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Asymmetric reductive arylation and alkenylation to access S-chirogenic sulfinamides

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Xiaowu Fang[1,5], Longlong Xi[1,5], Minyan Wang[1] ✉, Jieshuai Xiao[1], Yue Zhao[1], Michael C. Willis[2] ✉ & Zhuangzhi Shi[1,3,4] ✉

The study of the stereochemistry of organic sulfur compounds has been ongoing for over a century, with S-chirogenic pharmacophores playing an essential role in drug discovery within bioscience and medicinal chemistry. Traditionally, the synthesis of sulfinamides featuring stereogenic sulfur(IV) centers involves a complex, multistep process that often depends on chiral auxiliaries or kinetic resolution. Here, we introduce an effective and versatile method for synthesizing diverse classes of S-chirogenic sulfinamides through selective aryl and alkenyl addition to sulfinylamines. This process is catalysed by a chiral nickel or cobalt complex under reductive conditions, and eliminating the need for preformed organometallic reagents. The method facilitates the incorporation of a diverse array of aryl and alkenyl halides at the sulfur position, enabling their integration into various biologically significant sulfur pharmacophores. Our detailed mechanistic investigations and density functional theory calculations provide insights into the reaction pathway, particularly highlighting the enantiocontrol mode during addition process.

Enantiomerically enriched molecules with chiral sulfur centers, particularly in the oxidation states IV and VI, are pivotal across multiple fields such as catalysis, ligand design, materials science, agrochemistry, and pharmaceutical research[1–8]. Sulfinamides with S-chirogenic centers exemplify a unique balance between stability and chemical reactivity, making them essential for applications ranging from chiral auxiliaries[9,10] to ligands in metal catalysis[11] and as efficient organocatalysts[12]. Moreover, these compounds also function as valuable precursors for the stereoselective synthesis of a variety of S-chirogenic pharmacophores, including sulfinimidate esters, sulfinamides, sulfonimidoyl halides, and sulfoximines (Fig. 1a)[13–15]. These compounds have also been utilized as bifunctional chiral reagents through desulfinylation processes[16,17]. Conventional methods for producing these compounds typically involve complex, multistep procedures, often relying on chiral auxiliaries or kinetic resolutions[18,19]. Therefore, the development of a general and one-step approach to synthesize sulfinamides would represent a significant advancement, greatly enhancing the efficiency and simplicity of preparing chiral sulfur-containing molecules.

There has been a surge in the development of asymmetric nucleophilic substitution reactions involving sulfur(IV) nucleophiles using organocatalysts, aimed at synthesizing S-chirogenic sulfinyl compounds (Fig. 1b). The research conducted by the Tan group marks a significant advancement in this domain, as they have successfully synthesized enantioenriched arylsulfinate esters through an asymmetric condensation of sulfinates with alcohols, employing a chiral pentanidium catalyst[20]. An asymmetric deoxygenation of sulfones was further developed to form chiral sulfinate esters by utilizing a catalyst that interacts with arylsulfonyl nitriles with alcohol through hydrogen bonding[21]. However, neither of these approaches is effective for the

[1]State Key Laboratory of Coordination Chemistry, Chemistry and Biomedicine Innovation Center (ChemBIC), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, China. [2]Department of Chemistry, University of Oxford, Oxford, UK. [3]School of Chemistry and Materials Science, Nanjing Normal University, Nanjing, China. [4]School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan, China. [5]These authors contributed equally: Xiaowu Fang, Longlong Xi. ✉e-mail: wangmy@nju.edu.cn; michael.willis@chem.ox.ac.uk; shiz@nju.edu.cn

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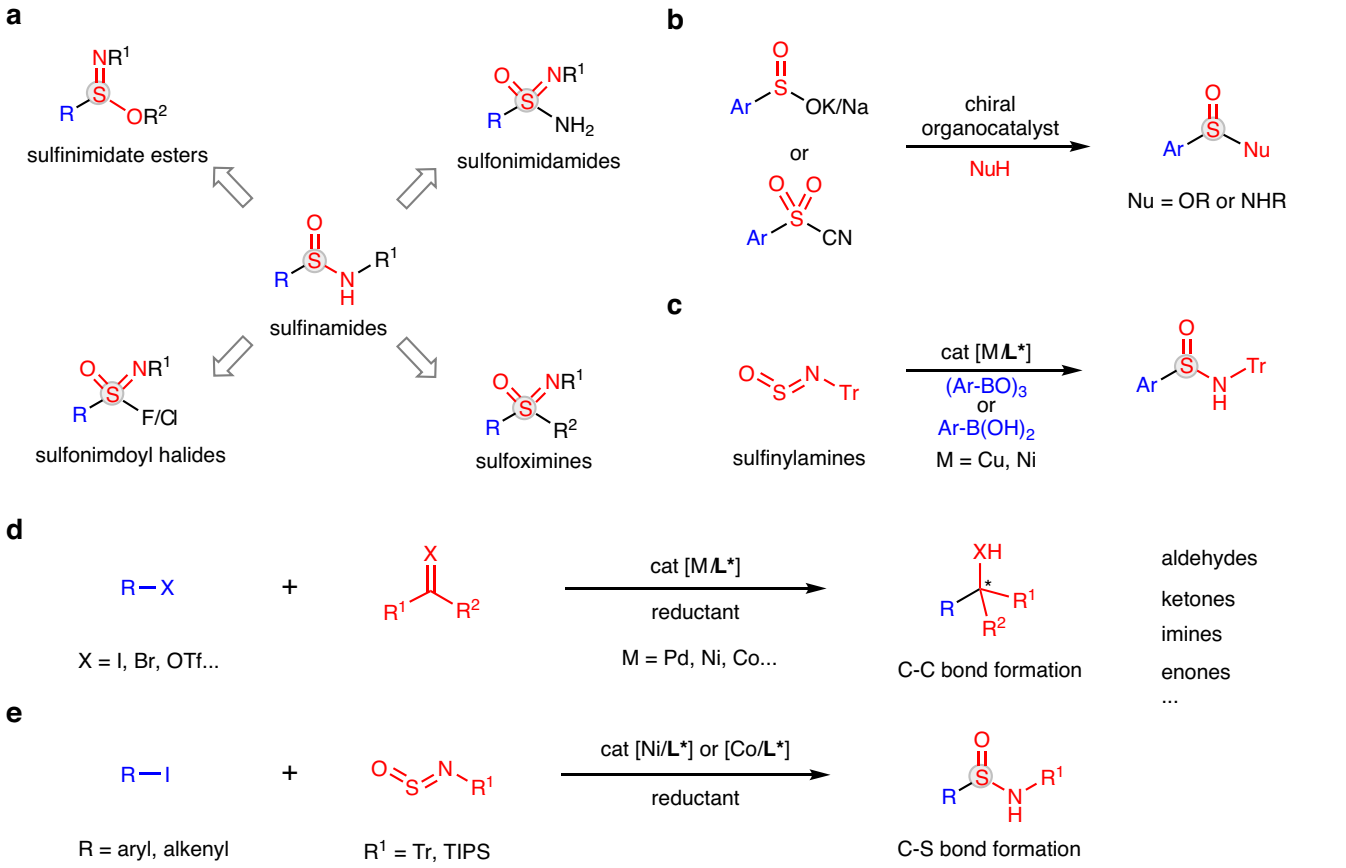

