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Catalytic C–H amination of alkanes with sulfonimidamides: silver(I)-scorpionates vs. dirhodium(II) carboxylates

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ABSTRACT

The silver complex $[Tp^{*,Br}Ag]_2$ ($Tp^{*,Br}$: hydrotris(4-bromo-3,5-dimethyl)pyrazolyl borate) and the rhodium complex Rh_2(*S*-nta)$_4$ (nta: *N*-(1,8-naphthoyl)-alanine) are competent catalysts for C–H bond functionalization by nitrene insertion. Both complexes display similar catalytic activity for the functionalization of benzylic C–H bonds, although the silver derivative does not provide the very high diastereoselection induced by the rhodium complex. On the other hand, when starting from 5 equiv of alkanes, such as pentane and other C_6–C_8 branched non-activated hydrocarbons, it is the silver catalyst that promotes the amination of the C–H bonds with yields of up to 70%, higher than those provided by the rhodium counterpart. When available, the tertiary C–H bonds of the substrate are preferentially derivatized, as a consequence of a stepwise mechanism in which carbon-centered radicals are involved.

1. Introduction

The ubiquity of nitrogen in natural products, pharmaceuticals, or agrochemicals makes the search for efficient syntheses of optically pure amines still a topic of paramount importance in organic chemistry.[1] New opportunities for C–N bond forming reactions, in this context, have arisen from recent investigations aimed at developing the direct amination of Csp^3–H bonds through the insertion of a metallanitrene. Various reagents and catalysts are described to this end, which are overviewed in several reviews published in the last five years.[2] Among these conditions, the most significant achievements in catalytic C–H amination have undoubtedly been made with the use of trivalent iodine oxidants[3] that have led to elegant applications in synthesis.[4] However, despite the discovery of processes, which occur in good yields and with high levels of selectivity, some issues remain to be addressed, one of the most challenging being the efficient selective catalytic C–H amination of simple alkanes.[5]

Highly active catalysts derived from group 11 elements and scorpionate ligands have been described in the context of catalytic nitrene transfers.[6] In particular, efficient selective Csp^3–H amination of hydrocarbons has been reported using PhI=NTs as the nitrene precursor. Whereas copper complexes have proved effective for the selective functionalization of alkyl aromatics and cyclohexane,[6a,c] the higher reactivity of silver-scorpionate complex $[Tp^{*,Br}Ag]_2$ **1** ($Tp^{*,Br}$: hydrotris(4-bromo-3,5-dimethyl)pyrazolyl borate, Fig. 1)[7] has allowed the C–H amination of linear and branched alkanes to be performed in good yields of up to 80% in the case of 2-methylbutane.[6d] Nevertheless, it should be mentioned that these very good results are observed for reactions carried out in neat alkanes at 80 °C.

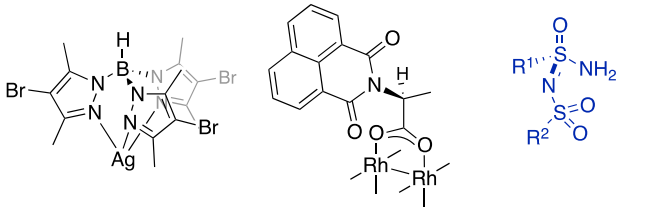

Fig. 1. The monomeric form of the silver catalyst $[Tp^{*,Br}Ag]_2$ **1**, the rhodium catalyst Rh_2(*S*-nta)$_4$ **2**, and (*S*)-sulfonimidamide **3a**.

The discovery of practical procedures for the generation in situ of nitrenes with iodine(III) oxidants,[3c,g,8] on the other hand, has led to greatly expand the scope of catalytic nitrene transfers in terms of

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nitrogen sources. Chiral nitrenes of high reactivity have therefore been generated from sulfonimidamides.[9] The combination of the chiral rhodium carboxylate Rh_2(*S*-nta)$_4$ **2** (nta: *N*-(1,8-naphthoyl)-alanine) with the (*S*)-*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide (*S*)-**3a**, especially, was optimal to develop the stereoselective Csp^3–H amination of benzylic and allylic substrates used as the limiting agent.[10] However, this pair of reagent has proved to be of low efficiency for the functionalization of alkanes, such as the branched derivative 2-methylbutane, though complete selectivity in favor of the tertiary site is observed.[10b]

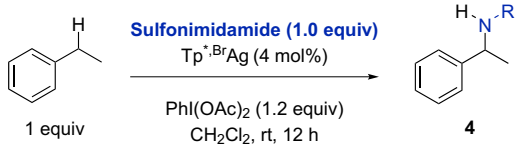
Based on the respective performance of both aforementioned systems, it was decided to combine the highly efficient nitrene precursor **3** with the very active silver catalyst **1** with the aim to observe a synergetic effect likely to help addressing the issue of alkane C–H amination. The results of our investigations are reported in this article, that also provides a direct comparison with the sulfonimidamide **3**/rhodium catalyst **2** system.

