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Synthesis of chiral *spiro*-indenes via Pd-catalyzed asymmetric (4 + 2) dipolar cyclization

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Abstract

Chiral indene skeletons are widely found in biologically active natural products and pharmaceutical molecules, making indene synthesis an ongoing research hotspot in organic synthetic chemistry. However, the construction of chiral *spiro*-indenes bearing all-carbon quaternary stereocenters via catalytic asymmetric synthesis remains challenging due to their inherent rigidity and hindrance. Herein, we present a solution to this unmet challenge through palladium-catalyzed asymmetric (4 + 2) dipolar cyclization by trapping π-allyl-Pd 1,4-dipoles with indene-involved ketenes generated *in situ* from 1-diazonaphthalene-2(1*H*)-ones via visible light-induced Wolff rearrangement. This protocol features mild reaction conditions, wide substrate scope, and high enantio- and diastereoselectivities [31 examples, up to 86% yield, 97% enantiomer excess (ee) and 19:1 diastereoisomer ratio (dr)].

Keywords: Asymmetric cyclization, indene, ketene, palladium catalysis

INTRODUCTION

Indenes bearing chiral quaternary stereocenters with unique carbocyclic structures serve as the key structural unit for many biologically active natural products and pharmaceutical agents[1-5]. As shown in Figure 1A, Dalesconol A and B display immunosuppressive activities comparable to the clinically used Cyclosporine A[6-8]. Cyanosporaside A and B from the marine actinomycete genus *Salinispora* show significant antimicrobial activity[9,10], and Dichroanal B is reported to have anti-inflammatory and anti-tumor activities[11]. In addition, indenes with unique three-dimensional structures and rigid skeletons are widely used as novel pharmacophores, e.g., in Chemokine[5]. Accordingly, many efforts have been devoted to constructing this important scaffold, which could be divided into two synthetic strategies. One is the construction of a chiral indene ring using aromatic compounds as substrates, including intramolecular cyclization[12-15] and intermolecular alkyne insertion[16-22] [Figure 1B]. Several elegant examples have been reported for accessing chiral indenes bearing quaternary stereocenters via this method through transition-metal-catalyzed domino reaction[23-29]. The other strategy involves direct enantioselective functionalization of the indene ring, such as benzofulvenes[30-32] and other indene derivatives[33,34]. However, generating chiral *spiro*-indenes bearing all-carbon quaternary stereocenters remains challenging, and only a few examples have been reported[23,24,29-33]. Some of them even suffer from the harsh reaction conditions, low efficiency and structural limitation of the substrate, which could be attributed to the rigid ring and steric hindrance of the indene skeleton, making chiral indene synthesis difficult. Furthermore, it is difficult to control the *spiro*-quaternary stereocenters.

Palladium-catalyzed dipolar cyclizations have proven to be one of the most unique and powerful strategies for synthesizing various heterocycles in a highly stereoselective manner. Since 2017, we have launched a program on developing asymmetric dipolar cyclizations for efficient construction of structurally diverse heterocycles by combining transition metal catalysis and photo-Wolff rearrangements[35]. Starting from readily available linear α-diazoketones, 5-10 membered oxa- and aza-heterocyclic products bearing chiral quaternary stereocenters have been constructed[36]. Following these successes, it is hypothesized that 1-diazonaphthalene-2(1*H*)-ones[37-39] could be used as efficient cyclic ketene precursors under visible light irradiation, which would subsequently trap π-allyl-Pd 1,4-dipoles to form the chiral *spiro*-indenes bearing all-carbon quaternary stereocenters [Figure 1C]. Although feasible in principle, challenges remain due to the rigidity and hindrance of the *spiro*-indene skeleton, which is difficult in the enantioselective formation of all-carbon quaternary stereocenters.

EXPERIMENTAL

Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Pd_2(dba)_3 \cdot CHCl_3$ (0.005 mmol, 5 mol%, "dba": dibenzylideneacetone), **L8** (0.02 mmol, 20 mol%) and anhydrous dichloromethane (DCM) (1.0 mL), and the resulting solution was stirred for 30 min at room temperature (rt). Then, vinylbenzoxazinanone **1a** (0.1 mmol, 1.0 equiv.), 1-diazonaphthalen-2(1*H*)-one **2a** (0.2 mmol, 2.0 equiv.) and anhydrous DCM (1.0 mL) were added to the reaction mixture. After that, the reaction solution was stirred under the irradiation of 6 W blue light-emitting diodes (LEDs) for 24 h at rt. The combined solution was concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate = 20/1 to 15/1) to afford the desired product **3aa**.