Fig. 1 | Background and new strategy to access S-chirogenic sulfinamides. **a** Reaction diversity of S-chirogenic sulfinamides. **b** Asymmetric synthesis of chiral sulfinyl compounds by organocatalysts. **c** Metal-catalysed synthesis of S-chirogenic sulfinamides using arylboron compounds. **d** Reported results on asymmetric reductive addition for constructing chiral C – C bonds. **e** Asymmetric reductive addition of aryl and alkenyl halides to sulfinylamines to form C – S bonds.

direct synthesis of sulfinamides. These challenges were later overcome, and chiral sulfinamides were synthesized through the nucleophilic substitution of arylsulfinates with amines, facilitated by bifunctional chiral 4-arylpyridine N-oxide catalysts[22]. Enantioenriched sulfinate esters and sulfinamides were also prepared via quinine-catalyzed reactions of activated sulfinates with alcohol and amine nucleophiles[23]. However, the limited commercial availability of S-containing substrates necessitates the de novo synthesis of the relevant substrates. Moving forward, there is a clear need for methods to prepare S-chirogenic sulfinamides that exploit commercially available reagents and substrates.

Sulfinylamines (R-NSO) have been pivotal as synthons in the synthesis of sulfinamides, which are typically generated through the nucleophilic addition of organometallic compounds such as Grignard and lithium reagents[24,25]. Building on this reactivity, the development of S-chirogenic sulfinamides using transition metal catalysts has become feasible (Fig. 1c)[26]. Recently, Zhang and Yang reported a copper-catalyzed asymmetric synthesis of sulfinamides via the addition of aryl boroxines to sulfinylamines[27]. In parallel, our group has discovered an asymmetric nickel-catalyzed arylation of sulfinylamines using more readily available arylboronic acids[28]. While many arylboron reagents are commercially available, specialized reagents like boroxines or arylboronic acids with complex frameworks still require pre-preparation. Moreover, alkenyl organometallic compounds are less readily available, thus rendering the synthesis of chiral alkenylsulfinamides particularly challenging and underexplored. Given that organohalides are frequently employed as precursors to the corresponding organometallic reagents, there is a pressing need to develop more efficient methodologies that permit the direct utilization of these abundant and structurally diverse feedstocks, thereby obviating the requirement for preformed organometallic reagents.

The Nozaki-Hiyama-Kishi (NHK) reaction is a classic example of reductive addition, typically used to produce allylic alcohols through the reaction of an aldehyde with an alkenyl halide in the presence of a terminal chromium reductant and a nickel catalyst[29,30]. Recent advancements in catalytic addition to aldehydes[31–34], ketones[35], imines[36–39], enones[40] with carbon electrophiles have significantly expanded the scope of this chemistry, enabling the formation of chiral C – C bonds under reductive conditions (Fig. 1d). Inspired by these developments, we hypothesized whether the direct addition of organohalides to sulfinylamines could lead to the formation of S-chirogenic centers[41].

Here, we introduce an enantioselective nickel-catalyzed process that facilitates the addition of aryl halides to sulfinylamines, leading to the formation of S-chirogenic sulfinamides (Fig. 1e). Additionally, this reductive process can be extended to cobalt catalysis, which allows for asymmetric additions of vinyl halides to sulfinylamines, leading to the formation of chiral alkenylsulfinamides. By employing metal catalysts in conjunction with chiral bisoxazoline ligands and a metal reductant, sulfinylamines substituted with N-trityl (Tr) or N-TIPS groups undergo aryl and vinyl addition, demonstrating remarkable enantioselectivity.

Results

Preliminary studies and optimization

The feasibility of the enantioselective addition was explored by examining the reaction of reagent **I** with iodoarene **1a** in the presence of a nickel catalyst (Fig. 2a). The optimum conditions for the reaction were achieved using 15 mol% $Ni(cod)_2$ as a catalyst and 18 mol% dibenzofuran-

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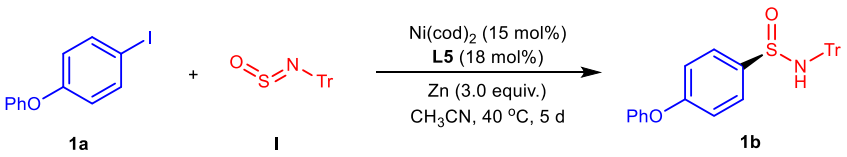
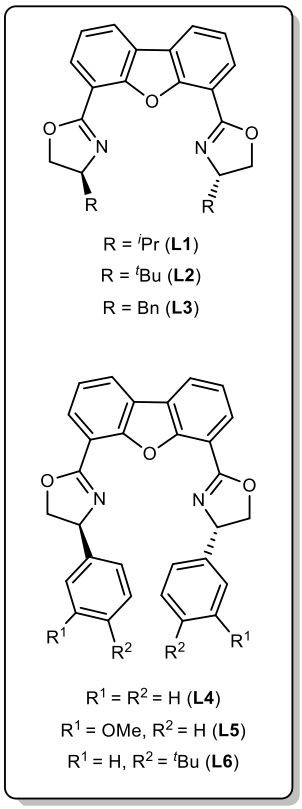
a



Entry	Deviation	Yield of **1b** (%)	E.r. of **1b** (%)
1	none	87	96/4
2	using **L1** as ligand	47	81/19
3	using **L2** as ligand	12	52/48
4	using **L3** as ligand	45	68/32
5	using **L4** as ligand	92	95/5
6	using **L6** as ligand	71	87/13
7	using $Ni(dme)Br_2$ as catalyst	85	74.5/25.5
8	using $Co(dme)Br_2$ as catalyst	trace	-
9	using $Ni(cod)_2$ (10 mol%) and **L5** (12 mol%)	30	95.5/4.5
10	at 60 °C	74	92.5/7.5
11	using Mn as reductant	46	87/13
12	without Zn	trace	-
13	using undehydrated CH_3CN	80	90.5/9.5
14	using 1-bromo-4-phenoxybenzene (**1a'**)	64	89/11
15	using 1-chloro-4-phenoxybenzene (**1a''**)	trace	-