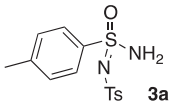
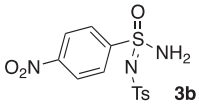
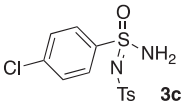
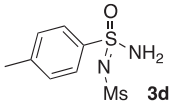
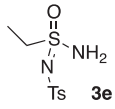
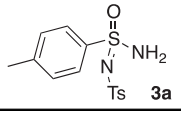
2. Results and discussion

2.1. Catalytic benzylic C–H amination

It was initially decided to focus on the catalytic amination of benzylic Csp^3–H bonds in order to test the relevance of our hypothetical combination. To this end, ethylbenzene used in stoichiometric amounts was chosen as a test substrate in the first experiments conducted at room temperature in dichloromethane (Table 1). The screening of various racemic substituted

Table 1
Screening of the sulfonimidamide reagent for the silver-catalyzed C–H amination of ethylbenzene

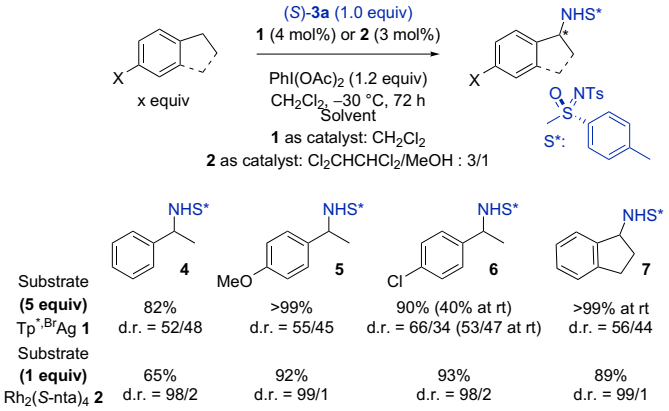


Entry	Sulfonimidamide	Yield %	d.r.[a]
1	 **3a**	20	68/32
2	 **3b**	<5	—
3	 **3c**	35	50/50
4	 **3d**	27	50/50
5	 **3e**	<5	—
6[b]	 **3a**	82	52/48

[a] Determined by ^{1}H NMR.
[b] Reaction run 3 days at −30 °C using 5 equiv of ethylbenzene.

sulfonimidamides led to the conclusion that the derivative **3a** (entry 1 vs. entries 2–5) affords the best compromise between reactivity, selectivity, and ease of preparation. However, the yields remain generally low in the 20–35% range whereas a modest diastereomeric ratio of 2:1 is observed in the case of **3a**.[11] Application of conditions inspired by the previous optimal protocol using rhodium,[10] i.e., carrying out the reaction at −30 °C for 3 days,[12] together by using 5 equiv of ethylbenzene, then allowed to improve the results. The expected C–H aminated product **4a** was thus obtained with a higher yield of 82% albeit with essentially no diastereoselectivity (entry 6).

These conditions were applied to the functionalization of various benzylic substrates in the presence of the enantiomerically pure (*S*)-**3a** with both the silver **1** or rhodium **2** catalysts (Scheme 1). Pleasingly, high conversions greater than 90% were observed with the silver-based catalyst. A test experiment run with *p*-chloroethylbenzene at room temperature, in addition, demonstrates the influence of the temperature since the corresponding product is formed with a lower conversion of 40%. By contrast, indan, which is efficiently aminated by this methodology, underwent C–H amination at room temperature with comparable levels of conversion. However, the diastereoselectivity remains low in all cases, a diastereomeric ratio of 2:1 being obtained in the case of *p*-chloroethylbenzene.[13]