RESULTS AND DISCUSSION

First, we determined the ultraviolet-visible (UV-vis) absorption spectra of 1-diazonaphthalen-2(1*H*)-ones with different electronic substituents (see Supplementary Figure 1 for details). Optically, this kind of cyclic α-diazoketone shows absorption around 450 nm. We then tested the feasibility of the above idea using vinylbenzoxazinanone **1a** and 1-diazonaphthalen-2(1*H*)-ones **2a** as model substrates under 6 W blue LEDs.

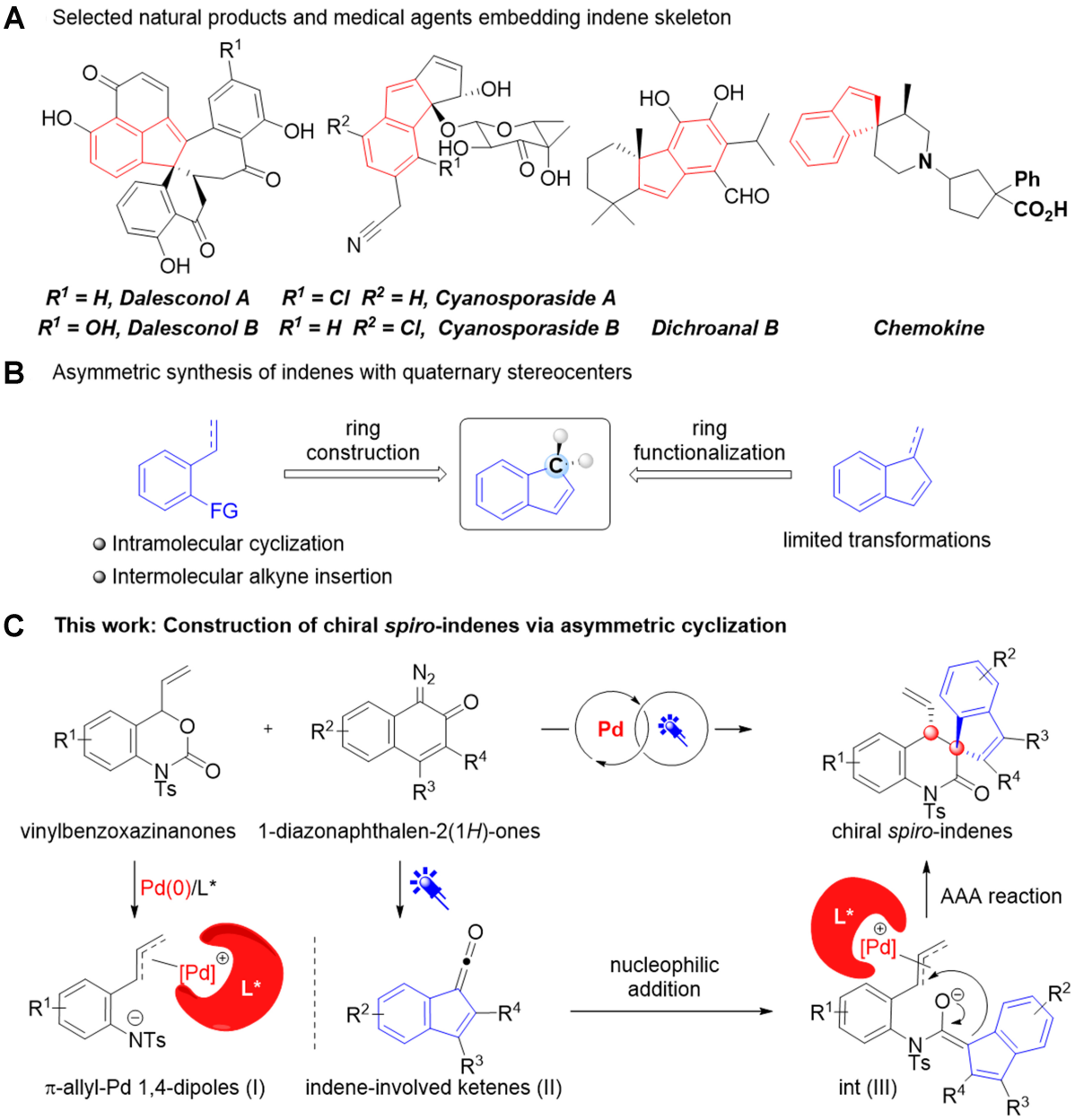
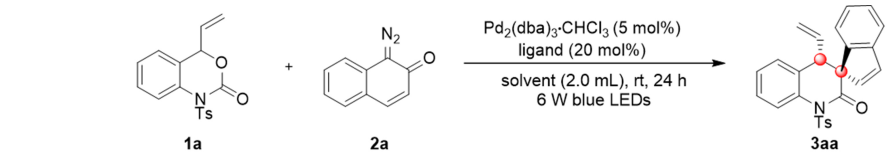
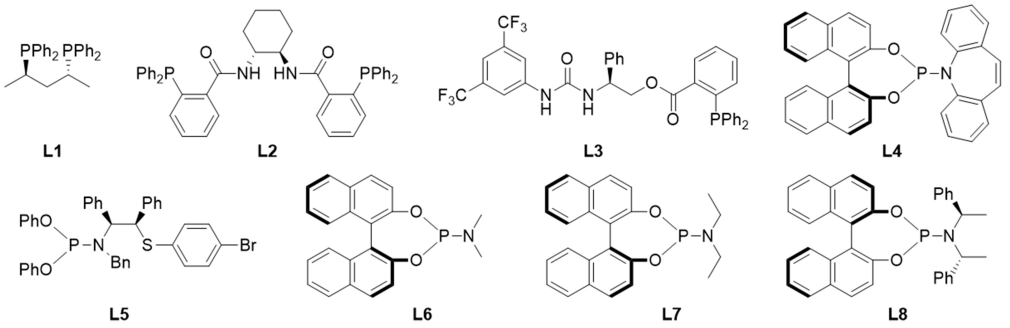