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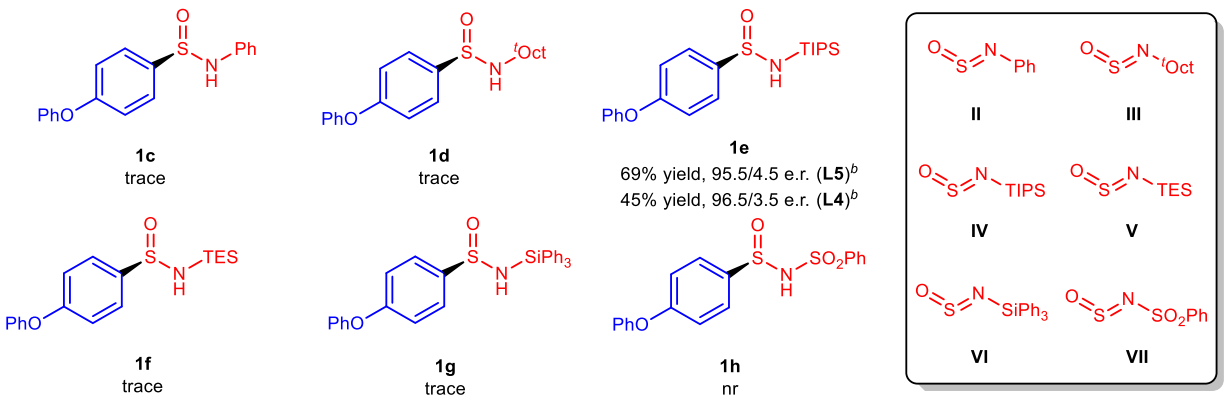

Fig. 2 | Reaction discovery and optimization. a Analysis of reaction parameters in the reaction of sulfinylamine **I** and iodoarene **1a**. **b** Evaluation of diverse sulfinylamines. [a]Reaction conditions: [Ni] (15 mol%), **L*** (18 mol%), **1a** (3.0 equiv., 0.3 mmol), sulfinylamine **I** (1.0 equiv., 0.1 mmol), Zn dust (3.0 equiv., 0.3 mmol) in CH_3CN (superdry, water ≤ 10 ppm) at 40 °C for 5 days under N_2 atmosphere. The yields mentioned are isolated yields. E.r. values were determined via chiral HPLC [b]React for 3 days with **1a** (1.0 equiv., 0.1 mmol) and **IV** (3.0 equiv., 0.3 mmol).

4,6-bis(oxazoline) ligand **L5** bearing two 3-methoxyphenyl substituents in a dry CH_3CN solvent, with a reaction time of 5 days at 40 °C (entry 1). Under these carefully selected conditions, the desired product **1b** was formed and isolated with a yield of 87%, and displaying 96/4 enantiomeric ratio (e.r.). When substituting the aryl group in the ligand with ^{i}Pr (**L1**), ^{t}Bu (**L2**) and Bn (**L3**), the formation of product **1b** was significantly compromised (entries 2-4). The use of phenyl-substituted ligand **L4** resulted in slightly lower enantioselectivity but still furnished compound **1b** with a yield of 92% (entry 5). Using a more sterically bulky ligand **L6**, which contains two *tert*-butylphenyl groups led to a much lower outcome in both yield and enantioselectivity (entry 6). When a divalent nickel species such as $Ni(dme)Br_2$ was employed as the catalyst, product **1b** was obtained with a yield of 85%, but with only modest enantioselectivity (entry 7). Using other earth-abundant metals, such as $Co(dme)Br_2$, only yielded trace amounts of the desired product **1b** (entry 8). Interestingly, reducing the catalyst loading from 15 to 10 mol% had a profound effect on the reaction's efficacy, resulting in a disappointing yield of 30%, while maintaining impeccable enantioselectivity (entry 9). Adjusting the reaction temperature to 60 °C under the established conditions led to a substantially poorer outcome (entry 10). The use of zinc powder as a reducing agent is essential for the reaction, as other reductants, such as manganese powder, resulted in much lower conversion (entry 11), and no conversion was observed in the absence of the reductant (entry 12). When using ordinary CH_3CN that has not been

