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ENANTIOSELECTIVE INTRAMOLECULAR C–H AMIDATION OF SULFAMATE ESTERS CATALYZED BY CHIRAL DIRHODIUM(II) CARBOXYLATES†

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Abstract – The chiral dirhodium(II) carboxylate-catalyzed enantioselective intramolecular C–H amidation reaction of sulfamate esters via in situ generated iminoiodinanes is described. The use of dirhodium(II) tetrakis[N-tetrafluorophthaloyl-(S)-tert-leucinate], Rh$_2$(S-TFPTTL)$_4$, as a catalyst and PhI(OAc)$_2$ as an oxidant provides cyclic sulfamidates in up to 48% ee.

The transition metal-catalyzed intramolecular C–H amidation of iminoiodinanes, which features C–N bond formation at an unactivated carbon atom, offers a potentially powerful strategy for the synthesis of heterocycles.† While the pioneering work of Breslow and Gellman in 1983 demonstrated that the Rh$_2$(OAc)$_4$-catalyzed intramolecular C–H amidation of [(2,5-diisopropyl)phenylsulfonylimino]phenyliodinane provided cyclic sulfonamide in high yield, it was not until several years ago that an efficient and general intramolecular C–H amidation procedure with in situ generated iminoiodinanes was developed. Du Bois and co-workers demonstrated that the oxidation of carbamates and sulfamate esters by PhI(OAc)$_2$ in the presence of MgO gives only low concentrations of iminoiodinanes, which undergo rapid C-H insertion under the influence of a dirhodium(II) catalyst to produce oxazolidinones and cyclic sulfamidates, respectively, with high regioselectivity and good to excellent diastereoselectivity. Since then, remarkable progress has been achieved in the development of intramolecular C–H amidations with effective metal catalysts derived from Ru(II), Mn(III), and Ag(I). Consequently, a great deal of effort has been directed toward the development of an enantioselective version of these catalytic processes. Che and co-workers demonstrated the first successful examples of

† Dedicated to Professor Satoshi Ōmura on the occasion of his 70th birthday.
the enantioselective intramolecular C–H amidation of sulfamate esters (up to 88% ee), using a chiral ruthenium(II) porphyrin-catalyst.\(^6\) Thereafter, Fruit and Müller reported enantioselective intramolecular C–H amidation reactions of sulfamate esters and sulfonamides catalyzed by chiral dirhodium(II) carboxylates, Rh\(_2\)(S-NTTL)\(_4\) (1g) and Rh\(_2\)(R-NTV)\(_4\) (1h), in up to 52% ee and 66% ee, respectively.\(^9\) More recently, the Che group explored the intramolecular C–H amidation of sulfamate esters in the presence of chiral manganese(III)-salen-catalysts, in which moderate to good enantioselectivities (up to 79% ee) were obtained.\(^7\) Recently, Che and co-workers reported enantioselective intramolecular aziridination of sulfonamides via \textit{in situ} generated iminoiodinanes (up to 76% ee), using a chiral dirhodium(II) carboxamidate catalyst Rh\(_2\)(4S-MEOX)\(_4\).

We recently reported that the enantioselective intermolecular benzylic C–H amidation of aromatic hydrocarbons (2) with [(4-nitrophenyl)sulfonylimino]phenyliodinane (3) catalyzed by chiral dirhodium(II) carboxylates provides sulfonamides in up to 84% ee [eqn. (1)].\(^10\) In this process, Rh\(_2\)(S-TCPTTL)\(_4\) (1a), characterized by the substitution of chlorine atoms for four hydrogen atoms on the phthalimido group in the parent dirhodium(II) complex, Rh\(_2\)(S-PTTL)\(_4\) (1c),\(^11,12\) proved to be the catalyst of choice in terms of product yield and enantioselectivity as well as catalyst activity. As a logical extension of our studies, we now address the issue of enantiocontrol in the intramolecular C–H amidation of sulfamate esters.

\[
\begin{align*}
\text{R}-\text{C}=\text{N} & \quad \xrightarrow{\text{Rh}_2(\text{S-TCPTTL})_4(1a)} \quad \text{NH}p\text{Ns} \\
\text{R} \quad \text{R} & \quad \text{R} \quad \text{R} \\
\text{CH}_2\text{Cl}_2, -23 \degree \text{C} & \\
\text{pNs} = 4-\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2 & \\
\text{up to 84\% ee}
\end{align*}
\]

