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# Enantioselective amination of silylketene acetals with (*N*-arylsulfonylimino)phenyliodinanes catalyzed by chiral dirhodium(II) carboxylates: asymmetric synthesis of phenylglycine derivatives

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**Abstract**—The first catalytic enantioselective amination of silylketene acetals with (*N*-arylsulfonylimino)phenyliodinanes is described. The reaction of silylketene acetals derived from methyl phenylacetates with [*N*-(2-nitrophenylsulfonyl)imino]phenyliodinane (NsN = IPh) under the catalysis of dirhodium(II) tetrakis[*N*-tetrachlorophthaloyl-(*S*)-*tert*-leucinate], $Rh_2$(*S*-TCPTTL)$_4$, proceeds in benzene at room temperature to give *N*-(2-nitrophenylsulfonyl)phenylglycine derivatives in high yields and with enantioselectivities of up to 99% ee.



The catalytic asymmetric amination of silylketene acetals is one of the most straightforward methods for the preparation of enantioenriched α-amino esters.[1,2] In 1999, Evans and Johnson described the first catalytic enantioselective amination of thioester silylketene acetals or silylketene aminals of acylpyrroles with azodicarboxylate derivatives, in which enantioselectivities up to 99% ee were achieved with the use of a Cu(OTf)$_2$-bis(oxazoline) catalyst.[3,4] Kobayashi and co-workers later reported that a $AgClO_4$-BINAP system catalyzed the amination of the silylketene acetal of phenyl propionate with dibenzyl azodicarboxylate with good enantioselectivity (51% ee).[5] In this context, the aziridination of silylketene acetals followed by ring opening of the aziridine intermediate provides a prototypical approach to catalytic asymmetric synthesis of α-amino esters.[6] In 1994, Evans et al. reported the first copper(I)-catalyzed amination of silylketene acetals using [(*p*-tolylsulfonyl)imino]phenyliodinane (TsN = IPh, **2a**) as a nitrene precursor,[7] and they concluded that this protocol does not represent a practical approach to the synthesis of α-amino esters. While high levels of enantiocontrol in aziridinations of alkenes have already been achieved using a variety of different chiral transition metal-catalysts,[8] the catalytic enantioselective amination reaction of silylketene acetals with (*N*-arylsulfonylimino)phenyliodinanes has, to the best of our knowledge, not been reported.[9]

Very recently, we demonstrated that the enantioselective amination of silyl enol ethers derived from acyclic ketones or enones with [(2-nitrophenylsulfonyl)imino]phenyliodinane (NsN = IPh, **2b**) catalyzed by chiral dirhodium(II) carboxylates provides *N*-(2-nitrophenylsulfonyl)-α-amino ketones with enantioselectivities of up to 95% ee.[10] In this process, $Rh_2$(*S*-TFPTTL)$_4$ (**1a**),[11] characterized by the substitution of fluorine atoms for four hydrogen atoms on the phthalimido group in the parent dirhodium(II) complex, $Rh_2$ (*S*-PTTL)$_4$ (**1c**),[12] proved to be the catalyst of choice in terms of product yield and enantioselectivity as well as catalytic activity. As a logical extension of our studies, we herein report that dirhodium(II) tetrakis[*N*-tetrachlorophthaloyl-(*S*)-*tert*-leucinate], $Rh_2$(*S*-TCPTTL)$_4$ (**1b**),[13] catalyzes enantioselective aminations of silylketene acetals derived from methyl phenylacetates with NsN = IPh (**2b**), to provide *N*-(2-nitrophenylsulfonyl)phenylglycine derivatives in high yields and with enantioselectivities of up to 99% ee.[14] While a number of methods,[15] such as the asymmetric Strecker

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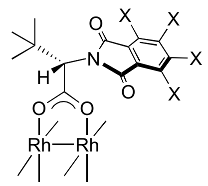
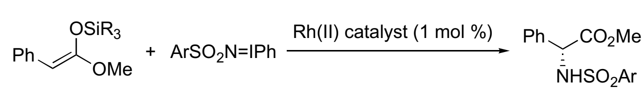
reaction,[16,17] the Sharpless asymmetric aminohydroxylation,[18] and the catalytic enantioselective hydrogenation of α-aryl imino esters,[19] have been used to synthesize optically active arylglycine derivatives,[20] this protocol provides a new, catalytic asymmetric approach to phenylglycine derivatives.