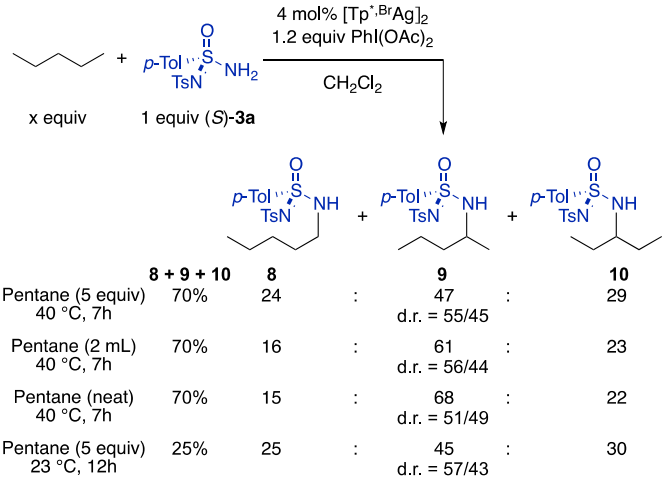


Scheme 1. Catalytic benzylic C–H amination with **1** or **2**.

The comparison of these results with those already reported using a combination of the rhodium catalyst **2** and the same nitrogen reagent (*S*)-**3a**[10b] clearly assesses the higher efficiency of this system since very good yields and high diastereoselectivities are obtained with only 1 equiv of benzylic substrates. Nonetheless, on the basis of the previous work[6d] in which complex **1** induced high yields of the alkane amidation reaction with PhI=NTs as the nitrene precursor, we decided to examine its potential with the (*S*)-**3a** reagent and a series of non-activated saturated hydrocarbons.[5,14]

2.2. Silver- and rhodium-catalyzed C–H amination of alkanes

Several reaction conditions were screened for the amination of *n*-pentane. As expected from the previous studies,[6d] a mixture of three products derived from the formal insertion of the nitrene moiety into the three different C–H bonds of pentane was obtained (Scheme 2). The first experiment carried out at 40 °C in dichloromethane gave an overall 70% conversion determined by ^{1}H NMR. The products **8**, **9**, and **10** were formed with a distribution of 24, 47, and 29%, respectively. Importantly, this result was obtained using 5 equiv of pentane with respect to the sulfonimidamide. This is a remarkable feature since the yield compares favorably with those described in our previous work that employed the alkane as the



	8 + 9 + 10	8		9		10
Pentane (5 equiv) 40 °C, 7h	70%	24	:	47 d.r. = 55/45	:	29
Pentane (2 mL) 40 °C, 7h	70%	16	:	61 d.r. = 56/44	:	23
Pentane (neat) 40 °C, 7h	70%	15	:	68 d.r. = 51/49	:	22
Pentane (5 equiv) 23 °C, 12h	25%	25	:	45 d.r. = 57/43	:	30

Scheme 2. C–H amination of *n*-pentane using sulfonimidamide (*S*)-**3a** and the silver complex **1** as catalyst.

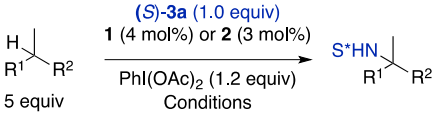
solvent (5 mL). We have also used the hydrocarbon in such that large excess, with 2 and 5 mL (17 or 43 mmol, respectively), in the presence of (*S*)-**3a**. The overall conversion, however, was identical to that observed with only 5 equiv, and the regioselectivity, intended as **8**:**9**:**10**, varied with a ca. 10% decrease into the product derived from the primary C–H bond functionalization.

The insertion of the nitrene group in the secondary site at C2 originates a stereocenter that in combination with the chirality of the sulfur center, provides the formation of diastereomers. Unfortunately, and in line with the aforementioned observations with the benzylic substrates, the diastereoselection induced by complex **1** was low in each case, the diastereomeric ratios ranging from 51/49 to 56/44. Carrying out the reaction at lower temperatures using the 5:1 ratio of pentane and (*S*)-**3a**, however, did not improve the results. The conversion dropped to 25% at room temperature, whereas the d.r. remains essentially in the same order of magnitude. These results, nevertheless, compare favorably with those recorded with rhodium(II) complexes since catalytic C–H amination of pentane in the presence of Rh_2(*S*-nta)$_4$ **2** only gives a low conversion of 14% at −30 °C for 3 days. Therefore, and at variance with the results discussed above on the functionalization of the benzylic sites, the silver complex **1** displays a pronounced catalytic activity toward the C_{sp3}–H bonds of pentane when compared with that of the rhodium complex **2**.