In an extension of our previous work, we initially explored the C–H amidation of indan-2-yl sulfamate (5a) using 2 mol % of Rh\(_2\)(S-TCPTTL)\(_4\) (1a), in the presence of 1.1 equiv. of PhI(OAc)\(_2\) and 2.3 equiv. of MgO. The reaction in dichloromethane at 23 \degree C proceeded smoothly to give the cyclic sulfamidate (6a), \([\alpha]_D^{25}+31.3\degree\) (c 0.87, THF), in 81% yield with complete \textit{cis} selectivity (Table 1, Entry 1). The
enantioselectivity of this reaction was determined to be 22% ee by HPLC analysis (Daicel Chiralcel OD-H). The preferred absolute stereochemistry of 6a was established as (3αR,8αS) by comparing the sign of the optical rotation with (3αR,8αS)-6a \([\alpha]_D^{24} +141^\circ\) (c 0.82, THF), prepared from (1R,2S)-1-aminooindan-2-ol according to the procedure of Harwood (SO\(_2\)Cl\(_2\), Et\(_3\)N, CH\(_2\)Cl\(_2\), 0 °C, 1 h, 67%).\(^{13}\) A survey of solvents revealed that benzene was the optimal solvent for this transformation, improving the enantioselectivity to 35% ee (Entry 2). Toluene was inferior to benzene in terms of both product yield and enantioselectivity (Entry 3).\(^{14}\) Using benzene as the solvent, we next evaluated the performance of other chiral dirhodium(II) carboxylates. While a uniform sense of asymmetric induction was observed in all cases, the ee values were dependent on the catalyst. As might be expected from the results for the enantioselective intermolecular amidation of indan, chiral dirhodium(II) carboxylate catalysts, Rh\(_2\)(S-PTA)\(_4\) (1d), Rh\(_2\)(S-PTPA)\(_4\) (1e), and Rh\(_2\)(S-PTV)\(_4\) (1f) were less effective than Rh\(_2\)(S-TCPTTL)\(_4\) (Entries 6–8).\(^{15}\) Somewhat surprisingly, Rh\(_2\)(S-TFPTTL)\(_4\) (1b)\(^{16}\) and Rh\(_2\)(S-PTTL)\(_4\) (1c) proved to be the catalysts of choice for this process, displaying higher enantioselectivities than Rh\(_2\)(S-TCPTTL)\(_4\) (48% and 43% ee, Entries 4 and 5). Although the enantioselectivities are modest, these ee values exceed those (22% and 30% ee)\(^{9b}\) reported previously by Fruit and Müller, using Rh\(_2\)(S-NTTL)\(_4\) (1g) and Rh\(_2\)(R-NTV)\(_4\) (1h). It is noteworthy that the isolated yield (98%) obtained using Rh\(_2\)(S-TFPTTL)\(_4\) is the highest ever reported for the intramolecular C–H amidation of 5a. In this respect,

**Table 1.** Enantioselective Intramolecular C–H Amidation of Indan-2-yl Sulfamate (5a) Catalyzed by Chiral Dirhodium(II) Carboxylates\(^{a}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Rh(II) catalyst</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>[\alpha]D (c, THF)</th>
<th>Ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh(_2)(S-TCPTTL)(_4) (1a)</td>
<td>CH(_2)Cl(_2)</td>
<td>3</td>
<td>81</td>
<td>+31.3° (0.87)</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>Rh(_2)(S-TCPTTL)(_4) (1a)</td>
<td>benzene</td>
<td>1</td>
<td>79</td>
<td>+48.9° (1.05)</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>Rh(_2)(S-TCPTTL)(_4) (1a)</td>
<td>toluene</td>
<td>1</td>
<td>37</td>
<td>+30.0° (0.63)</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>Rh(_2)(S-TFPTTL)(_4) (1b)</td>
<td>benzene</td>
<td>1</td>
<td>98</td>
<td>+68.3° (1.03)</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>Rh(_2)(S-PTTL)(_4) (1c)</td>
<td>benzene</td>
<td>2</td>
<td>75</td>
<td>+52.0° (1.13)</td>
<td>43</td>
</tr>
<tr>
<td>6</td>
<td>Rh(_2)(S-PTA)(_4) (1d)</td>
<td>benzene</td>
<td>1</td>
<td>61</td>
<td>+15.7° (1.01)</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>Rh(_2)(S-PTPA)(_4) (1e)</td>
<td>benzene</td>
<td>1.5</td>
<td>70</td>
<td>+21.5° (0.86)</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>Rh(_2)(S-PTV)(_4) (1f)</td>
<td>benzene</td>
<td>2</td>
<td>79</td>
<td>+16.8° (1.20)</td>
<td>19</td>
</tr>
<tr>
<td>9(^d)</td>
<td>Rh(_2)(S-TFPTTL)(_4) (1b)</td>
<td>benzene</td>
<td>1</td>
<td>98</td>
<td>+64.2° (0.93)</td>
<td>45</td>
</tr>
<tr>
<td>10(^d)</td>
<td>Rh(_2)(S-PTTL)(_4) (1c)</td>
<td>benzene</td>
<td>0.5</td>
<td>51</td>
<td>+56.3° (0.75)</td>
<td>38</td>
</tr>
</tbody>
</table>