X = F: $Rh_2$(*S*-TFPTTL)$_4$ (**1a**)
X = Cl: $Rh_2$(*S*-TCPTTL)$_4$ (**1b**)
X = H: $Rh_2$(*S*-PTTL)$_4$ (**1c**)

On the basis of our previous work,[10] we initially explored the amination of triethylsilylketene acetal **3a** (*Z*:*E* = 97:3, 1.2 equiv) derived from methyl phenylacetate with NsN = IPh (**2b**) using 1 mol % of $Rh_2$(*S*-TFPTTL)$_4$. The reaction in $CH_2Cl_2$ proceeded smoothly at 0 °C to completion in less than 15 min, giving *N*-(2-nitrophenylsulfonyl)phenylglycine methyl ester (**4b**)[21] in 95% yield after column chromatography on silica gel (Table 1, entry 1). The enantioselectivity of this reaction was determined to be 88% ee by HPLC analysis with a connected series of Daicel Chiralcel OD-H and Chiralpak IB columns. The preferred absolute stereochemistry of **4b** [$[\alpha]_D^{24}$ −156.4 (*c* 1.36, $CHCl_3$)] was assigned as *R* by comparing the sign of optical rotation with (*R*)-**4b** [$[\alpha]_D^{24}$ −172.3 (*c* 1.01, $CHCl_3$)], which was prepared from (*R*)-phenylglycine methyl ester hydrochloride (NsCl, pyridine, $CH_2Cl_2$, 0 °C, 2 h, 87%).[21,22] Gratifyingly, switching the catalyst from $Rh_2$(*S*-TFPTTL)$_4$ to $Rh_2$(*S*-TCPTTL)$_4$ greatly improved the enantioselectivity, providing **4b** in 98% yield with 97% ee (entry 2), although lowering the reaction temperature to –20 °C had little impact on the enantioselectivity (98% ee, entry 3). In this system, $Rh_2$(*S*-PTTL)$_4$ was also less effective in terms of both reactivity and enantioselectivity (entry 4). Using $Rh_2$(*S*-TCPTTL)$_4$ as the catalyst, we next evaluated the performance of other nitrene precursors, [(4-nitrophenylsulfonyl)imino]phenyliodinane (*p*NsN = IPh, **2c**), [(2,4-dinitrophenylsulfonyl)imino]-phenyliodinane (DNsN = IPh, **2d**), and TsN = IPh (**2a**) (entries 5–7). This screening revealed that NsN = IPh (**2b**) was the optimal nitrene precursor for this transformation (entries 2 vs 5–7), although the reason for the advantage of **2b** is not clear at this time. A survey of solvents revealed that the use of benzene was the superior choice as nearly perfect enantiocontrol (99% ee) was achieved at room temperature (entry 8). The product **4b** was also formed with a similar high enantioselectivity in toluene (99% ee, entry 9), but the reaction time (6 h) was longer than that in benzene (3 h). It is noteworthy that the amination of silylketene acetal **3a** (*Z*:*E* = 23:77) with **2b** using $Rh_2$(*S*-TCPTTL)$_4$ produced **4b** with the same sense of asymmetric induction as above in only 18% yield with 99% ee, along with 60% recovery of methyl phenylacetate (entry 10). This observation indicates that only the *Z*-isomer of **3a** is responsible for the formation of **4b** in the present catalytic process. Therefore, it is not necessary to use geometrically pure

**Table 1.** Enantioselective amination of silylketene acetals with [*N*-(arylsufonyl)imino]phenyliodinanes catalyzed by chiral dirhodium(II) carboxylates[a]