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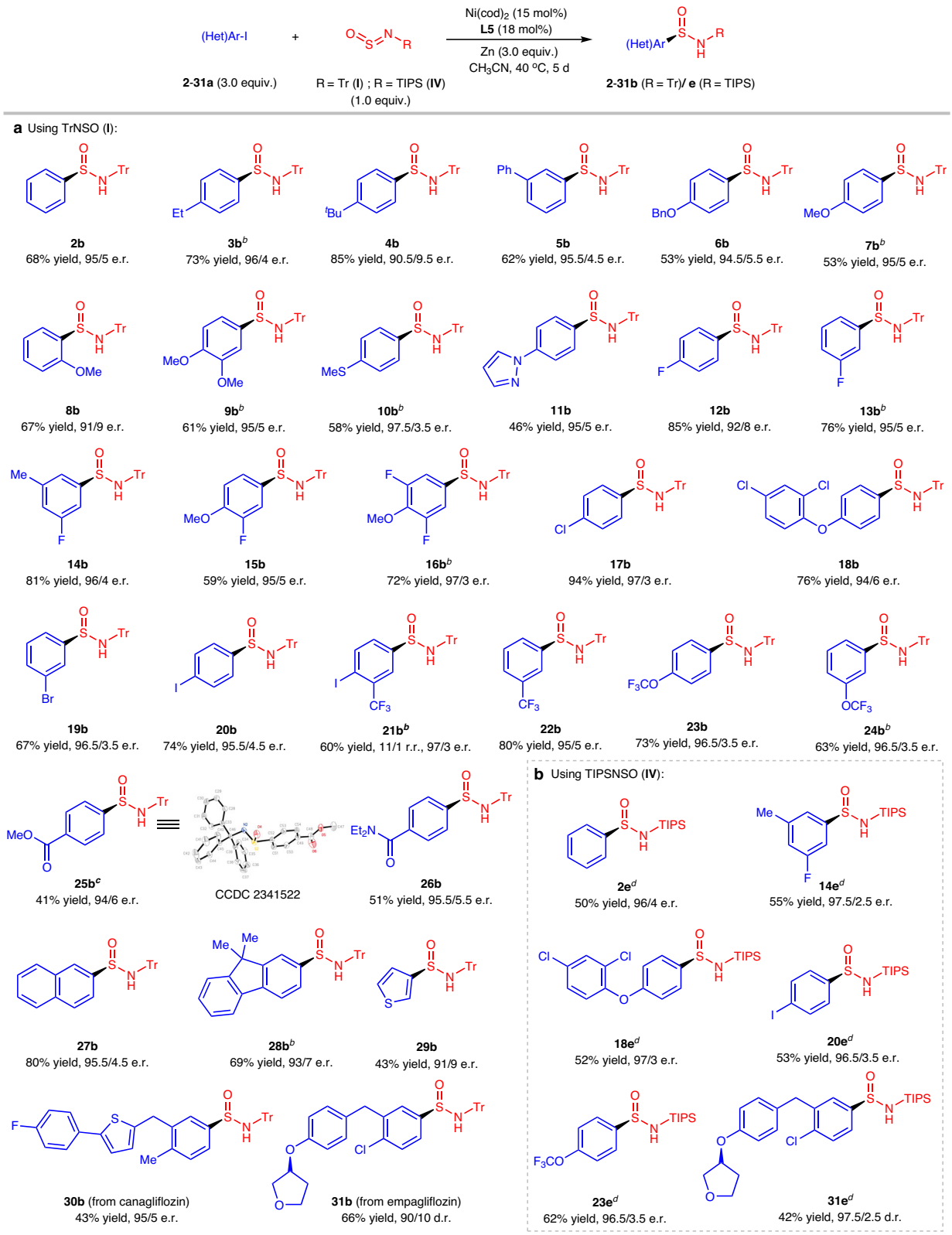

Fig. 3 | Substrate scope. a Scope of iodoarenes with sulfinylamine **I**. **b** Selected examples of iodoarenes with sulfinylamine **IV**. [a]Reaction conditions: $Ni(cod)_2$ (15 mol%), **L5** (18 mol%), **2-31a** (3.0 equiv., 0.3 mmol), **I** (1.0 equiv., 0.1 mmol), Zn dust (3.0 equiv., 0.3 mmol) in CH_3CN (superdry, water ≤10 ppm, 0.1 M) at 40 °C for 5 days under N_2 atmosphere; Isolated yields; E.r. values determined by chiral HPLC. [b]Using **L4** instead of **L5**. [c]React for 5 days at 10 °C. [d]Shortened to 3 days with **2-31a** (1.0 equiv., 0.1 mmol) and **IV** (3.0 equiv., 0.3 mmol).

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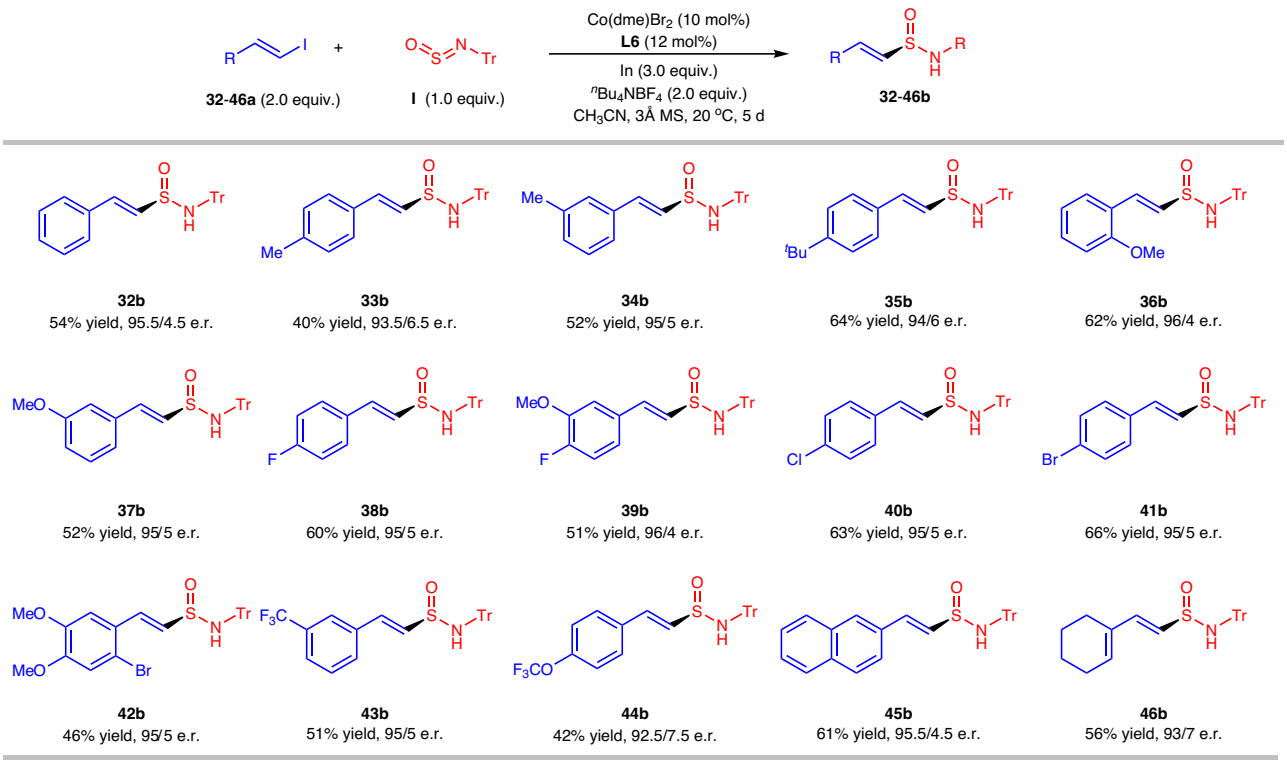

Fig. 4 | Substrate scope. Reaction conditions: $Co(dme)Br_2$ (10 mol%), **L6** (12 mol%), **32-46a** (2.0 equiv, 0.2 mmol), **I** (1.0 equiv., 0.1 mmol), In dust (3.0 equiv., 0.3 mmol), $^nBu_4NBF_4$ (2.0 equiv., 0.2 mmol) and 3 Å MS (50 mg) in CH_3CN (superdry, water ≤10 ppm, 0.5 M) at 20 °C for 5 days under N_2 atmosphere; Isolated yields; E.r. values determined by chiral HPLC.