\(^{a}\) All reactions were performed on a 0.2 mmol scale. \(^{b}\) Isolated yield. \(^{c}\) Determined by HPLC (Daicel Chiralcel OD-H column). \(^{d}\) The reaction was carried out in the absence of MgO.
it is interesting to note that the reaction with Rh$_2$(S-TFPTTL)$_4$ in the absence of MgO as an AcOH scavenger gave nearly the same result as that in the presence of MgO (Entry 4 vs. 9), which is in marked contrast with the results for Rh$_2$(S-PTTL)$_4$ (Entry 5 vs. 10). These results demonstrate the robust nature and high reactivity of Rh$_2$(S-TFPTTL)$_4$.

We then investigated the applicability of the present catalytic system to sulfamate esters other than 5a. Some representative results are presented in Table 2. To our disappointment, the method was found to be highly sensitive to the structure of the substrate. The reaction of cyclopentyl sulfamate ester (5b) under the influence of Rh$_2$(S-TFPTTL)$_4$ or Rh$_2$(S-PTTL)$_4$ gave the cyclic sulfamidate (6b) in low yields with complete cis selectivity, wherein ee values were significantly lower than those in the case of 5a (Entries 1 and 2). These results strongly suggest that the presence of a phenyl ring is required for both product yield and enantioselectivity in the five-membered ring insertion process. It was also found that the formation of the six-membered cyclic sulfamidate (6c), the preferred pathway in the C–H amidation of acyclic, conformationally mobile sulfamate esters, resulted in disappointing enantioselectivities (Entries 3 and 4). In this reaction, Rh$_2$(S-PTTL)$_4$ exhibited a higher enantioselectivity than Rh$_2$(S-TFPTTL)$_4$. The intramolecular insertion of aromatic sulfamate ester (5d) into a benzylic C–H bond provided the tricyclic sulfamidate (6d) in low to moderate yields with ca. 60% substrate conversion and only a poor enantioselectivity (Entries 5 and 6).

### Table 2. Enantioselective Intramolecular C–H Amidation of Sulfamate Esters (5b-d)$^a$)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sulfamate ester</th>
<th>Rh(II) catalyst</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield (%)$^b$</th>
<th>Ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="https://example.com/5b.png" alt="5b" /></td>
<td>Rh$_2$(S-TFPTTL)$_4$ (1b)</td>
<td>1</td>
<td><img src="https://example.com/6b.png" alt="6b" /></td>
<td>30</td>
<td>27$^c$</td>
</tr>
<tr>
<td>2</td>
<td><img src="https://example.com/5b.png" alt="5b" /></td>
<td>Rh$_2$(S-PTTL)$_4$ (1c)</td>
<td>1</td>
<td><img src="https://example.com/6b.png" alt="6b" /></td>
<td>34</td>
<td>14$^c$</td>
</tr>
<tr>
<td>3</td>
<td><img src="https://example.com/5c.png" alt="5c" /></td>
<td>Rh$_2$(S-TFPTTL)$_4$ (1b)</td>
<td>10</td>
<td><img src="https://example.com/6c.png" alt="6c" /></td>
<td>87</td>
<td>10$^d$</td>
</tr>
<tr>
<td>4</td>
<td><img src="https://example.com/5c.png" alt="5c" /></td>
<td>Rh$_2$(S-PTTL)$_4$ (1c)</td>
<td>30</td>
<td><img src="https://example.com/6c.png" alt="6c" /></td>
<td>67</td>
<td>21$^d$</td>
</tr>
<tr>
<td>5</td>
<td><img src="https://example.com/5d.png" alt="5d" /></td>
<td>Rh$_2$(S-TFPTTL)$_4$ (1b)</td>
<td>2</td>
<td><img src="https://example.com/6d.png" alt="6d" /></td>
<td>49(39)$^e$</td>
<td>14$^f$</td>
</tr>
<tr>
<td>6</td>
<td><img src="https://example.com/5d.png" alt="5d" /></td>
<td>Rh$_2$(S-PTTL)$_4$ (1c)</td>
<td>2</td>
<td><img src="https://example.com/6d.png" alt="6d" /></td>
<td>9(45)$^e$</td>
<td>–16$^f$</td>
</tr>
</tbody>
</table>