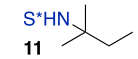
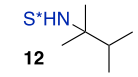
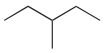
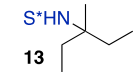
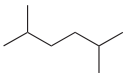
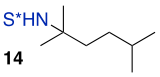
Once demonstrated the catalytic performance of **1** for the amination of pentane with (*S*)-**3a**, we targeted a series of C_5–C_8 alkanes, such as 2-methylbutane, 2,3-dimethylbutane, 3-methylpentane, and 2,5-dimethylhexane. The reactions were performed at 40 °C for 7 h, generally using a 5:1 ratio of the alkane and (*S*)-**3a**. The results are shown in Table 2. In all cases, the only product observed was that derived from the formal insertion of the nitrene group into the tertiary sites. This is in contrast with our previous report,[6d] in which, for example, 2-methylbutane gave a ca. 9:1 mixture of products corresponding to the functionalization of the tertiary and secondary sites. The yields range from 25 to 60% but these can be improved by increasing the relative amount of alkanes. This resulted beneficial for the reaction outcome in most cases, as inferred from the values in Table 1, entries 1 and 2.

In addition, a series of experiments with the rhodium catalyst **2** was performed using 5 or 10 equiv of alkanes, though at −30 °C and in a 3/1 mixture of 1,1,2,2-tetrachloroethane/MeOH. The products observed, when the reaction proceeded to a certain extend, were the same as with the silver catalyst, i.e., those from the functionalization of the tertiary C–H bonds. 2-Methylbutane gave 35% yield, a value higher than that induced by complex **1**, whereas

Table 2
C–H amination of alkanes with (*S*)-**3a** and complexes **1** or **2** as the catalysts



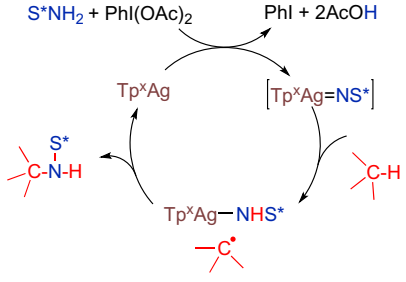
1 as catalyst: CH_2Cl_2, 7h, 40 °C
2 as catalyst: $Cl_2CHCHCl_2$/MeOH : 3/1, 72 h, –35 °C

Entry	Substrate	Product	Yield %[a] with **1**	Yield %[b] with **2**
1		 **11**	25 70[c]	35
2		 **12**	30 75[c]	nr[d,e]
3		 **13**	25	nr[d,e]
4		 **14**	60	23[d]

[a] Determined by ^{1}H NMR.
[b] Isolated yields.
[c] Reaction performed in the presence of 0.5 mL (ca. 30 equiv) of alkane.
[d] Reaction performed in the presence of 10 equiv of alkane.
[e] nr: no reaction observed.

2,5-dimethylhexane led to the opposite behavior. In addition, 2,3-dimethylbutane and 3-methylpentane did not react in the presence of **2**. Despite the different conditions,[15] these data are in accordance with a higher capacity of the silver complex **1** to mediate the C–H amination of non-activated alkanes.

The absence of products arising from the functionalization of primary and secondary C–H bonds is at variance with the metal-catalyzed carbene insertion reaction from diazocompounds. For example, the silver complexes Tp^{Br3}Ag(acetone)[7a] and F_{21}-$Tp^{4Bo,3CF3}$Ag(acetone)[16] induce the functionalization of 2-methylbutane giving rise to a mixture of products upon insertion of the carbene group into the tertiary, secondary, and primary sites. These data support the different nature of both reactions, in spite of the use of the same catalysts. The carbene transfer reaction has been proposed to occur in a concerted manner[5,17] whereas the C–H amination seems to proceed with the intermediacy of carbon-centered radicals in the presence of silver,[6d] ruthenium[18], and cobalt complexes.[5] Scheme 3 shows a plausible mechanistic picture for the silver-based catalyst based on previous experiments,[6d] the formation of a metallanitrene species being the first step of the reaction pathway. Hydrogen abstraction would lead to an Ag-amido species along with an organic radical that, upon a step similar to the so-called rebound mechanism,[5] extensively proposed in C–H hydroxylation reactions, would liberate the amidated C–H bond and the metal center to re-start the catalytic cycle. This would be in



Scheme 3. Plausible mechanistic pathway for the Ag-catalyzed C–H amination of alkane using (*S*)-**3a** as the nitrene source.

agreement with the preferential functionalization of the tertiary sites since they would originate the most stable radical along the reaction pathway. In the case of pentane, both primary and secondary sites were functionalized since there is not a very large difference in energy between their corresponding radicals.

