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Torsional strain inversed chemoselectivity in a Pd-catalyzed atroposelective carbonylation reaction of dibenzothiophenium†

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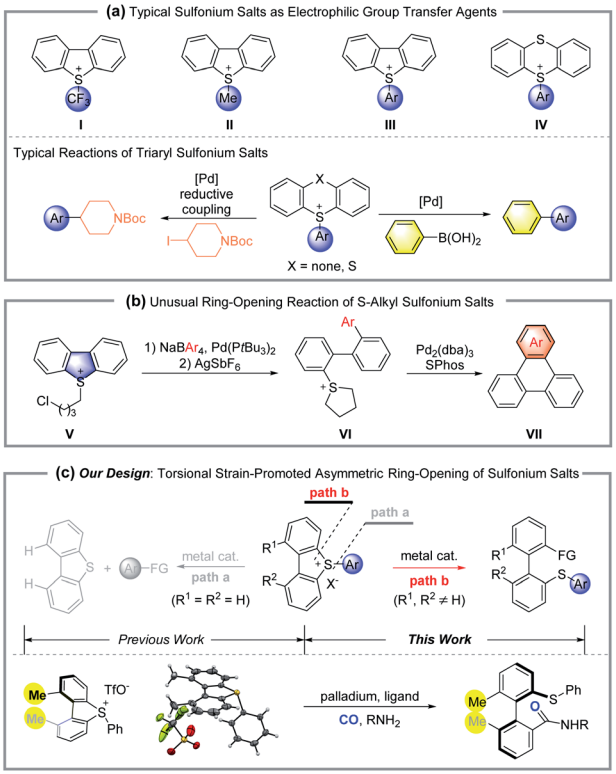
A palladium-catalyzed enantioselective ring-opening/carbonylation of cyclic diarylsulfonium salts is reported. In comparison to thioethers, the sulfonium salts displayed high reactivity and enabled the reaction to be performed under mild conditions (room temperature). The steric repulsion of the two non-hydrogen substituents adjacent to the axis led cyclic diarylsulfonium salts to be distorted, which enabled the ring-opening reaction to proceed with significant preference for breaking the exocyclic C–S bond.

Introduction

Organosulfur compounds are important in synthetic organic chemistry, as they are both widely used as synthetic reagents and exist in many natural products and bioactive drugs. Importantly, dibenzo[*b*,*d*]thiophene and thianthrene derived sulfonium salts (**I**, **II**, **III** and **IV**) are widely used as electrophilic agents in organic synthesis, where the exo group usually works as the transferred functionality (Scheme 1a).[1–4] The Umemoto reagent (**I**) is well-known as a powerful, thermally stable electrophilic trifluoromethylating agent. Sulfonium salts **III** and **IV**, prepared from the activation of sulfoxides, followed by the electrophilic thiolation of arenes, are efficient arylation transfer agents in transition-metal catalyzed cross-coupling, such as the Heck reaction, Sonogashira coupling, carbonylation *etc.* It was generally observed that the cleavage of the exocyclic *S*–aryl bond proceeded with significant preference for the cyclic *S*–aryl bond. In contrast, in 2015, Yorimitsu and co-workers reported a palladium-catalyzed ring-opening reaction of S–alkyl sulfonium salt (**V**), where the cyclic C–S bond was selectively cleaved to give acyclic biaryl compounds (Scheme 1b).[5]

Atropisomers are an important class of compounds, which result from restricted rotation of a single C–C, C–N, C–O bond *etc.*[6] They not only can be found in many bioactive natural products and drugs,[7] but also are the leading skeleton for chiral ligands and catalysts. In view of the importance of axially chiral structures and their unique characters, several strategies have been developed for enantioselective synthesis of these kinds of compounds. Classic methods include asymmetric aryl–aryl cross-coupling,[8] *de novo* asymmetric aryl ring construction,[9] desymmetrization or resolution,[10] and point-to-axial chirality transfer.[11] Bringmann and coworkers realized the asymmetric ring-opening reaction of lactones based on the fast dynamics of



Scheme 1 The selectivity of C–S bond cleavage for cyclic sulfonium salts.