**3** **2** **4**

| Entry | Silylketene acetal | | | Iminoiodinane | | Rh(II) catalyst | Solvent | Temperature (°C) | Time (h) | α-Amino ester | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $R_3Si$ | *Z*:*E* | | Ar | | | | | | Yield[b] (%) | ee[c] (%) |
| 1 | **3a** | $Et_3Si$ | 97:3 | **2b** | 2-$NO_2C_6H_4$ | $Rh_2$(*S*-TFPTTL)$_4$ (**1a**) | $CH_2Cl_2$ | 0 | 0.2 | **4b** | 95 | 88 |
| 2 | **3a** | $Et_3Si$ | 97:3 | **2b** | 2-$NO_2C_6H_4$ | $Rh_2$(*S*-TCPTTL)$_4$ (**1b**) | $CH_2Cl_2$ | 0 | 0.2 | **4b** | 98 | 97 |
| 3 | **3a** | $Et_3Si$ | 97:3 | **2b** | 2-$NO_2C_6H_4$ | $Rh_2$(*S*-TCPTTL)$_4$ (**1b**) | $CH_2Cl_2$ | −20 | 2.5 | **4b** | 91 | 98 |
| 4 | **3a** | $Et_3Si$ | 97:3 | **2b** | 2-$NO_2C_6H_4$ | $Rh_2$(*S*-PTTL)$_4$ (**1c**) | $CH_2Cl_2$ | 0 | 1 | **4b** | 80 | 64 |
| 5 | **3a** | $Et_3Si$ | 97:3 | **2c** | 4-$NO_2C_6H_4$ | $Rh_2$(*S*-TCPTTL)$_4$ (**1b**) | $CH_2Cl_2$ | 0 | 0.2 | **4c** | 92 | 59[d] |
| 6 | **3a** | $Et_3Si$ | 97:3 | **2d** | 2,4-$(NO_2)_2C_6H_3$ | $Rh_2$(*S*-TCPTTL)$_4$ (**1b**) | $CH_2Cl_2$ | 0 | 2 | **4d** | 70 | 92[d] |
| 7 | **3a** | $Et_3Si$ | 97:3 | **2a** | 4-$MeC_6H_4$ | $Rh_2$(*S*-TCPTTL)$_4$ (**1b**) | $CH_2Cl_2$ | 0 | 16 | **4a** | 40 | 88[e] |
| 8 | **3a** | $Et_3Si$ | 97:3 | **2b** | 2-$NO_2C_6H_4$ | $Rh_2$(*S*-TCPTTL)$_4$ (**1b**) | Benzene | 23 | 3 | **4b** | 98 | 99 |
| 9 | **3a** | $Et_3Si$ | 97:3 | **2b** | 2-$NO_2C_6H_4$ | $Rh_2$(*S*-TCPTTL)$_4$ (**1b**) | Toluene | 23 | 6 | **4b** | 91 | 99 |
| 10 | **3a** | $Et_3Si$ | 23:77 | **2b** | 2-$NO_2C_6H_4$ | $Rh_2$(*S*-TCPTTL)$_4$ (**1b**) | Benzene | 23 | 3 | **4b** | 18[f] | 99 |
| 11 | **3b** | $Me_3Si$ | 97:3 | **2b** | 2-$NO_2C_6H_4$ | $Rh_2$(*S*-TCPTTL)$_4$ (**1b**) | Benzene | 23 | 3 | **4b** | 88 | 95 |
| 12 | **3c** | *t*-$BuMe_2Si$ | 96:4 | **2b** | 2-$NO_2C_6H_4$ | $Rh_2$(*S*-TCPTTL)$_4$ (**1b**) | Benzene | 23 | 3 | **4b** | 63 | 97 |

[a] The following is a representative procedure (entry 8): **2b** (80.8 mg, 0.2 mmol) was added in one portion to a solution of **3a** (63.4 mg, 0.24 mmol) and $Rh_2$(*S*-TCPTTL)$_4$·2EtOAc (**1b**) (3.8 mg, 0.002 mmol, 1 mol %) in benzene (0.5 mL) at 23 °C. The mixture was concentrated in vacuo and chromatographed on silica gel to afford **4b** (68.7 mg, 98%) as a white solid.