$^a$ All reactions were performed on a 0.2 mmol scale with 2 mol % of Rh(II) catalyst, 1.1 equiv. of PhI(OAc)$_2$ and 2.3 equiv. of MgO in benzene at 23 °C. $^b$ Isolated yield. $^c$ Determined by HPLC (Daicel Chiralpak AD column) after conversion to the corresponding benzyl carbamate. $^d$ Determined by HPLC (Daicel Chiralcel OD column). $^e$ Values in parentheses refer to the yields of sulfamate esters recovered. $^f$ Determined by HPLC (Daicel Chiralpak IA column).
In summary, we have reported one-pot enantioselective C–H amidation of sulfamate esters with the use of chiral dirhodium(II) carboxylate catalysts and PhI(OAc)_2 as an oxidant. Rh_2(S-TFPTTL)_4 is the most effective catalyst for this process (up to 48% ee). In contrast to the enantioselective intermolecular amidation of benzylic C–H bonds, there is considerable room for improvement in the intramolecular amidation of sulfamate esters catalyzed by chiral dirhodium(II) complexes. The design and synthesis of a new class of chiral bridging ligands to further enhance enantioselectivity is currently in progress.

**EXPERIMENTAL**

**General.** Melting points were recorded on a Büchi 535 digital melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer and absorbance bands are reported in wavenumber (cm\(^{-1}\)). \(^1\)H NMR spectra were recorded on JEOL JNM-AL 400 (400 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane; \(\delta_\text{H} 0.00\) or acetone-\(d_6\); \(\delta_\text{H} 2.04\)). Data are presented as follows: chemical shift (\(\delta\), ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant and integration. \(^13\)C NMR spectra were recorded on a JEOL JNM-AL 400 (100 MHz) spectrometer. Chemical shifts are reported relative to internal standard (CDCl_3; \(\delta 77.0\), acetone-\(d_6\); \(\delta 29.8\)). Optical rotations were measured on a JASCO P-1030 digital polarimeter at the sodium D line (589 nm). EI-MS spectra were obtained on a JEOL JMS-HX 110 spectrometer. Column chromatography was carried out on Kanto silica gel 60 N (63-210 mesh). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F\(_{254}\) plates with visualization by ultraviolet, anisaldehyde stain solution or phosphomolybdic acid stain solution. Analytical high performance liquid chromatography (HPLC) was performed on JASCO PU-1580 intelligent HPLC pump with JASCO UV-1575 intelligent UV/VIS detector. Detection was performed at 254 nm. Chiralcel OD, OD-H, Chiralpak IA and AD columns (0.46 cm \(\times\) 25 cm) from Daicel were used. Retention times (\(t_R\)) and peak ratio were determined with Shimadzu C-R8A chromatopac integrator or JASCO-Borwin analysis system.

All non-aqueous reactions were carried out in flame-dried glassware under argon atmosphere. Reagents and solvents were purified by standard means. Dehydrated THF, CH\(_2\)Cl\(_2\) and toluene were purchased from Kanto Chemical Co., Inc. Benzene was distilled from Na/benzophenone ketyl. Sulfamoyl chloride was prepared according to the procedure of Appel and Berger.\(^{17}\)

**General procedure for sulfamate ester preparation: indan-2-yl sulfamate (5a).**\(^{3b, 9b}\) The sulfamate ester (5a) was prepared according to the procedure of Okada.\(^{18}\) Sulfamoyl chloride (2.25 g, 15.0 mmol, 1.5 equiv) was added to a solution of 2-indanol (1.3 g, 10 mmol) in \(N,N\)-dimethylacetamide (40 mL, 0.25 M) at 0 °C. The mixture was stirred at 23 °C for 1 h and poured into cold brine (100 mL). The whole
mixture was extracted with EtOAc (2 × 100 mL), and the combined organic layers were washed with H₂O (50 mL) and brine (2 × 50 mL), and dried over Na₂SO₄. Filtration and evaporation gave the crude product (2.4 g), which was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) followed by recrystallization from benzene to provide 5a (1.8 g, 84%) as colorless needles; Rₚ = 0.54 (5:1 CH₂Cl₂/EtOAc); mp 99.5-100.5 °C (lit., 98 mp 89 °C); IR (KBr) ν 3370, 3281, 1346, 1179 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.26 (dd, J = 3.6, 17.0 Hz, 2H, C1-H and C3-H), 3.33 (dd, J = 5.8, 17.0 Hz, 2H, C1-H and C3-H), 4.94 (br-s, 2H, NH₂), 5.40 (tt, J = 3.6, 5.8 Hz, 1H, C2-H), 7.17-7.24 (m, 4H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ 39.81 (CH₂), 83.58 (CH), 124.54 (CH), 127.04 (CH), 139.14 (C); HRMS (EI) calcd for C₉H₁₅NO₃S (M⁺) 213.0460, found 213.0450; Anal. Calcd for C₉H₁₅NO₃S: C, 50.60; H, 5.20; N, 5.67; S, 15.04. Found: C, 50.60; H, 5.15; N, 6.64; S, 15.20.