Figure 1. Significance and synthesis of chiral indenes. AAA: Asymmetric allylic alkylation.

As shown in Figure 2, using $Pd_2(dba)_3{\cdot}CHCl_3$ as a precatalyst, the chiral diphosphine ligand **L1**, Trost's ligand **L2**[40], Zi's chiral ligand **L3**[41] and Carreira's ligand **L4**[42], which are widely used in Pd-catalyzed dipolar cyclizations, failed to give the desired product. Our chiral P,S ligand **L5**[35] was found to promote the reaction with good enantioselectivity but in low yield [22% yield, 90% enantiomer excess (ee) and 3:1 diastereoisomer ratio (dr)]. Subsequently, we turned our attention to chiral phosphoramidite ligands[43] by extensively exploring different substituents on the N atom (**L6**-**L8**). It is noted that chiral ligands **L6** and **L7**, which have two identical substituent groups, e.g., Me, Et on the N atom, gave the desired products with the improved results and dr values and the comparable enantioselectivity (**L6**: 46% yield, -93% ee and 5:1 dr; **L7**: 72% yield, -84% ee and 10:1 dr). When using Feringa's ligand **L8**, a satisfactory result with a higher yield and similar enantio- and diastereoselectivities was observed (84% yield, 94% ee and 14:1 dr). Furthermore, a





