (heptet, 2H, $J = 6.8$ Hz, $CH(CH_3)_2$), 2.46 (d, 2H, $J = 12.4$ Hz, CH_{olef}), 2.38 (d, 2H $J = 9.6$ Hz, CH_{olef}), 1.07 (d, 6H, $J = 6.8$ Hz, $CH(CH_3)_2$), 0.81 (d, 6H, $J = 6.8$ Hz, $CH(CH_3)_2$), 0.70 (d, 6H, $J = 6.8$ Hz, $CH(CH_3)_2$), 0.69 (d, 6H, $J = 6.8$ Hz, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 204.1 (C_{carb}), 123.8, 123.8, 125.2, 126.7, 129.2, 137.0, 145.3, 146.2, 146.2 (CH_{arom}), 126.7 (CH_{imid}), 72.3 (CH_{olef}), 49.2 (CH_{olef}), 28.4 (CH(Me)$_2$), 27.7 (CH(Me)$_2$), 26.4 (CH(*Me*)$_2$), 24.8 (CH(*Me*)$_2$), 22.1 (CH(*Me*)$_2$), 21.5 (CH(*Me*)$_2$). IR (Nujol mull): 1497 cm^{-1} (ν(C=C)). Anal. Calcd for $C_{43}H_{52}N_2Ni\cdot THF$: C, 77.58; H, 8.31; N, 3.85. Found: C, 77.98; H, 8.25; N, 3.34.

General Catalytic Procedure for the Nickel-Catalyzed Amination of Aryl Tosylates. The catalyst (0.05 mmol), the aryl tosylate (1 mmol), and the base LiO^{t}Bu (1.5 mmol) were added in turn to an ampule equipped with a magnetic bar. The amine (1.5 mmol) and dioxane (1 mL) were added under a nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 15 min to 5 h in an oil bath. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (2 × 10 mL), and filtered through Celite. The clean solution was evaporated to dryness, and the residue was purified by flash chromatography on silica gel with ethyl acetate/petroleum ether (by default 1/10 otherwise indicated) to afford the desired product.

Crystal Data for 1: $C_{43}H_{52}N_2Ni$, $M_w = 655.58$, single crystal of suitable size, yellow prism (0.43 × 0.42 × 0.40 mm^3) crystallized from THF/petroleum ether, coated with dry perfluoropolyether, mounted on a glass fiber and fixed in a cold nitrogen stream (173(2) K) to the goniometer head, monoclinic, space group $P2_1/c$, $a = 32.150(3)$ Å, $b = 12.3620(11)$ Å, $c = 28.190(3)$ Å, $V = 11193.2(19)$ Å^3, $Z = 12$, $\rho_{calcd} = 1.167$ g cm^{-3}, λ(Mo Kα_1) = 0.710 73 Å, $F(000) = 4224$, $\mu = 0.551$ mm^{-1}. A total of 124 827 reflections were collected from a Bruker-Nonius X8Apex-II CCD diffractometer in the range $1.27 < 2\theta < 26.38°$, and 22 845 independent reflections (R(int) = 0.1257) were used in the structural analysis. The data were reduced (SAINT) and corrected for Lorentz−polarization effects and absorption by multiscan methods applied by SADABS.[31,32] The asymmetric unit of **1** is formed by three independent complexes. The structure was solved by direct methods (SIR-2002)[33] and refined against all F^2 data by full-matrix least-squares techniques (SHELXL97);[34] the structure converged to final R1 = 0.0597 ($I > 2\sigma(I)$) and wR2 = 0.1224 for all data, with a goodness of fit on F^2 (S) of 0.972 and 1249 parameters.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and a CIF file giving detailed experimental procedures, analytical and spectroscopic data, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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