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these biaryl fused lactones.[12] Following that, the corresponding lactams, hemiacetals and *N*,*O*-acetals were successfully applied in atropisomer synthesis *via* ring-opening reactions.[13] Recently, the ring-opening of diaryl fused iodonium salts,[14] 4,5-disubstituted 9*H*-fluoren-9-ols,[15] silafluorenes[16] and dinaphtho[2,1-*b*:1′,2′-*d*]furans[17] showed excellent potential in functionalized axially chiral molecule synthesis.

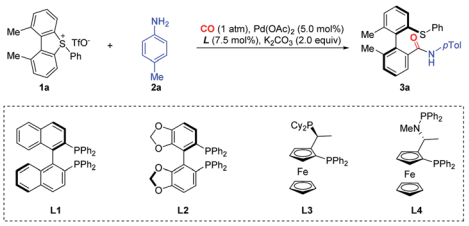
In 2002, Hayashi reported a nickel-catalyzed atropisomer synthesis *via* the ring-opening reaction of dinaphtho[2,1-*b*:1′,2′-*d*]thiophene, which displayed low functional group tolerance by employing aryl Grignard reagents as the coupling partners.[18] Alternatively, we reasoned that the corresponding sulfonium salts would show higher reactivity than dinaphthothiophene. Thus, the coupling partners can be extended to mild agents with excellent functional group tolerance. However, the concomitant challenge of this design is the chemoselectivity for cleavage of different C–S bonds (path a *vs.* path b) (Scheme 1c). Our previous studies indicated that the introduction of *ortho*, *ortho*′-disubstituents into dibenzo compounds would create torsional strain due to steric repulsion.[14a] Furthermore, the torsional strain would promote the subsequent ring-opening/bond breaking reactions. Herein, we report a palladium-catalyzed asymmetric ring-opening reaction of cyclic sulfonium salts for the synthesis of axially chiral biaryl thioethers, where the torsional strain of cyclic sulfonium not only promotes the C–S bond breaking, but also increases the chemoselectivity between different C–S bonds.

Results and discussion

Optimization

In the initial trials, we investigated a palladium-catalyzed ring-opening/carbonylation reaction by choosing 1,9-dimethyl-5-phenyl-5*H*-dibenzo[*b*,*d*]thiophen-5-ium triflate (**1a**) as the model substrate, whose distorted structure was confirmed by crystallographic analysis. In the atmosphere of CO (1 atm), the reaction catalyzed by $Pd(OAc)_2$/(*R*)-BINAP (**L1**) gave moderate yield of ring-opening product **3a** with 55% ee (Table 1, entry 1). In our survey of various chiral phosphine or related ligands, (S_a,*R*)-BoPhoz (**L4**) gave the best selectivity (entries 2–4). In terms of the solvent effect, THF displayed the same efficacy as 1,4-dioxane while using DMSO led to very low productivity (entries 5 and 6). Aromatic hydrocarbon solvents, *i.e.* toluene or *p*-cymene (*p*CM), led to a notable selectivity enhancement, which reached 73% ee and 84% ee, respectively (entries 7 and 8). Using a degassed and dried solvent does not provide a better ee value (entry 9). The reaction proceeded as efficiently at room temperature as at 60 °C (entry 10), however, further decreasing the temperature to 0 °C almost completely halted the reaction (entry 11). Further optimization of the solvent system indicated a beneficial effect of certain amounts of THF (*p*-cymene/THF), which improved both the yield and stereoselectivity and about 1% amount of THF showed the best result for stereoselectivity (entry 12–14). The base K_3PO_4 had a slightly better performance than K_2CO_3 (entry 15). Pd_2dba_3 gave a high yield and excellent enantioselectivity with a prolonged reaction time (entry 16).

Table 1 Reaction condition optimization[a]



Entry	Ligand	Solvent	*T*/°C	Yield/%	ee/%
1	**L1**	Dioxane	60	44	55
2	**L2**	Dioxane	60	42	50
3	**L3**	Dioxane	60	21	52
4	**L4**	Dioxane	60	55	60
5	**L4**	THF	60	48	60
6	**L4**	DMSO	60	NR	—
7	**L4**	Toluene	60	34	73
8	**L4**	*p*CM	60	48	84
9	**L4**	*p*CM[e]	60	61	78
10	**L4**	*p*CM	25	53	82
11[b]	**L4**	*p*CM	0	Trace	—
12	**L4**	*p*CM/THF (1 : 1)	25	77	83
13	**L4**	*p*CM/THF (4 : 1)	25	76	85
14	**L4**	*p*CM/THF (100 : 1)	25	73	88
15[c]	**L4**	*p*CM/THF (100 : 1)	25	80	89
16[c,d]	**L4**	*p*CM/THF (100 : 1)	25	92	90