3. Conclusion

The silver complex $[Tp^{*,Br}Ag]_2$ catalyzes the functionalization of C–H bonds using a chiral sulfonimidamide as the nitrene source with moderate to high yields. When compared to the rhodium $[Rh_2(S\text{-nta})_4]$ catalyst, the relative catalytic capabilities depend on the nature of the hydrocarbon. For benzylic sites, both catalysts induce similar conversions, although the rhodium catalyst secures excellent levels of diastereocontrol. For non-activated C–H bonds, such as those found in pentane and other alkanes, the silver complex seems to be more active and the yields obtained are higher than those previously reported starting from PhI=NTs, taking in consideration the lower amounts of alkanes. The combination of silver complex **1** and nitrene precursor **3a** thus proves to improve the efficiency of catalytic nitrene transfer in this case. However, none of both catalytic systems provide noticeable diastereoselectivity. As a result of this work, it seems feasible that more elaborated silver-based complexes could exert better diastereoselection following an appropriate design, which is currently under investigation.

4. Experimental section

4.1. General methods

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or inside a glovebox. Solvents were dried and degassed before use. All the substrates were purchased from Aldrich. The sulfonimidamides[9] and the complexes $[Tp^{*,Br}Ag]_2$,[19] and $Rh_2(S\text{-nta})_4$[10] were prepared according to the literature. NMR experiments were recorded on a Varian Mercury 400 MHz spectrometer in $CDCl_3$ as solvent.

4.2. General catalytic C–H amination using $[Tp^{*,Br}Ag]_2$ 1

A Teflon-capped ampoule containing a magnetic stirring bar was charged with sulfonimidamide **3a** (0.486 g, 0.15 mmol), $Tp^{*,Br}Ag$ **1** (0.038 g, 0.006 mmol calculated as monomeric unit $Tp^{*,Br}Ag$), and $PhI(OAc)_2$ (0.058 g, 0.18 mmol). After deoxygenation, 5 mL of anhydrous dichloromethane were added. The mixture was stirred for 5 min before addition of the substrate (0.75 mmol or the corresponding amount), being then covered with aluminum foil to maintain the reaction mixture in the dark. The vessel was either stored in the freezer (−30 °C) for 3 days or stirred at room temperature or at 40 °C in an oil bath. After the reaction time, volatiles were removed under vacuum. The residue was dissolved in $CDCl_3$ and, then, investigated by ^1H NMR. The new products as well as unreacted sulfonimidamide were identified. Accordingly, conversions and yields were estimated upon integration of representative resonances.[6d]

4.3. General procedure for catalytic C–H amination using $Rh_2(S\text{-nta})_4$ 2

In an oven-dried tube were introduced activated 4 Å molecular sieves (100 mg), $Rh_2[(S)\text{-nta}]_4$ **2** (7.7 mg, 0.006 mmol), and (−)-*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide (−)-(*S*)-**3a** (78 mg, 0.24 mmol). The tube was capped with a rubber septum and purged with argon. Anhydrous and degassed 1,1,2,2-tetrachloroethane (0.75 mL) and methanol (0.25 mL) were added under argon, and the mixture was stirred for 5 min before addition of the substrate (0.2 mmol). The tube was cooled to −78 °C, and bis(*tert*-butylcarbonyloxy)iodobenzene (115 mg, 0.28 mmol) was added. The mixture was stirred at −35 °C for 3 days. After dilution with dichloromethane (3 mL), the molecular sieves were removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The oily residue was purified by flash chromatography on silica gel, affording the following C–H insertion products.