[b] Isolated yield.

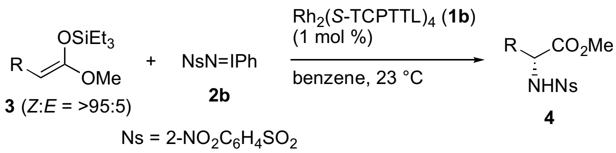
[c] Determined by HPLC (column: Daicel Chiralcel OD-H followed by Daicel Chiralpak IB, eluent: 5:1 hexane/*i*-PrOH, flow rate: 1.0 mL/min) unless otherwise stated.

[d] Determined by HPLC (column: Daicel Chiralpak AD-H, eluent: 1:1 hexane/*i*-PrOH, flow rate: 1.0 mL/min).

[e] Determined by HPLC (column: Daicel Chiralpak AD-H (2 × 250 mm), eluent: 9:1 hexane/*i*-PrOH, flow rate: 1.0 mL/min).

[f] 60% of methyl phenylacetate was recovered.

**Table 2.** Enantioselective amination of silylketene acetals with **2b** catalyzed by $Rh_2$(*S*-TCPTTL)$_4$ (**1b**)



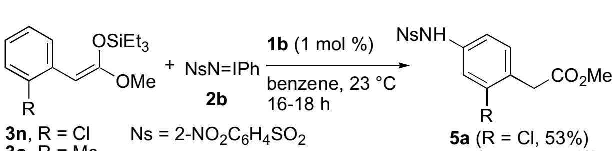

| Entry | Silylketene acetal | | Time (h) | Phenylglycine derivatives | | |
|---|---|---|---|---|---|---|
| | R | | | | Yield[a] (%) | ee[b] (%) |
| 1 | **3a** | $C_6H_5$ | 3 | **4b** | 98 | 99 |
| 2 | **3d** | 4-$CF_3C_6H_4$ | 3 | **4e** | 95 | 97 |
| 3 | **3e** | 4-$FC_6H_4$ | 3 | **4f** | 95 | 97 |
| 4 | **3f** | 4-$ClC_6H_4$ | 2 | **4g** | 98 | 96 |
| 5 | **3g** | 4-$BrC_6H_4$ | 3 | **4h** | 93 | 96 |
| 6 | **3h** | 4-$MeC_6H_4$ | 6 | **4i** | 95 | 98 |
| 7 | **3i** | 4-$MeOC_6H_4$ | 4 | **4j** | 98 | 80 |
| 8 | **3j** | 3-$CF_3C_6H_4$ | 2 | **4k** | 92 | 97 |
| 9 | **3k** | 3-$ClC_6H_4$ | 3 | **4l** | 94 | 98 |
| 10 | **3l** | 3-$MeC_6H_4$ | 4 | **4m** | 93 | 98 |
| 11 | **3m** | 3-$MeOC_6H_4$ | 3 | **4n** | 48 | 98 |

[a] Isolated yield.

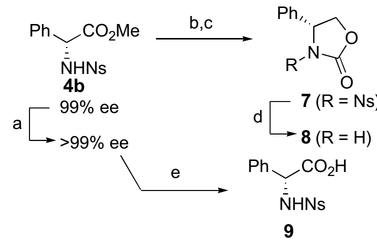
[b] Determined by HPLC. See the Supplementary data for details.

silylketene acetals to achieve high enantioselection. We also examined the effect of the silicon substituents of silylketene acetals **3a–c** on enantioselectivity. Variation in the silyl group revealed that the triethylsilyl functionality was optimal for this process (entries 8 vs 11 and 12).