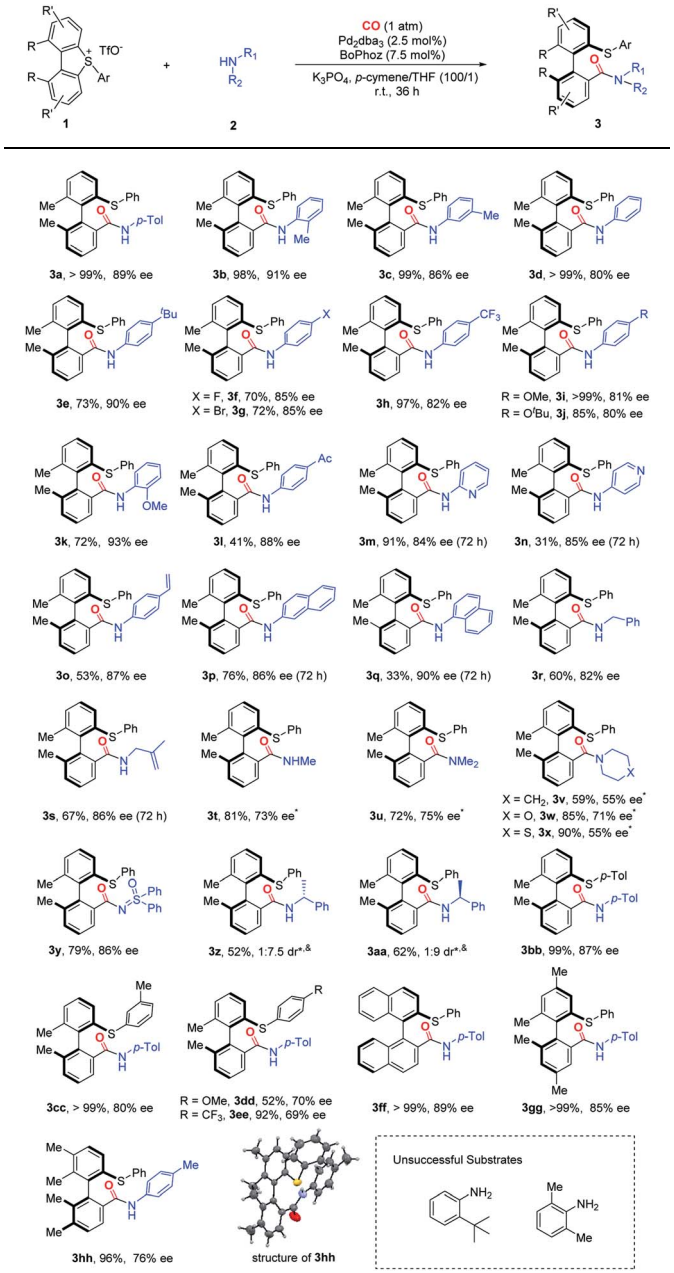
[a] Conditions: **1a** (43.9 mg, 0.10 mmol, 1.0 equiv.), **2a** (21.4 mg, 0.20 mmol, 2.0 equiv.), CO (1 atm), $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol, 5.0 mol%), ligand (0.0075 mmol, 7.5 mol%), K_2CO_3 (27.6 mg, 0.20 mmol, 2.0 equiv.) in 1 mL of solvent for 24 h. [b] Reaction time is 3 days. [c] K_3PO_4 (1.0 equiv.) was used. [d] $Pd_2(dba)_3$ (2.5 mol%) was used. [e] The solvent was degassed and dried by 4 Å MS.

Substrate scope

With the optimal conditions in hand, we started investigating the substrate scope of this asymmetric carbonylation reaction (Table 2). Substituted aromatic amines were tested, whose reactivities significantly depend on the nature of the substituents. Aniline derivatives bearing *para*, *meta* and *ortho* alkyl groups, as well as β-, or α-naphthalenamine, displayed good reactivity and selectivity, except the very bulky 2-*tert*-butyl aniline or 2,6-dimethyl aniline (**3a–3e**, **3p** and **3q**). Although it is a palladium(0)-catalyzed reaction, aryl–Br bonds and terminal alkene groups in the aniline substrates are tolerable, and the reaction provided comparable yields of the products (**3g** and **3o**). Both electron-donating (**3i**, **3j**) and electron-withdrawing (**3h**) groups at the *para* position of aniline slightly reduced stereoselectivity, while *o*-toluidine produced high enantioselectivity (**3k**). 2- and 4-Pyridinamines were equally effective substrates, although the latter gave the corresponding product in a dropped yield (31%) (**3m** and **3n**).