Entry	L	solvent	light source	Yield (%)[a]	dr[b]	ee (%)[c]
1[d]	**L1**	DCM	456 nm	ND	-	-
2[d]	**L2**	DCM	456 nm	ND	-	-
3[d]	**L3**	DCM	456 nm	ND	-	-
4[d]	**L4**	DCM	456 nm	ND	-	-
5[d]	**L5**	DCM	456 nm	22	3:1	90
6	**L6**	DCM	456 nm	46	5:1	-93
7	**L7**	DCM	456 nm	72	10:1	-84
8	**L8**	DCM	456 nm	84 (84)[e]	14:1	94
9	**L8**	DMF	456 nm	ND	-	-
10	**L8**	$CHCl_3$	456 nm	41	8:1	93
11	**L8**	Toluene	456 nm	35	9:1	93
12	**L8**	Acetone	456 nm	38	10:1	94
13	**L8**	EtOAc	456 nm	51	11:1	91
14	**L8**	Et_2O	456 nm	44	9:1	90
15	**L8**	THF	456 nm	21	6:1	92
16	**L8**	DCM	390 nm	57	11:1	92
17	**L8**	DCM	370 nm	52	10:1	91
18	**L8**	DCM	-	ND	-	-

Figure 2. Condition optimization. Conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd_2(dba)_3·CHCl_3$ (5 mol%) and chiral ligand (20 mol%) in 2.0 mL anhydrous DCM at rt under the irradiation of 6 W blue LEDs for 24 h. [a]Determined by analyzing the ^{1}H NMR of reaction mixture with 1,3,5-trimethoxybenzene as an internal standard. [b]Determined by chiral HPLC analysis of the purified products. [c]Determined by ^{1}H NMR analysis of the reaction mixture. [d]Ligand (10 mol%) was used instead. [e]Isolated yield. dba: Dibenzylideneacetone; rt: room temperature; LEDs: light-emitting diodes; dr: diastereoisomer ratio; ee: enantiomer excess; DCM: dichloromethane; ND: not detected; DMF: N,N-dimethylformamide; THF: tetrahydrofuran; NMR: nuclear magnetic resonance; HPLC: high performance liquid chromatography.