Cyclopentyl sulfamate (5b).¹⁹ The sulfamate ester (5b) was prepared according to the general procedure, using cyclopentanol (861.4 mg, 10 mmol) and sulfamoyl chloride (4.50 g, 30 mmol). The crude product (1.9 g) was purified by column chromatography (3:1 hexane/EtOAc) followed by recrystallization from 1:1 PrOH/hexane to afford 5b (1.51 g, 67%) as colorless plates; Rₚ = 0.60 (1:1 hexane/EtOAc); mp 181.5-182.5 °C (dec.) (lit., 19 mp 58-60 °C); IR (KBr) ν 3360, 3264, 1345, 1181, 1155 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.60-1.68 (m, 2H, CH₂), 1.77-1.81 (m, 2H, CH₂), 1.84-1.94 (m, 2H, CH₂), 1.99-2.03 (m, 2H, CH₂), 4.68 (br-s, 2H, NH₂), 5.10 (quintet, J = 2.8 Hz, 1H, CHOSO₂NH₂); ¹³C NMR (100 MHz, CDCl₃) δ 23.24 (CH₂), 33.11 (CH₂), 86.45 (CH); HRMS (EI) calcd for C₅H₁₀NO₃S (MH⁺) 166.0538, found 166.0534.

3-Phenylpropyl sulfamate (5c).³⁰ According to the general procedure, 5c was prepared from 3-phenylpropanol (1 g, 7.3 mmol) and sulfamoyl chloride (1.64 g, 11 mmol). The crude product (1.5 g) was purified by column chromatography (silica gel, 3:1 hexane/EtOAc) followed by recrystallization from 3:1 ether/hexane to afford 5c (1.3 g, 82%) as colorless needles; Rₚ = 0.53 (1:1 hexane/EtOAc); mp 56.5-57.0 °C; IR (KBr) ν 3370, 3285, 1350, 1184 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.02-2.19 (m, 2H, CH₂CH₂CH₂), 2.74 (t, J = 7.5 Hz, 2H, PhCH₂), 4.20 (t, J = 6.4 Hz, 2H, OCH₂), 4.92 (br-s, 2H, NH₂), 7.17-7.31 (m, 5H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ 30.28 (CH₂), 31.55 (CH₂), 70.52 (CH₂), 126.14 (CH), 128.37 (CH), 128.44 (CH), 140.32 (C); HRMS (EI) calcd for C₉H₁₅NO₃S (M⁺) 215.0616, found 215.0609; Anal. Calcd for C₅H₁₃NO₃S: C, 50.21; H, 6.09; N, 6.51; S, 14.90. Found: C, 50.15; H, 5.98; N, 6.47; S, 15.19.

1,2,3,4-Tetrahydrobenzthalen-8-yl sulfamate (5d).³² According to the general procedure, 5d was prepared from 1,2,3,4-tetrahydrobenzthalen-8-ol (1.5 g, 10 mmol) and sulfamoyl chloride (2.25 g, 15
mmol). The crude product (3.0 g) was purified by column chromatography (silica gel, 5:1 hexane/EtOAc) followed by recrystallization from benzene to afford 5d (2.2 g, 98%) as colorless needles; \( R_f = 0.50 \) (2:1 hexane/EtOAc); mp 87.5-88 °C; IR (KBr) ν 3387, 3279, 1346, 1175 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.77-1.80 (m, 4H, C1-H, C4-H), 2.79-2.81 (m, 4H, C2-H, C3-H), 5.03 (br-s, 2H, NH\(_2\)), 7.02 (d, \( J = 7.8 \) Hz, 1H, ArH), 7.11 (dd, \( J = 7.8, 7.8 \) Hz, 1H, ArH), 7.18 (d, \( J = 7.8 \) Hz, 1H, ArH); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 22.36 (CH\(_3\)), 22.55 (CH\(_2\)), 23.70 (CH\(_3\)), 29.44 (CH\(_2\)), 118.35 (CH), 125.95 (CH), 127.94 (CH), 130.56 (C), 139.98 (C), 148.45 (C); HRMS (EI) calcd for C\(_{16}\)H\(_{13}\)NO\(_3\)S (M\(^+\)) 227.0616, found 227.0612; Anal. Calcd for C\(_{16}\)H\(_{13}\)NO\(_3\)S: C, 52.85%; H, 5.77%; N, 6.16%; S, 14.11. Found: C, 52.93%; H, 5.66%; N, 6.06%; S, 14.16.