dehydrated, the reaction yields are significantly reduced, and the ee is also greatly affected (entry 13). Additionally, substituting bromoarene **1a'** with substrate **1a** in the system led to a 64% yield of **1b** with an e.r. of 89/11 (entry 14). Furthermore, using chloroarene **1a''** as the substrate produced only trace amounts of the desired product **1b** (entry 15). With the optimized conditions in hand, we proceeded to investigate the effect of different S-substituents in sulfinylamine (Fig. 2b). Substrates bearing phenyl (**II**)[42] and *tert*-octyl (**III**) groups exhibited only minimal formation of the desired products **1c** and **1 d** under the current reaction conditions. Encouragingly, when the sulfinylamine **IV** contained a TIPS group, the corresponding product **1e** was obtained in good yield with high enantioselectivities using ligands **L4** or **L5**. However, other silyl substitutes, such as TES (**V**) and $SiPh_3$ (**VI**), displayed sluggish reactivity. Finally, the reaction of $PhSO_2$–NSO (**VII**)[43] did not yield any aryl addition product.

We initially explored the versatility of the reaction by assessing the range of aromatic iodides combined with sulfinylamine **I** (Fig. 3a). Ligand **L4** was also employed in some cases, exhibiting better enantioselectivity compared to ligand **L5**. Iodobenzene (**2a**) and its analogues, incorporating alkyl and aryl groups such as ethyl (**3a**), *tert*-butyl (**4a**), and phenyl (**5a**), yielded the corresponding products **2-5b** in yields ranging from 62% to 85%, with good enantioselectivities. Furthermore, iodoarenes carrying electron-donating groups, such as benzyloxy (**6a**), methoxy (**7-9a**), methylthio (**10a**), and pyrazol (**11a**), at para, meta and ortho position exhibited excellent compatibility. Notably, the presence of one or more halogen groups including F (**12-16a**), Cl (**17-18a**), and Br (**19a**) did not influence the reaction. Of particular interest is the utilization of 1,4-diiodobenzene (**20a**), where one C–I bond could be retained under the reaction conditions, resulting in the formation of the corresponding product **20b** with a yield of 74% and an e.r. of 95.5/4.5. Meanwhile, non-symmetric 1,4-diiodobenzene (**21a**) exhibited surprising regioselectivity and can obtain product **21b** with a r.r. of 11/1 and an e.r. of 97/3. Aryl iodides with electron-withdrawing substituents, such as trifluoromethyl (**22a**) and trifluoromethoxy (**23-24a**), delivered products **22-24b** in good yields and enantioselectivities. It is worth noting that carbonyl compounds, such as ester (**25a**) and amide (**26a**), which products **25-26b** with delightful yields and enantioselectivitys. Among them, the absolute configuration of product **25b** was determined to be *R* via X-ray crystallography. Expanding on this strategy, polycyclic arenes such as 2-iodonaphthalene (**27a**) and 2-iodo-9,9-dimethyl-9H-fluorene (**28a**) could be employed with satisfactory enantioselectivities. Heteroaryl iodides, such as thiophene **29a**, readily underwent conversion into the corresponding product **29b** with moderate outcomes. Unfortunately, other heteroaryl iodides, such as 4-iodopyridine, and 8-iodoquinoline, were not compatible and the corresponding products cannot be obtained (not shown in the Fig. 3). In addition, substrates derived from canagliflozin (**30a**) and empagliflozin (**31a**) proved to be compatible with this transformation. Building upon the success of asymmetric reductive addition, we further investigated the utilization of sulfinylamine **IV** bearing the TIPS group in these catalytic systems. As depicted in Fig. 3b, selected iodoarenes provided sulfinamides **2e, 14e, 18e, 20e, 23e** and **31e** with commendable enantioselectivities.

Based on the above results, we further explored the use of alkenyl halides as substrates in our strategy for constructing S-chirogenic alkenylsulfinamides. Unfortunately, when aromatic iodides were replaced with alkenyl iodide **32a**, the reaction with sulfinylamine **I** under the initial conditions produced only trace amounts of the desired product. Through systematic screening (see Supplementary information for details), we identified an optimized reaction protocol using $Co(dme)Br_2$ as the catalyst, ligand **L6**, indium dust as the reductant, and $^nBu_4NBF_4$ and 3 Å molecular sieves (MS) as additives in CH_3CN solvent at 20 °C for 5 days (Fig. 4). Under these conditions, we isolated product **32b** with a yield of 54% and an e.r. of 95.5/4.5. We then investigated the reactivity of sulfinylamine **I** with various alkenyl