This method is also amendable to apply to substrates with the amino group attached to sp^3-hybridized carbon. Both benzylamine and 2-methylallylamine reacted smoothly with cyclic diarylsulfonium salts and the products were formed with good stereoselectivity (**3r** and **3s**). Aliphatic amines showed relatively

Table 2 Substrate scope[a]



[a] *60 °C for 24 h; [&]optically pure amine was used.

lower reactivity, which was possibly attributed to the potential saturated coordination of the metal center with aliphatic amines. Therefore, the corresponding reactions with aliphatic amines should be conducted at a higher temperature (60 °C) (**3t–3x**). Either primary or secondary (both acyclic and cyclic) amines gave decreased enantioselectivity. In addition, sulfoximine can take part in this reaction, and resulted in a similar yield and ee value in comparison with aromatic amines (**3y**). Pre-installed chiral elements at amines had a marginal effect on the stereoselectivity: both the reactions with (*R*)- and (*S*)-1-phenylethan-1-amine gave a pair of diastereomers with the dr values being 1 : 7.5 and 9 : 1, respectively (**3z** and **3aa**).

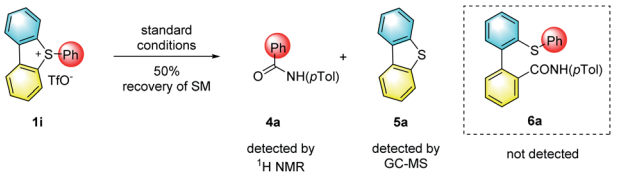
We further studied the substituent effect of cyclic diarylsulfonium salts. Both electron-donating and electron-withdrawing substituents on the acyclic phenyl ring caused a decrease of the ee values (**3bb–3ee**). Replacement of the biphenyl skeleton with the binaphthyl structure produced a similar yield and enantioselectivity (**3ff**). Introducing *p*,*p*′-dimethyl groups to the biphenyl structure (**3gg**) did not have a significant effect on the results, while the corresponding *m*,*m*′-dimethyl substituted sulfonium salt gave a reduced ee value (76%) (**3hh**). Notably, a single crystal structure of **3hh** was obtained by slow evaporation of a mixed solvent (DCM/Et_3N = 1 : 3), which finally determined the absolute configuration of the axial chirality to be *R*.

In support of the role of torsional strain, we investigated the ring-opening reaction with sulfonium salt **1i**, which bears two hydrogen atoms at the two adjacent positions of the biaryl axis (Scheme 2). Notably, the reaction became sluggish under standard conditions, and 50% of starting material **1i** was recovered even with a prolonged reaction time (5 days). The loss of torsional strain results in no yield of the ring-opening product. The formation of *N*-(*p*-tolyl)benzamide **4a** and dibenzothiophene **5a** were confirmed by crude ^{1}H NMR or GC-mass spectroscopy. These results indicated that 1,9-disubstituents on the sulfonium salt, which create the torsional strain, are crucial for both reactivity and selectivity for this ring-opening reaction.