General procedure for the enantioselective intramolecular C–H amidation reaction (Table 1, Entry 4): (3aR,8aS)-3,3a,8,8a-tetrahydroindeno[1,2-d]-1,2,3-oxathiazole 2,2-dioxide (6a).\(^{3b,6a,9b}\) To a suspension of 5a (42.6 mg, 0.2 mmol), MgO (18.5 mg, 0.46 mmol, 2.3 equiv.) and Rh\(_2\)(S-TFPTTL)\(_4\)2EtOAc (6.8 mg, 0.004 mmol, 2 mol %) in benzene (5 mL) was added PhI(OAc)\(_2\) (70.9 mg, 0.22 mmol, 1.1 equiv.) in one portion at 23 °C. After stirring at this temperature for 1 h, the whole mixture was filtered through a pad of Celite. The filter cake was rinsed with EtOAc and the combined filtrates were evaporated under reduced pressure. The residue (113 mg) was purified by column chromatography (silica gel, 5:1 hexane/EtOAc) to provide (3aR,8aS)-6a (40.9 mg, 98%) as a white solid; \( R_f = 0.32 \) (2:1 hexane/EtOAc); mp 169-170 °C; \([\alpha]_D^{22} = +68.3^\circ \) (c 1.03, THF) for 48% ee; IR (KBr) ν 3283, 1350, 1187 cm\(^{-1}\); \(^1\)H NMR (400 MHz, acetone-\(d_6\)) \( \delta \) 3.29 (d, \( J = 18.1 \) Hz, 1H, C8-CH), 3.46 (dd, \( J = 6.2, 18.1 \) Hz, 1H, C8-CH), 5.44 (t, \( J = 6.2 \) Hz, 1H, C3a-CH), 5.61 (m, 1H, C8a-CH), 7.03 (br-d, \( J = 6.2 \) Hz, 1H, NH), 7.29-7.32 (m, 3H, ArH), 7.39-7.41 (m, 1H, ArH); \(^{13}\)C NMR (100 MHz, acetone-\(d_6\)) \( \delta \) 38.07 (CH\(_2\)), 65.12 (CH), 86.95 (CH), 125.77 (CH), 126.29 (CH), 128.19 (CH), 129.90 (CH), 139.56 (C), 140.63 (C); HRMS (EI) calcd for C\(_9\)H\(_9\)NO\(_3\)S (M\(^+\)) 211.0303, found 211.0294. The enantiomeric excess of 6a was determined to be 48% by HPLC with a Chiralcel OD-H column (9:1 hexane/i-PrOH, 1.0 mL/min); \( t_8 \) (minor) = 26.5 min for (3aS,8aR)-enantiomer; \( t_8 \) (major) = 31.5 min for (3aR,8aS)-enantiomer. The absolute configuration of 6a was determined to be 3aR, 8aS by chemical correlation (vide infra).

Determination of absolute configuration of 6a: (3aR,8aS)-3,3a,8,8a-tetrahydroindeno[1,2-d]-1,2,3-oxathiazole 2,2-dioxide (6a) from (1R,2S)-1-aminooindan-2-ol. The cyclic sulfamidate (6a) was prepared according to the procedure of Harwood.\(^{13}\) To a solution of (1R,2S)-1-aminoo-2-ndanol (>99% ee, purchased from Aldrich, 100 mg, 0.67 mmol) and Et\(_3\)N (102 mg, 1.0 mmol) in CH\(_2\)Cl\(_2\) (3 mL) was added SO\(_2\)Cl\(_2\) (136 mg, 1.0 mmol) at 0 °C. After stirring at this temperature for 1 h, the reaction mixture was poured into cold water (10 mL), and the whole was extracted with EtOAc (3 × 10 mL). The combined
organic layers were washed with saturated NaHCO₃ solution (10 mL), water (10 mL) and brine (2 × 10 mL), and dried over Na₂SO₄. Filtration and evaporation gave the crude product (118.7 mg), which was purified by column chromatography (silica gel, 3:1 hexane/EtOAc) followed by recrystallizations from 1:1 PrOH/hexane to furnish (3aR,8aS)-6a (94.5 mg, 67%) as colorless needles; mp 187–188 °C (dec); [α]D₂⁴ +141.2° (c 0.82, THF) for >99% ee of (3aR,8aS)-6a; Anal. Calcd for C₁₀H₁₉NO₅S: C, 51.17; H, 4.29; N, 6.63; S, 15.18. Found: C, 51.15; H, 4.33; N, 6.53; S, 15.29. The enantiomeric excess was determined to be >99% by HPLC.