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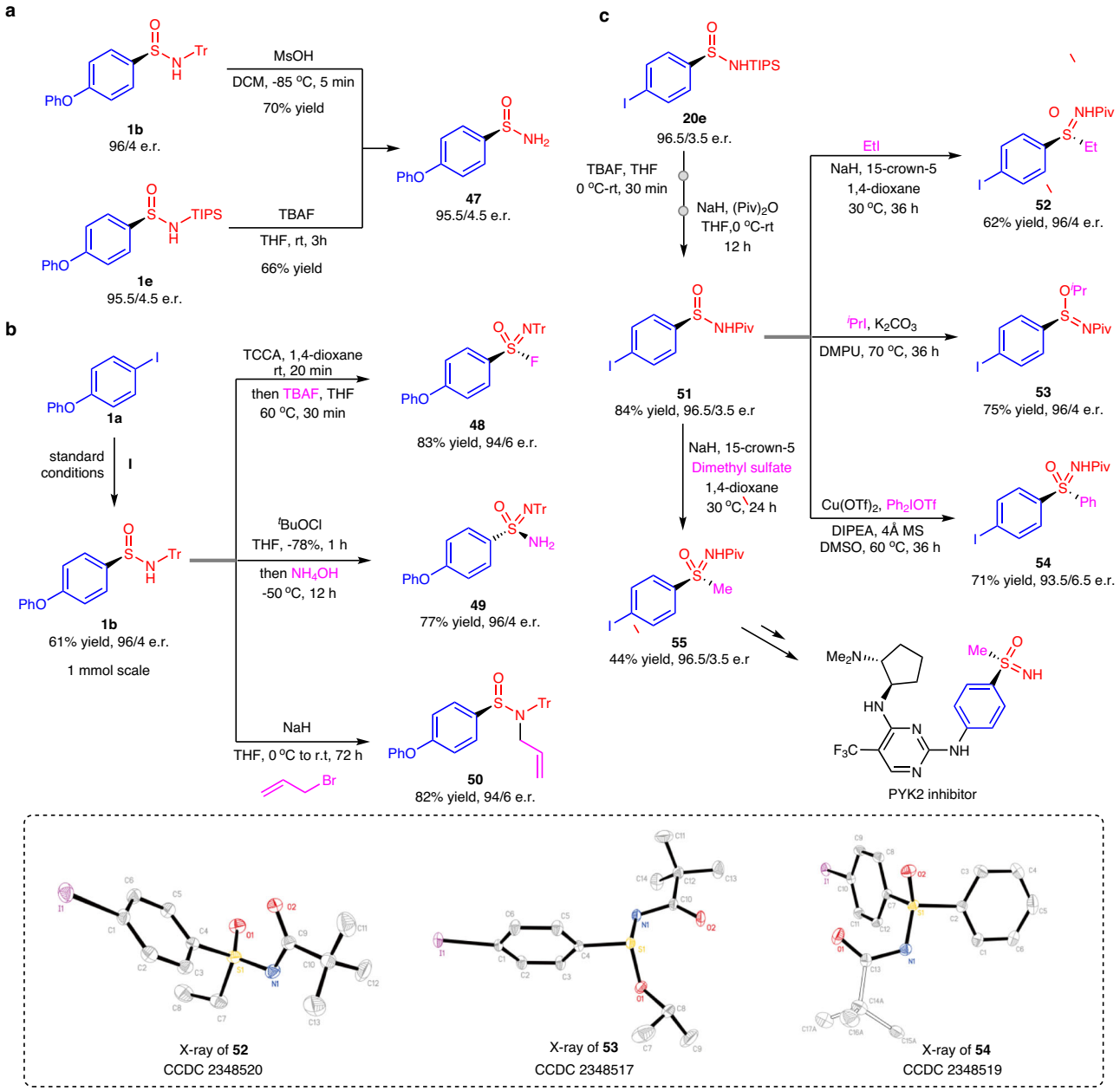

Fig. 5 | Synthetic applications. a Deprotection of compounds 1b and 1e. **b** Scale-up synthesis and follow-up transformations of chiral product 1b. **c** Subsequent transformations of chiral product 20e.

iodides. Substrates featuring the styrenyl motif with methyl (**33a, 34a**) and *tert*-butyl (**35a**) groups were successfully incorporated into the reaction, generating products **33b**-**35b** with satisfactory yields and enantioselectivities. Styrenyl iodides containing methoxy groups (**36a, 37a**) were also compatible, yielding the desired products **36b** and **37b** with good enantioselectivities. Halide-containing substrates, including those with fluorine (**38a, 39a**), chlorine (**40a**), and bromine (**41a, 42a**), reacted smoothly with sulfinylamine **I**. Furthermore, substrates bearing electron-withdrawing groups, such as trifluoromethyl (**43a**) and trifluoromethoxy (**44a**), were equally compatible. The reaction of 2-vinylnaphthalene **45a** under the current conditions resulted in satisfactory enantioselectivity. Additionally, a diene-substituted sulfinamide **46b** was prepared in modest yield from alkenyl iodide **46a** under the optimized reaction conditions. However, simple alkenyl iodides, such as iodoethene and 1-iodocyclohex-1-ene, produced only trace amounts of the desired products under the current reaction conditions (not shown in the Fig. 4).

To further demonstrate the synthetic utility of this approach, a series of experiments were then conducted (Fig. 5). Both type of products can undergo deprotection effectively (Fig. 5a). For example, anhydrous MsOH effectively served as a deprotecting agent, converting N-Tr sulfinamide **1b** into primary sulfinamide **47** with a 70% yield while maintaining enantioselectivity. N-TIPS Sulfinamide **1e** can also be deprotected to yield product **47** using TBAF under milder reaction conditions. Utilizing iodoarene **1a** and sulfinylamine **I** as substrates, a 1.0 mmol-scale synthesis was performed smoothly under standard conditions, yielding product **1b** with a 61% yield and retaining enantioselectivity (Fig. 5b). Sulfonimidoyl fluorides are valuable intermediates in chemical synthesis due to their potential for conversion into other significant compound classes through sulfur(VI) fluoride exchange (SuFEx) reactions[44–46]. The treatment of **1b** with TBAF resulted in the formation of a sulfonimidoyl fluoride **48**, containing a chiral sulfur(VI) center, achieved in a satisfactory yield, with only a slight decrease in enantioselectivity. Traditionally, sulfonimidamides

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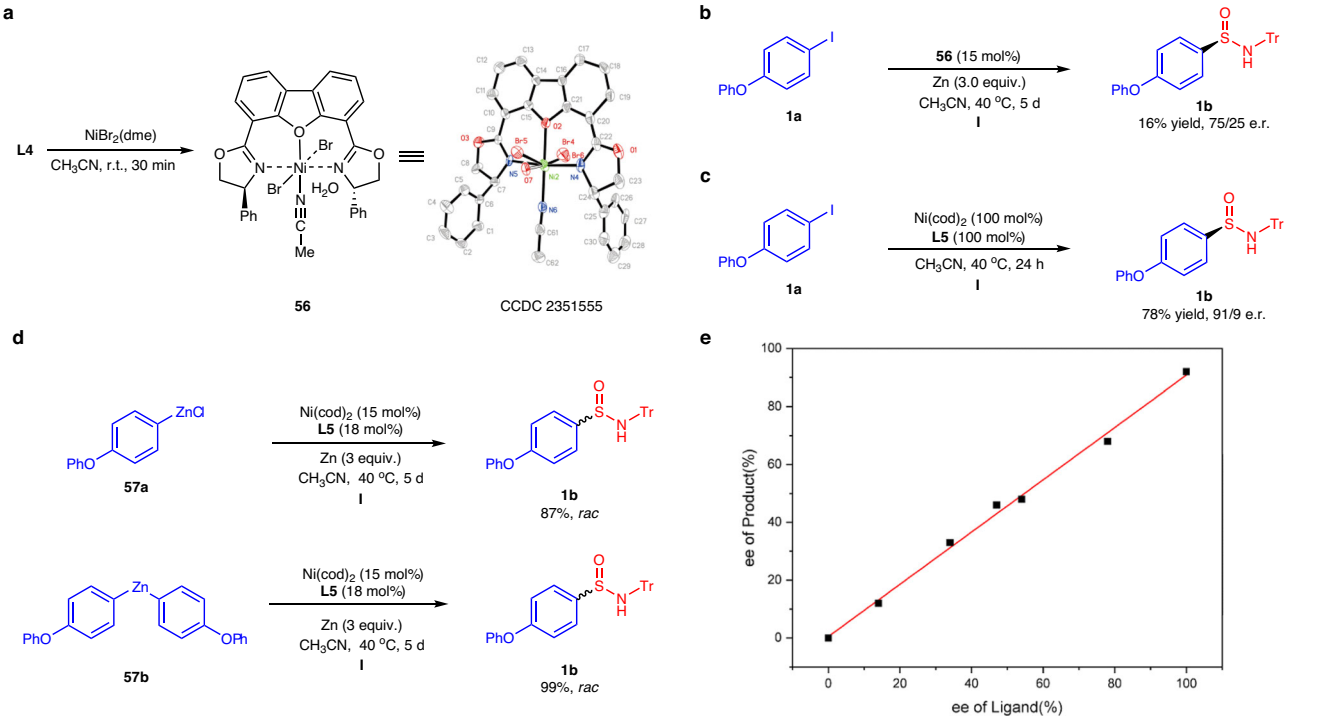