Having demonstrated the effectiveness of the combination of $Rh_2$(*S*-TCPTTL)$_4$ as the catalyst, NsN = IPh as the nitrene precursor, and benzene as the solvent, the applicability of this catalytic system to a range of silylketene acetals was then investigated (Table 2). High yields and excellent enantioselectivities were consistently observed at room temperature with electron-withdrawing substituents such as trifluoromethyl and chlorine at the *para* or *meta* position on the benzene ring (96–98% ee, entries 2–5, 8, and 9). The reaction with silylketene acetals **3h** and **3l** bearing a methyl group at the *para* or *meta* position also afforded the corresponding phenylglycine derivatives **4i** and **4m** in high yields and very high enantioselectivities (98% ee, entries 6 and 10). However, the introduction of a methoxy group at the *para* or *meta* position had a detrimental effect on product yield or enantioselectivity. The use of *para*-methoxy-substituted silylketene acetal **3i** resulted in only modest enantioselection (80% ee, entry 7). Although a high enantioselectivity (98% ee) was achieved with *meta*-methoxy-substituted silylketene acetal **3m**, a marked decrease in product yield was observed (entry 11). Surprisingly, the introduction of methyl or chlorine substituents at the *ortho* position on the benzene ring gave aromatic C–H amination products **5a** and **5b** as the sole products instead of the expected phenylglycine derivatives (Eq. 1).[23]




(1)




**Scheme 1.** Reagents and conditions: (a) recrystallization from EtOH, 91%; (b) DIBAL-H, $CH_2Cl_2$, −78–0 °C, 0.5 h; (c) triphosgene, $Et_3N$, $CH_2Cl_2$, 0 °C, 1 h, 88% (two steps); (d) PhSH, $Cs_2CO_3$, DMF, 23 °C, 1 h, 81%; (e) LiI, EtOAc, reflux, 6 h, 94%.

The *N*-(2-nitrophenylsulfonyl)phenylglycine derivatives are potentially useful for the synthesis of chiral ligands[24] and novel oligopeptide structures[21,25] (Scheme 1). A single recrystallization of **4b** (99% ee) from EtOH produced an optically pure sample [mp = 103.0–104.0 °C, $[\alpha]_D^{23}$ −172.0 (*c* 1.00, $CHCl_3$)] in 91% yield. Reduction of **4b** with DIBAL-H followed by treatment with triphosgene produced the *N*-Ns-protected oxazolidinone **7** [$[\alpha]_D^{23}$ −629.7 (*c* 0.50, $CHCl_3$)] in 93% yield with no racemization.[22] Removal of the Ns-group under standard Fukuyama conditions[26] furnished an Evans auxiliary (*R*)-**8**,[24] [$[\alpha]_D^{23}$ −57.0 (*c* 1.01, $CHCl_3$), lit.,[24b] $[\alpha]_D^{22}$ +58.0 (*c* 1.00, $CHCl_3$) for (*S*)-**8**] in 81% yield. In addition, methyl ester cleavage of **4b** with LiI in refluxing ethyl acetate[25] provided (*R*)-*N*-(2-nitrophenylsulfonyl)phenylglycine (**9**) [$[\alpha]_D^{25}$ −181.5 (*c* 1.01, $CHCl_3$)] in 94% yield and in enantiomerically pure form.[22]

In summary, we have developed the first catalytic enantioselective amination of silylketene acetals with (*N*-arylsulfonylimino)phenyliodinanes. The reaction of *Z* -triethylsilylketene acetals derived from methyl phenylacetates with NsN = IPh is catalyzed by $Rh_2$(*S*-TCPTTL)$_4$ at room temperature to give *N*-Ns-protected phenylglycine derivatives in high yields and with excellent enantioselectivities, although the efficiency of the present protocol depends on the substitution pattern on the benzene ring. Further studies to expand the range of substrates as well as mechanistic and stereochemical studies are currently underway.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.10.087.

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