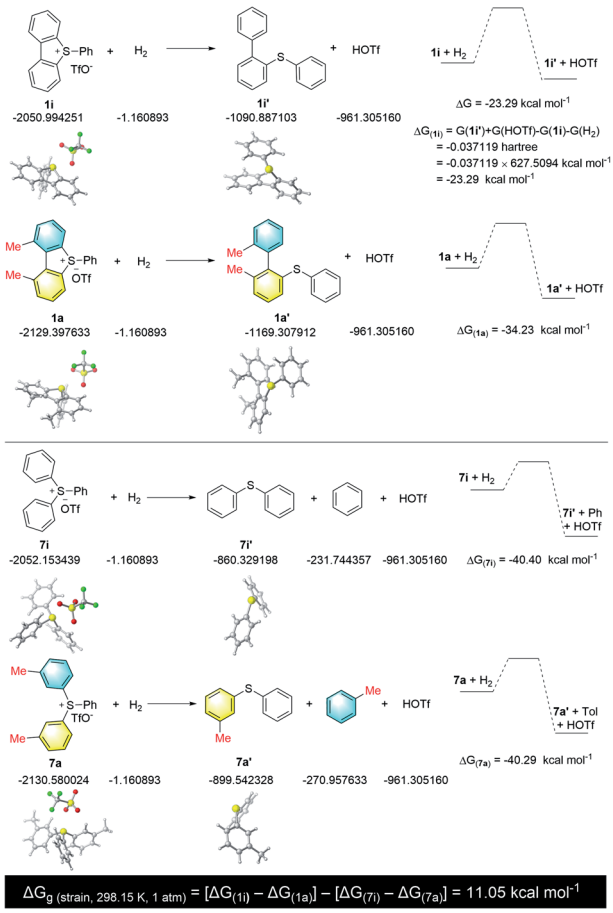
To further support our hypothesis that the torsional strain enhances the reactivity and selectivity, we calculated the torsional strain of **1a** at the B3LYP level of theory.[19] By following the calculation methods of ring strain for cyclic hydrocarbons,[20] we determined the torsional strain of **1a** by calculating the hydrogenation free energy difference between compound **1a** and **1i** by breaking one C–S bond. In order to avoid the discrepancy caused by the two methyl groups, we further calculated the hydrogenation free energy difference between compound **7a** and **7i** (Scheme 3). Thus, the torsional strain of **1a** is estimated to be $\{\Delta G_{(strain)} = [\Delta G_{(1i)} - \Delta G_{(1a)}] - [\Delta G_{(7i)} - \Delta G_{(7a)}]\} = 11.05$ kcal mol^{-1}.

Mechanistic studies

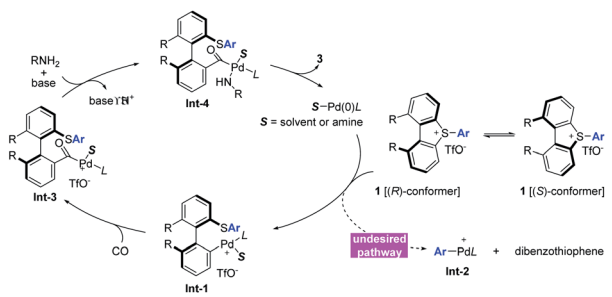
Following the above studies and previous reports,[4,5] a tentative catalytic cycle with canonical organometallic steps is proposed (Scheme 4). The (*R*)-conformer and (*S*)-conformer of sulfonium salt **1** have a fast equilibrium at ambient temperature, and the oxidative addition of Pd(0)/(S_a,*R*)-BoPhoz and (*R*)-conformer is preferred over that of the (*S*)-conformer, which gave the



Scheme 2 Reaction of sulfonium salt **1i**.



Scheme 3 Calculation of torsional strain.



Scheme 4 Plausible mechanism.

palladium intermediate **Int-1** with *R* axial chirality of the biaryl skeleton. Alternatively, the oxidative addition of Pd(0) with the exocyclic C–S bond would give **Int-2** and is concomitant with the formation of dibenzothiophene. This undesired pathway became unfavourable due to torsional strain caused by the steric repulsion. Acylpalladium **Int-3** would be formed upon the interaction of **Int-1** and CO *via* a migration/insertion process. Subsequently, the amine coordination, followed by deprotonation and reductive elimination, produced amide **3** and therefore regenerated the Pd(0) catalyst.

Conclusions

We reported a palladium-catalyzed enantioselective ring-opening/carbonylation reaction of cyclic diarylsulfonium salts to form thioether-containing axially chiral biaryls. The success of this reaction benefited from the torsional strain created by steric repulsion, which enabled the high chemoselectivity of bond breaking between the exocyclic C–S bond and the cyclic one.

Data availability

All experimental and characterization data, as well as DFT calculation data are available in the ESI.† Crystallographic data for compounds **1a** and (*R*)-**3hh** have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under accession numbers CCDC 2129903 and 2129904.

Author contributions

Q. Z. initiated this work. Q. Z. and B. H. performed the experiments. X. X. performed the DFT calculations. Q. Z. and Z. G. designed the project and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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