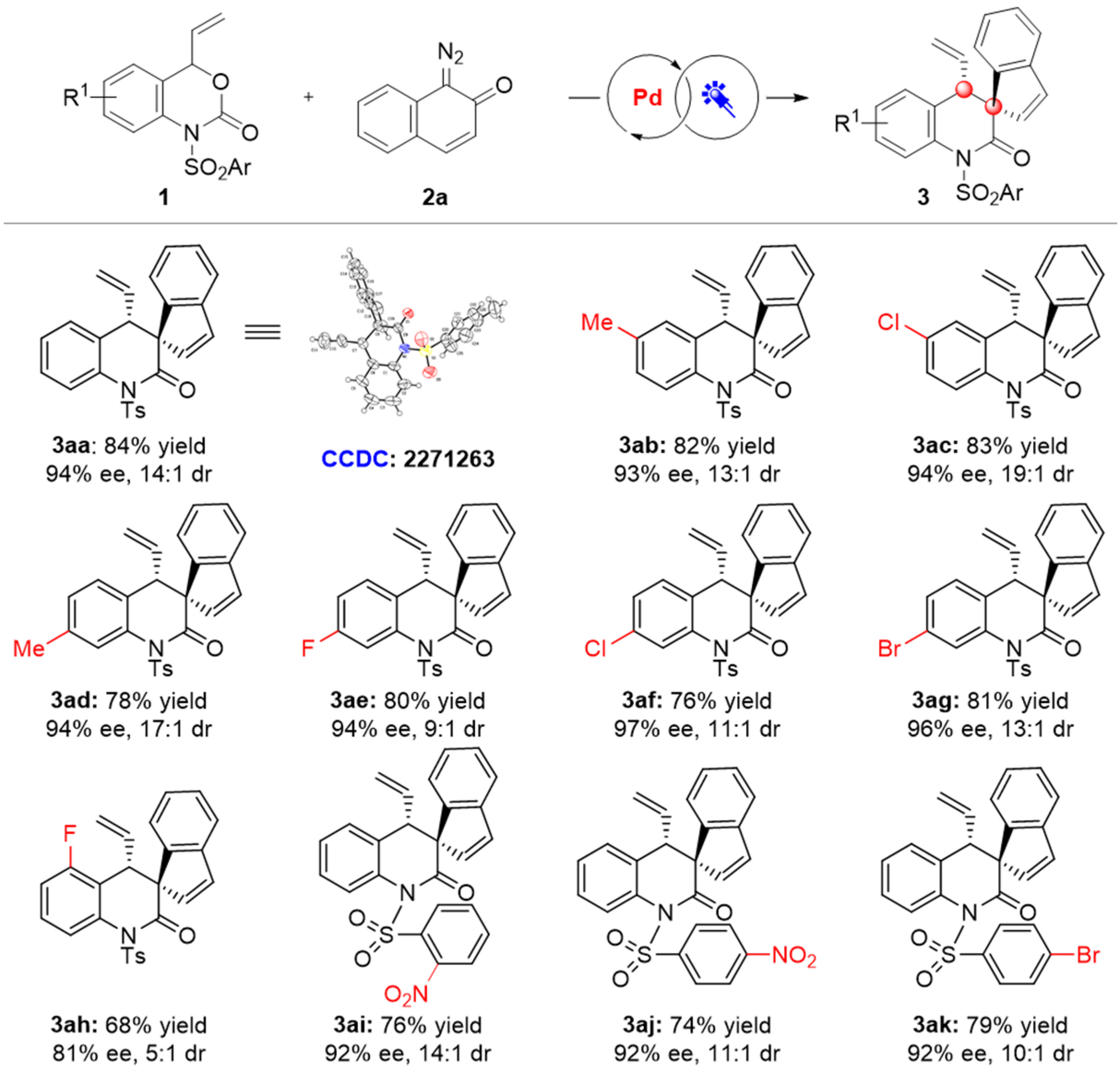


Figure 3. The scope of vinylbenzoxazinanones. Standard conditions: **1** (0.1 mmol), **2** (0.2 mmol), $Pd_2(dba)_3$·$CHCl_3$ (5 mol%) and **L8** (20 mol%) in 2.0 mL anhydrous DCM at rt under the irradiation of 6 W blue LEDs for 24 h. Isolated yields. ee: Enantiomer excess; dr: diastereoisomer ratio; dba: dibenzylideneacetone; DCM: dichloromethane; rt: room temperature; LEDs: light-emitting diodes.

number of solvents were screened, and the results showed that the use of DCM led to the highest reaction efficiency. Replacement of the 456 nm light source with other light sources, such as 390 or 370 nm, all promoted the formation of **3aa** with similar overall enantio- and diastereoselectivities but with moderate yields (entries 16 and 17). In the absence of the light source, no product was determined, so, as expected, the control experiment demonstrated that light irradiation is crucial to the reaction (entry 18).

With the optimal conditions in hand, we first explored the substrate scope of vinylbenzoxazinanones for this reaction. As summarized in Figure 3, the electronically varied substituents at the 6- or 7-position of the benzene ring, such as H, Me, F, Cl, and Br, were found to be applicable to generate chiral *spiro*-indenes in good yields with no obvious influence on the enantio- and diastereoselectivities (**3aa**-**3ag**, 76%-84% yields, 93%-97% ee and 9:1-19:1 dr). It could be speculated that vinylbenzoxazinones bearing an electron-donating