Fig. 6 | Mechanistic experiments. a Synthesis of nickel complex 56. **b** Testing the catalytic reactivity of complex 56. **c** Evaluation of the reaction with stoichiometric amounts of nickel and ligand. **d** Reaction of sulfinylamine I with zinc reagents 57a-b. **e** Nonlinear effect experiments involving ligand L4, sulfinylamine I and 1a.

are synthesized by reacting amines with sulfonimidoyl chlorides, which are obtained from the electrophilic chlorination of sulfinamides[47]. Building on our initial findings, treating compound sulfinamide **1b** with *tert*-butyl hypochlorite led to a complete conversion to sulfonimidoyl chloride, which was then reacted with ammonium hydroxide to efficiently produce sulfonimidamide **49** with high enantioselectivity. Furthermore, compound **1b** was efficiently transformed into tertiary sulfinamide **50** through a substitution reaction with allyl bromide. Enantioenriched sulfinamides are extremely versatile intermediates in organic synthesis, capable of being converted into other important compound families (Fig. 5c). Deprotection of **20e** with TBAF, followed by reaction with pivalic anhydride, yielded sulfinamide **51** with an 84% yield and 96.5/3.5 e.r. Treatment of **51** with EtI using NaH resulted in the synthesis of chiral sulfoximine **52** through a stereospecific S-alkylation[48]. A stereospecific, oxygen-selective alkylation of **51** using isopropyl iodide, K_2CO_3, and DMPU formed chiral sulfimide **53** with a 75% yield and an e.r. of 96/4. In the presence of a copper catalyst, the asymmetric synthesis of chiral sulfoximine **54** with an aryl group was successful using diphenyliodonium salt as a coupling partner. To gain a more comprehensive understanding of the product structures, X-ray crystallographic analysis was performed on products **52-54**, unequivocally confirming their absolute configurations. Finally, sulfinamide **51** was smoothly converted to the *S*-methylated product **55**, a key precursor for the synthesis of proline-rich tyrosine kinase 2 (PYK2) inhibitor C, potentially offering a new anabolic treatment for osteoporosis[49].

Discussion

Mechanistic investigation

To deepen our understanding of the reaction pathway, we conducted several mechanistic studies (Fig. 6). When equimolar amounts of ligand **L4** were mixed with $NiBr_2$(dme), the formation of a bivalent nickel complex **56** was confirmed *via* X-ray analysis (Fig. 6a). Nevertheless, further testing showed that compound **56** was an ineffective catalyst, delivering the product **1b** with only a 16% yield and a 75/25 e.r. (Fig. 6b). This result suggests that the reduction of Ni(II) to Ni(I) to initiate the reaction is not the main pathway of the reaction. In contrast, reacting stoichiometric amounts of $Ni(cod)_2$ with ligand **L5** yielded the product **1b** with a 78% yield and a 91/9 e.r., aligning with the outcomes observed in catalytic systems (Fig. 6c). These results highlight the critical role of the oxidative addition of Ni(0) species to iodoarenes, which form Ni(II) entities that subsequently undergo insertion into sulfinylamine. Moreover, arylzinc reagents **57a** and **57b** exhibited high reactivity in the nucleophilic addition to sulfinylamine **I**, yet both yielded the racemic product **1b** (Fig. 6d). It rules out the in situ formation of arylzinc species, confirming zinc's role as a reductant in the system. Lastly, the absence of nonlinear effects observed in the reaction between substrates **I** and **1a** indicate that the active catalytic species is a monomeric nickel complex associated with a single ligand **L4** (Fig. 6e).

Based on the results described above, density functional theory (DFT) was utilized to investigate the detailed mechanism and the origin of enantioselectivity in the model reaction between aromatic iodide **1a** and sulfinylamine **I** (Fig. 7). The chiral Ni(0) catalyst **INT1A** initially coordinates with **1a**, followed by oxidative addition of the C–I bond through transition state **TS3A** to form the nickel(II) intermediate **INT3A**, with an activation free energy of 7.5 kcal·mol^{-1}. Subsequently, this intermediate **INT3A** undergoes ligand exchange with reagent **I** to generate the cationic nickel intermediate **INT4A**. The migration insertion of the S = N bond of reagent **I** is crucial for determining enantioselectivity. Computational results indicate that the formation of the *R* configuration via transition state **TS5A**-*R* in the migration insertion process is kinetically favored, exhibiting significantly lower energy compared to the pathway through transition state **TS5A**-*S* (9.4 kcal·mol^{-1} vs 11.2 kcal·mol^{-1} relative to intermediate **INT4A**), consistent with our experimental observation. To gain deeper insights into the stereoselectivity, the non-covalent interactions of **TS5A**-*R* and **TS5A**-*S* have been systematically analyzed using the NCI (Non-Covalent Interaction) approach[50]. Structural analysis reveals the stereochemical preferences in transition state **TS5A**-*R*, where a significant S –O···H interaction is observed between the chiral skeleton of the ligand and the oxygen atom of the sulfinylamine. This interaction plays