Compounds **4**–**7** have been previously reported.[10b] In addition, the compounds **8**–**14** have been described for the NTs derivatives.[6d]

*4.3.1. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-1-(1-aminoethyl)benzene (**4**).* (1*R*-**4**) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.26 (d, *J*=6.9 Hz, 3H), 2.31 (s, 3H), 2.33 (s, 3H), 4.39 (q, *J*=7.0 Hz, 1H), 6.14 (d, *J*=6.8 Hz, 1H), 6.84–7.32 (m, 8H), 7.40–7.80 (m, 4H).

(1*S*-**4**) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.48 (d, *J*=6.9 Hz, 3H), 2.25 (s, 3H), 2.34 (s, 3H), 4.39 (q, *J*=7.0 Hz, 1H), 6.29 (d, *J*=6.8 Hz, 1H), 6.84–7.32 (m, 8H), 7.40–7.80 (m, 4H).

*4.3.2. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-4-(1-aminoethyl)anisole (**5**).* (1*R*-**5**) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.32 (d, *J*=6.9 Hz, 3H), 2.39 (s, 3H), 2.41 (s, 3H), 3.79 (s, 3H), 4.46 (m, 1H), 6.30 (br s, 1H), 6.79–6.90 (m, 2H), 7.07–7.25 (m, 6H), 7.71–7.86 (m, 4H).

(1*S*-**5**) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.54 (d, *J*=6.9 Hz, 3H), 2.41 (s, 3H), 3.72 (s, 3H), 4.46 (m, 1H), 6.44 (br s, 1H), 6.79–6.90 (m, 2H), 7.07–7.25 (m, 6H), 7.71–7.86 (m, 4H).

*4.3.3. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-1-(1-aminoethyl)-4-chlorobenzene (**6**).* (Major diastereoisomer-**6**) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.41 (d, *J*=6.9 Hz, 3H), 2.49 (br s, 6H), 4.52 (m, 1H), 6.64 (d, *J*=6.9 Hz, 1H), 6.99–7.34 (m, 4H), 7.79–7.91 (m, 8H).

(Minor diastereoisomer-**6**) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.59 (d, *J*=6.9 Hz, 3H), 2.43 (s, 3H), 2.47 (s, 3H), 4.52 (m, 1H), 6.80 (d, *J*=6.9 Hz, 1H), 6.99–7.34 (m, 4H), 7.79–7.91 (m, 8H).

*4.3.4. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-1-aminoindane (**7**).* (1*R*-**7**) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.67–1.76 (m, 1H), 2–2.16 (m, 1H), 2.41 (s, 3H), 2.44 (s, 3H), 2.65–2.72 (m, 1H), 2.84–2.89 (m, 1H), 4.79 (q, *J*=7.8 Hz, 1H), 6.28 (d, *J*=8.3 Hz, 1H), 7.09–7.26 (m, 6H), 7.30–7.38 (m, 2H), 7.79–7.91 (m, 4H).

(1*S*-**7**) 2.03–2.11 (m, 1H), 2.35–2.52 (m, 1H), 2.40 (s, 3H), 2.44 (s, 3H), 2.72–2.80 (m, 1H), 2.95–3.02 (m, 1H), 4.70 (q, *J*=7.8 Hz, 1H), 6.20 (d, *J*=8.9 Hz, 1H), 7.09–7.26 (m, 6H), 7.30–7.38 (m, 2H), 7.79–7.91 (m, 4H).

*4.3.5. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-1-amino-pentane (**8**).* ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.91 (t, *J*=7.5 Hz, 3H), 0.96–1.57 (m, 6H), 2.39 (s, 3H), 2.40 (s, 3H), 3.22 (q, *J*=8.5 Hz, 1H), 5.48 (m, 1H), 7.09–7.35 (m, 4H), 7.64–7.85 (m, 4H).

*4.3.6. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-2-amino-pentane (**9**).* (Major diastereoisomer-**9**) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.64 (t, *J*=7.3 Hz, 3H), 0.85 (d, *J*=6.5 Hz, 3H), 1.00–2.06 (m, 4H), 2.42 (br s, 6H), 3.25–3.34 (m, 1H), 5.92 (m, 1H), 7.09–7.35 (m, 4H), 7.64–7.85 (m, 4H).

(Minor diastereoisomer-**9**) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.64 (t, *J*=7.3 Hz, 3H), 1.22 (d, *J*=6.5 Hz, 3H), 1.00–2.06 (m, 8H), 2.42 (br s, 12H), 3.25–3.34 (m, 2H), 5.92 (m, 2H), 7.09–7.35 (m, 8H), 7.64–7.85 (m, 8H).