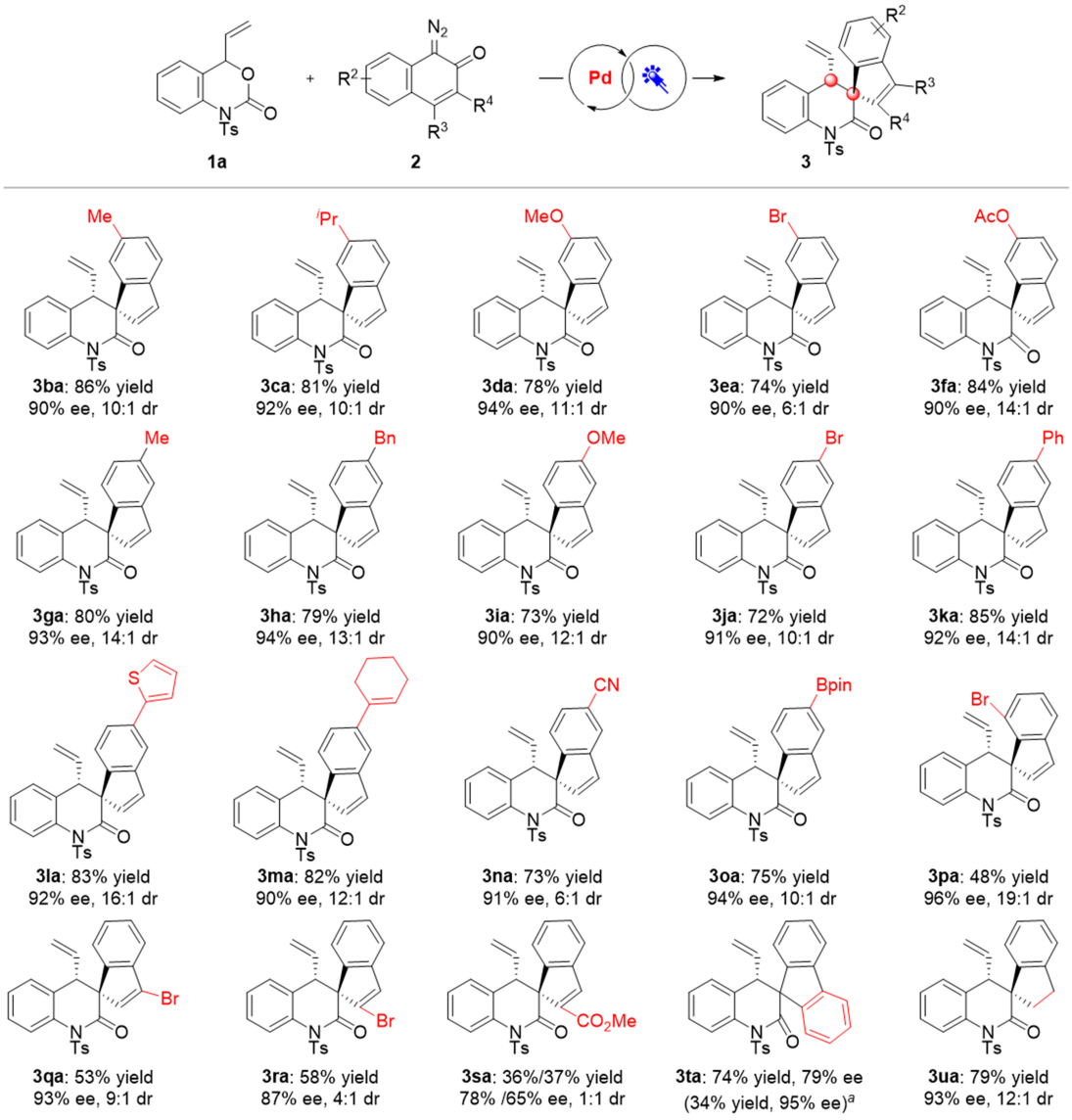


Figure 4. The scope of 1-diazonaphthalen-2(1*H*)-ones. Standard conditions: **1** (0.1 mmol), **2** (0.2 mmol), $Pd_2(dba)_3$·$CHCl_3$ (5 mol%) and **L8** (20 mol%) in 2.0 mL anhydrous DCM at rt under the irradiation of 6 W blue LEDs for 24 h. Isolated yields. [a]Chiral ligand **L9** (10 mol%) was used instead of **L8**.ee: Enantiomer excess; dr: diastereoisomer ratio; dba: dibenzylideneacetone; DCM: dichloromethane; rt: room temperature; LEDs: light-emitting diodes.

or electron-withdrawing group display comparable reactivity at the 6- or 7-position of the benzene ring. The absolute configuration of the resulting product **3aa** was assigned to 3*S*,4*S* by X-ray single-crystal diffraction analysis. In addition, the substrate with fluorine at the 5-position was successfully converted to the desired product **3ah**, while the one with Me was infeasible, possibly due to steric hindrance. Next, we briefly investigated the effect of sulfonyls on the nitrogen atom and found that the replacement of *p*-toluene with 2-nitro-, 4-nitro-, and 4-bromobenzenes can also afford products **3ai**-**3ak** in 74%-79% yields with 92% ee and 10:1-14:1 dr.