Tetrahydro-3(3aH)-cyclopent-1,2,3-oxathiazole (6b). According to the general procedure for C–H amidation, 6b was prepared from 5b (33.0 mg, 0.20 mmol), PhI(OAc)₂ (70.9 mg, 0.22 mmol), MgO (18.5 mg, 0.46 mmol), and Rh₂(S-TFPTTL)₂2EtOAc (6.8 mg, 0.004 mmol, 2 mol %). The crude product (76 mg) was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide 6b (9.7 mg, 30%) as a colorless oil; Rf = 0.38 (2:1 hexane/EtOAc); [α]D₂⁴ +1.21° (c 0.58, CHCl₃) for 27% ee; IR (neat) ν 3268, 1354, 1188 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.75 (m, 1H), 1.83-2.05 (m, 4H), 2.17 (m, 1H), 4.28 (ddt J = 3.2, 9.6, 6.4 Hz, 1H, C₃a-H), 4.40 (br-s, 1H, NH), 5.17 (dt, J = 1.9, 6.4 Hz, 1H, C₆a-H); ¹³C NMR (100 MHz, CDCl₃) δ 22.58 (CH₃), 32.70 (CH₂), 33.15 (CH₂), 59.77 (CH), 86.84 (CH); HRMS (EI) calcld for C₅H₉NO₅S (M⁺) 163.0303, found 163.0299. The enantiomeric excess of 6b was determined to be 27% by HPLC after conversion to the corresponding benzyl carbamate (vide infra). The absolute stereochemistry of 6b was not determined.

Benzyl tetrahydro-3(3aH)-cyclopent-1,2,3-oxathiazole-3-carboxylate. A solution of 6b (8.1 mg, 0.05 mmol) in THF (0.4 mL) was added to a solution of sodium tert-butoxide (10 mg, 0.1 mmol) in THF (0.6 mL) at 0 °C. After 0.5 h of stirring at this temperature, benzyl chloroformate (34 mg, 0.2 mmol) was added to the mixture. After 5 min of stirring at the same temperature, the reaction was quenched by crushed ice, and the whole mixture was extracted with EtOAc (20 mL). The organic layer was washed with water (5 mL) and brine (2 × 5 mL), and dried over Na₂SO₄. Filtration and evaporation in vacuo followed by column chromatography (silica gel, 20:1 toluene/EtOAc) provided benzyl tetrahydro-3(3aH)-cyclopent-1,2,3-oxathiazole-3-carboxylate (10.3 mg, 70%) as a colorless oil; Rf = 0.60 (1:1 hexane/EtOAc); [α]D₂³ +6.51° (c 0.85, CHCl₃); IR (neat) ν 1740, 1380, 1335,1305,1196 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.83-1.90 (m, 2H), 1.96-2.06 (m, 3H), 2.21 (m, 1H), 4.60 (dt J = 2.7, 5.4 Hz, 1H, C₆a-H), 5.21 (t, J = 5.4 Hz, 1H, C₃a-H), 5.30 (d, J = 12.4 Hz, 1H, PhCH), 5.34 (d, J = 12.4 Hz, PhCH), 7.32-7.41 (m, 5H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ 22.69 (CH₃), 32.31 (CH₂), 32.63 (CH₂), 61.52 (CH), 69.26 (CH₂), 84.13 (CH), 127.83 (CH), 128.51 (CH), 128.59 (CH), 134.40 (C), 150.05 (C=O); HRMS (EI) calcld for C₁₃H₁₅NO₅S (M⁺) 297.0671, found 297.0681. The enantiomeric excess was
determined to be 27% by HPLC [Daicel Chiralpak AD column (9:1 hexane/i-PrOH, 1.0 mL/min): \( t_R \) (major) = 17.9 min; \( t_R \) (minor) = 21.0 min].