*4.3.7. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-3-amino-pentane (**10**).* ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.57 (t, *J*=7.4 Hz, 6H),

1.05–1.43 (m, 4H), 2.39 (s, 3H), 2.40 (s, 3H), 3.00–3.09 (m, 1H), 5.97 (d, *J*=8.6 Hz, 1H), 7.09–7.35 (m, 4H), 7.64–7.85 (m, 4H).

*4.3.8. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-2-amino-2-methylbutane (**11**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.86 (t, *J*=7.5 Hz, 3H), 1.05 (s, 3H), 1.19 (s, 3H), 1.46 (m, 1H), 1.60 (m, 1H), 2.39 (s, 3H), 2.40 (s, 3H), 6.19 (br s, 1H), 7.22–7.26 (m, 4H), 7.78–7.84 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.5, 21.6, 26.2, 27.5, 36.0, 38.6, 59.7, 126.8 (2C), 127.7 (2C), 129.2 (2C), 129.6 (2C), 136.5, 140.6, 142.7, 144.6. IR (neat) ν_{max} 3240, 2973, 1596, 1300, 1148, 1103, 1089, 1065, 1017 cm^{-1}. HRMS (ESI): MNa^+, found 417.1243. $C_{19}H_{26}N_2NaO_3S_2$ requires 417.1283.

*4.3.9. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-2-amino-2,3-dimethylbutane (**12**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.85 (d, *J*=6.8 Hz, 3H), 0.93 (d, *J*=6.8 Hz, 3H), 0.95 (s, 3H), 1.23 (s, 3H), 1.72 (m, 1H), 2.39 (s, 3H), 2.40 (s, 3H), 6.27 (br s, 1H), 7.17–7.35 (m, 4H), 7.53–7.88 (m, 4H).

*4.3.10. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-3-amino-3-methylpentane (**13**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.75 (t, *J*=7.4 Hz, 3H), 0.85 (t, *J*=7.2 Hz, 3H), 1.25 (s, 3H), 1.35 (m, 2H), 1.51 (m, 2H), 2.39 (s, 3H), 2.40 (s, 3H), 6.14 (br s, 1H), 7.16–7.34 (m, 4H), 7.64–7.86 (m, 4H).

*4.3.11. [N-(p-Toluenesulfonyl)-p-toluenesulfonimidoyl]-2-amino-2,5-dimethylhexane (**14**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.80 (d, *J*=6.6 Hz, 3H), 0.83 (d, *J*=6.6 Hz, 3H), 1.07 (s, 3H), 1.19 (s, 3H), 1.33 (m, 2H), 1.37 (m, 1H), 1.50 (m, 2H), 2.39 (s, 3H), 2.40 (s, 3H), 6.20 (br s, 1H), 7.20–7.34 (m, 4H), 7.64–7.84 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.6, 22.4, 22.5, 26.9, 28.0, 28.3, 32.6, 41.2, 59.6, 126.8 (2C), 127.7 (2C), 129.2 (2C), 129.6 (2C), 138.8, 140.4, 142.8, 144.3. IR (neat) ν_{max} 3234, 2954, 1597, 1467, 1387, 1312, 1301, 1260, 1149, 1104, 1090, 1068, 1017 cm^{-1}. HRMS (ESI): MH^+, found 437.1932. $C_{22}H_{32}N_2O_3S_2$ requires 437.1933.

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11. It should be pointed out that the previous study with this catalyst (see Ref. 6d) was carried out with PhI=NTs as the nitrene source, in contrast to the present strategy based on the in situ generation of the imidoiodinane from a sulfonimidamide and $PhI(OAc)_2$.
12. The optimal protocol requires the use of methanol as a cosolvent. However, such a protic source is not compatible with a nitrene transfer catalyzed by a metal-scorpionate complex due to a side reaction currently under investigation.
13. These poor diastereoselectivities are comparable to those observed with sulfonimidamides either in the aziridination of styrene catalyzed by non-chiral copper complexes (see Ref. 9) or in the benzylic C–H amination using $Rh_2(OAc)_4$. Accordingly, the sole chirality of the sulfur reagent is not sufficient to provide the stereoselective addition of the nitrene. Good stereocontrol is thus obtained only when the sulfonimidamide is combined with an appropriate chiral catalyst as the result of matched effects (see Ref. 10b).
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