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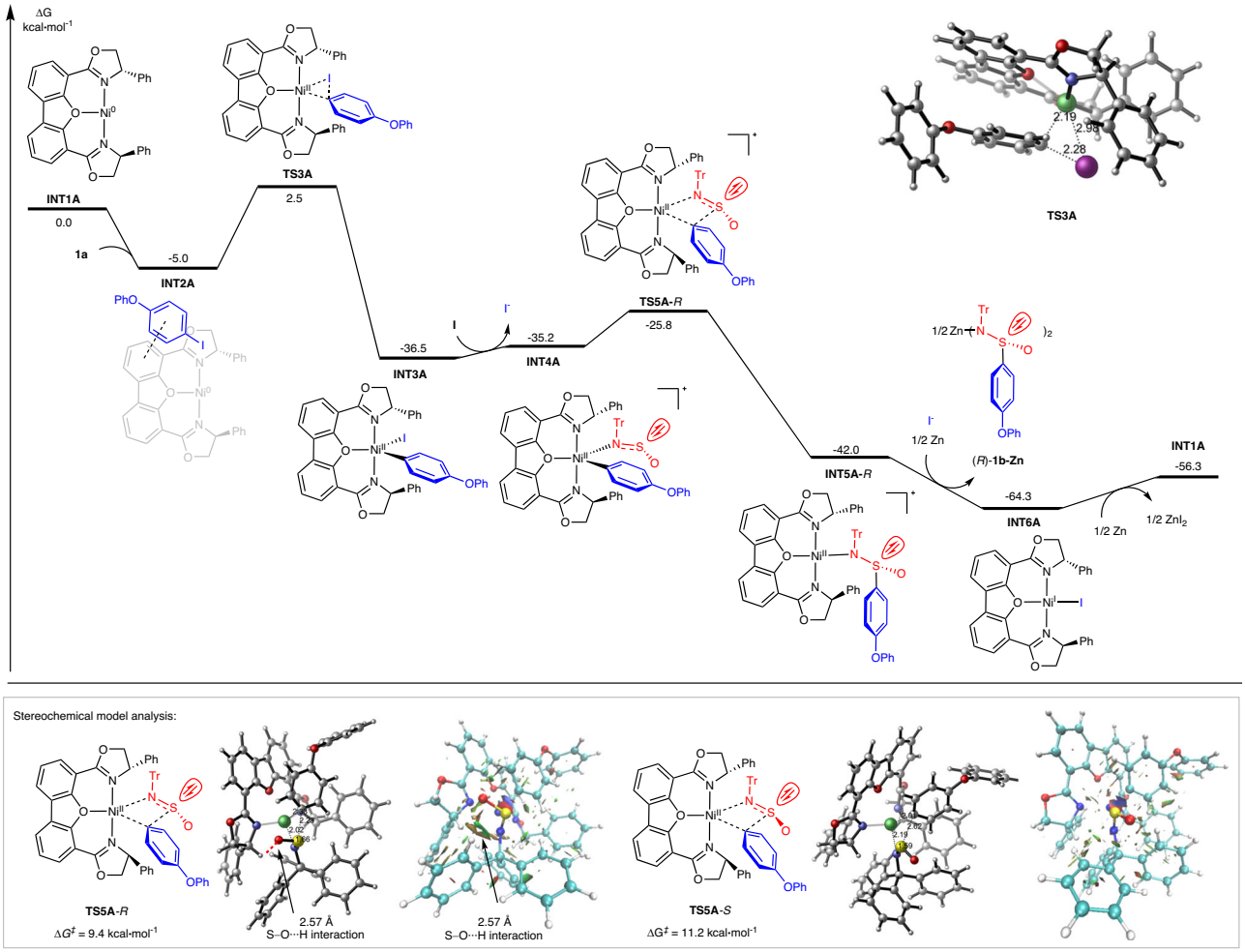

Fig. 7 | Proposed mechanism. DFT-computed reaction pathways for the reaction of aromatic iodide **1a** with sulfinylamine **I** (M06-D3/6-311 + G(d,p)-SDD(Ni, Zn, and I), SMD(MeCN)//B3LYP-D3/6-31 G(d,p)-SDD(Ni, Zn, and I)).

a crucial role in stabilizing the preferred transition state, thereby influencing the observed stereoselectivity. Subsequently, an excess amount of reducing agent facilitates the reduction of nickel(II) species **INT5A**-*R* to generate the zinc salt (*R*)-**1b-Zn**. This zinc salt undergoes protonolysis during the workup process to yield the final product (*R*)-**1b**[51,52]. In the presence of a substantial reducing agent, **INT6A** reduces to regenerate Ni(0) species, thereby completing the catalytic cycle[53].

In summary, we have devised an efficient and selective process for reductive addition of aryl and alkenyl halides into sulfinylamines, generating chiral sulfinamides featuring S(IV) stereocenters, with the aid of a chiral nickel and cobalt catalysts. The resultant compounds facilitate the synthesis of assorted S-stereogenic derivatives through stereoselective manipulations. Insight into the reaction mechanism that delivers the selective aryl addition processes was gleaned through an integrated analysis of experimental and computational evidence. Given the burgeoning interest in chiral S-stereogenic derivatives for their potential applications in the pharmaceutical and agrochemical sectors, we anticipate a broad implementation of the methodologies delineated in this investigation.

Methods

General procedure for synthesizing S-chirogenic arylsulfinamides

In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $Ni(cod)_2$ (15 mol%), **L4** or **L5** (18 mol%) and CH_3CN (1 mL, superdry, water ≤ 10 ppm). The resulting solution was stirred for 30 min at room temperature. Then iodoarene **1-31a** (0.3 mmol, 3.0 equiv.), sulfinylamine **I** (0.1 mmol, 1.0 equiv.) and Zn powder (0.3 mmol, 3.0 equiv) were added. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 40 °C for 5 days. Afterwards, the mixture was cooled to room temperature. Then, the work-up was performed by filtering through a short plug of silica gel, eluting with ethyl acetate (ca. 10 mL). The solvent was evaporated under reduced pressure. Purification via flash column chromatography afforded the desired products **1-31b**.

Data availability

Crystallographic data for the structures of **25b**, **52**, **53**, **54** and **56** reported in this paper have been deposited at the Cambridge Crystallographic Data Center under deposition numbers CCDC 2341522, 2348520, 2348517, 2348519 and 2351555. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/getstructures. All other data supporting the findings of the study, including experimental procedures and compound characterization, are available within the article and its Supplementary Information, or from the corresponding author upon request.

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Author contributions

X.F., L.X., J.X. performed the experiments and analysed the data. M.W. performed the DFT calculation. Y. Z performed the crystallographic studies. M.C.W., Z.S. conceived and designed the study and wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Minyan Wang, Michael C. Willis or Zhuangzhi Shi.

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