**Tetrahydro-4-phenyl-1,2,3-oxathiazine 2,2-dioxide (6c).**\(^{3b} \) According to the general procedure for C–H amidation, 6c was prepared from 5c (43.1 mg, 0.20 mmol), Phl(OAc)\(_2\) (70.9 mg, 0.22 mmol), MgO (18.5 mg, 0.46 mmol), and Rh\(_2\)(S-PTTL)\(_2\)·2EtOAc (5.69 mg, 0.004 mmol, 2 mol %). The crude product (70 mg) was purified by column chromatography (silica gel, 6:1 hexane/EtOAc) to provide 6c (28.4 mg, 67%) as a white solid; \( R_f = 0.44 \) (2:1 hexane/EtOAc); mp 120–120.5 °C; [\( \alpha \)]\(_D\)\(^{23} \)+1.09° (c 0.99, THF) for 21% ee; IR (KBr) \( \nu = 3212, 1355, 1180 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 2.00 \) (dq, \( J = 14.7, 1.8 \) Hz, 1H, C\(_5\)ax-H), 2.25 (ddt, \( J = 4.9, 14.7, 12.8 \) Hz, 1H, C\(_5\)eq-H), 4.50 (br-d, \( J = 9.1 \) Hz, 1H, NH), 4.64 (ddd, \( J = 1.8, 4.9, 11.8 \) Hz, 1H, C\(_6\)eq-H), 4.81–4.88 (m, 2H, C\(_4\)-H and C\(_6\)ax-H), 7.33–7.41 (m, 5H, ArH); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 30.13 \) (CH\(_2\)), 58.94 (CH\(_3\)), 71.91 (CH\(_2\)), 126.17 (CH), 128.76 (CH), 129.02 (CH), 137.84 (C); HRMS (EI) calcld for C\(_9\)H\(_{14}\)NO\(_3\)S (M\(^+\)) 213.0459, found 213.0462. The enantiomeric excess of 6c was determined to be 21% by HPLC with a Chiralcel OD column (3:1 hexane/i-PrOH, 0.5 mL/min): \( t_R \) (major) = 26.4 min; \( t_R \) (minor) = 30.1 min. The absolute stereochemistry of 6c was not determined.

**3a,4,5,6-Tetrahydro-3H-naphth[1,8-de]-1,2,3-oxathiazine 2,2-dioxide (6d).**\(^{3c} \) According to the general procedure for C–H amidation, 6d was prepared from 5d (45.5 mg, 0.20 mmol), Phl(OAc)\(_2\) (70.9 mg, 0.22 mmol), MgO (18.5 mg, 0.46 mmol), and Rh\(_2\)(S-TFPTTL)\(_2\)·2EtOAc (6.8 mg, 0.004 mmol, 2 mol %). The crude product (102 mg) was purified by column chromatography (silica gel, 3:1 hexane/EtOAc) to provide 6d (22.2 mg, 49%) as an orange solid, along with recovered 5d (17.6 mg, 39%). 6d: \( R_f = 0.47 \) (2:1 hexane/EtOAc); mp 123-124 °C; [\( \alpha \)]\(_D\)\(^{24} \)+5.28° (c 0.90, MeOH) for 14% ee; IR (KBr) \( \nu = 3259, 1370, 1174 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 1.62 \) (dq, \( J = 3.6, 12.4 \) Hz, 1H, C\(_4\)-H), 1.87 (m, 1H, C\(_5\)-H), 2.11 (m, 1H, C\(_5\)-H), 2.24 (m, 1H, C\(_4\)-H), 2.82 (ddd, \( J = 6.2, 11.3, 17.5 \) Hz, 1H, C\(_6\)-H), 2.91 (ddd, \( J = 2.4, 7.0, 17.5 \) Hz, 1H, C\(_6\)-H), 4.52 (br-s, 1H, NH), 4.71 (dt, \( J = 5.1, 11.5 \) Hz, 1H, C\(_3\)a-H), 6.78 (d, \( J = 7.9 \) Hz, 1H, ArH), 6.95 (d, \( J = 7.9 \) Hz, 1H, ArH), 7.20 (t, \( J = 7.9 \) Hz, 1H, ArH); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 21.29 \) (CH\(_2\)), 27.97 (CH\(_2\)), 28.06 (CH\(_2\)), 53.39 (CH), 114.86 (CH), 119.87 (C), 125.04 (CH), 128.97 (CH), 137.51 (C), 151.80 (C); HRMS (EI) calcld for C\(_{10}\)H\(_{16}\)NO\(_3\)S (M\(^+\)) 225.0460, found 225.0461. The enantiomeric excess of 6d was determined to be 14% by HPLC with a Chiralpak IA column (3:1 hexane/i-PrOH, 1.0 mL/min): \( t_R \) (major) = 17.2 min; \( t_R \) (minor) = 19.0 min. The absolute stereochemistry of 6d was not determined.

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REFERENCES AND NOTES


14. The use of ethyl acetate required 20 h for completion of the reaction, giving 6a in 87% yield with 15% ee.

15. While our studies were in progress, Fruit and Müller reported that the intramolecular C–H amidation of 5a using 3.5 mol % of Rh$_2$(S-PTPA)$_4$ [PhI(OAc)$_2$, MgO, CH$_2$Cl$_2$, 40 °C, 3.5 h] provides 6a with 18% ee, see Ref. 8b.