Subsequently, the substrate range of 1-diazonaphthalen-2(1*H*)-ones, which were easily prepared from 2-naphthol derivatives, was investigated. As shown in Figure 4, the introduction of electron-donating (e.g.,

Me and OMe) and electron-withdrawing (e.g., Br) groups at the 6- or 7-position of the naphthol ring of 1-diazonaphthalen-2(1*H*)-one was well tolerated in this reaction, and corresponding *spiro*-indenes **3ba**-**3ja** were obtained in 72%-86% yields with up to 94% ee and 14:1 dr. In addition, aryl substituents, such as phenyl and thiophenyl, were accommodated at the 6-position, giving the products of **3ka** and **3la** with good results. Significantly, the success of these transformations was further extended to substrates with different functional groups at the 6-position, such as cyclohexanyl (**3ma**, 82% yield, 90% ee and 12:1 dr), CN (**3na**, 73% yield, 91% ee and 6:1 dr) and Bpin (**3oa**, 75% yield, 94% ee and 10:1 dr). These results proved the good tolerance of functional groups with this asymmetric dipolar cyclization. The reactivity was slightly affected by the substituents at the 3-, 4- and 8-positions of the naphthol ring and the target products **3pa**-**3ra** were obtained in the moderate yields even with extended reaction time. 1-Diazonaphthalen-2(1*H*)-one with an extended fused ring system was also an efficient substrate for conversion to the product **3ta**. Dihydrodiazonaphthoquinone was also suitable for this reaction and was successfully converted to *spiro*-indane product **3ua** in 79% yield with 93% ee and 12:1 dr.

To demonstrate the utility of this methodology, a gram-scale reaction was carried out under the irradiation of two Kessil lamps (456 nm) and comparable enantio- and diastereoselectivities were observed (Figure 5A, 68% yield, 94% ee and 14:1 dr). Additionally, the reaction directly using sunlight as a light source worked well, yielding the corresponding product comparable to that in the laboratory [Figure 5B]. Furthermore, four additional synthetic transformations of **3aa** were carried out [Figure 5C]. Firstly, regioselective olefin epoxidation was successfully conducted, giving the product **4a** with excellent enantio- and diastereoselectivities. Reduction of the amide group with lithium tetrahydridoaluminate allowed for the smooth production of **4b**. Then, the *p*-tosyl group was easily removed under reductive conditions to afford compound **4c** in excellent yield with no loss of enantiopurity. Last, the *spiro*-indene product **3aa** underwent a facile hydrogenation reaction in the presence of Pd/C and H_2, which easily afforded the target product *spiro*-indane **4d**.

Quantum chemical calculations were carried out to explore the origin of regioselectivity in the reductive elimination processes (**L6** was employed in the calculations; the process involving two ligands was calculated based on the result of the nonlinear effect experiments in Section 7.1 of the Supplementary Materials). The calculated energy profiles [Figure 6A] indicate that **TS1*a***$_{RR}$, the transition state (TS) leading to chiral *spiro*-indenes, was predicted to be most stable compared with TSs in other pathways, agreeing with the experimentally observed good regio- and chemo-selectivity. Intriguingly, we found that the trend of relative stability of TSs was generally consistent with the trend of thermodynamics of the cyclization products. Herein, we examined the geometries of different plausible products to understand the regio- and chemoselectivity according to the Evans-Polanyi principle. As shown in Figure 6B, compared with **3aa**, the lone pair of the tosyl N atom of **3b** loses conjugated stabilization with the phenyl group. In both **3c** and **3d**, the double bonds were highly distorted due to the ring strain, resulting in a significant increase in energy.

CONCLUSIONS

In summary, we have developed a novel route to chiral *spiro*-indenes via the Pd-catalyzed asymmetric (4 + 2) dipolar cyclization of vinylbenzoxazinanones and 1-diazonaphthalene-2(*1H*)-ones. This reaction allows the one-pot preparation of a range of chiral *spiro*-indenes bearing all-carbon quaternary stereocenters in moderate to good yields and with generally high enantio- and diastereoselectivities. A key factor contributing to the success of this method is the formation of indene-involved ketenes by photo-Wolff rearrangement, which serves as efficient acceptors for Pd-containing 1,4-dipoles to proceed with the subsequent asymmetric dipolar cyclization. We believe that the strategy of combining asymmetric palladium catalysis with photo-Wolff rearrangement would find more potential applications in the chiral carbo- and heterocycle synthesis.

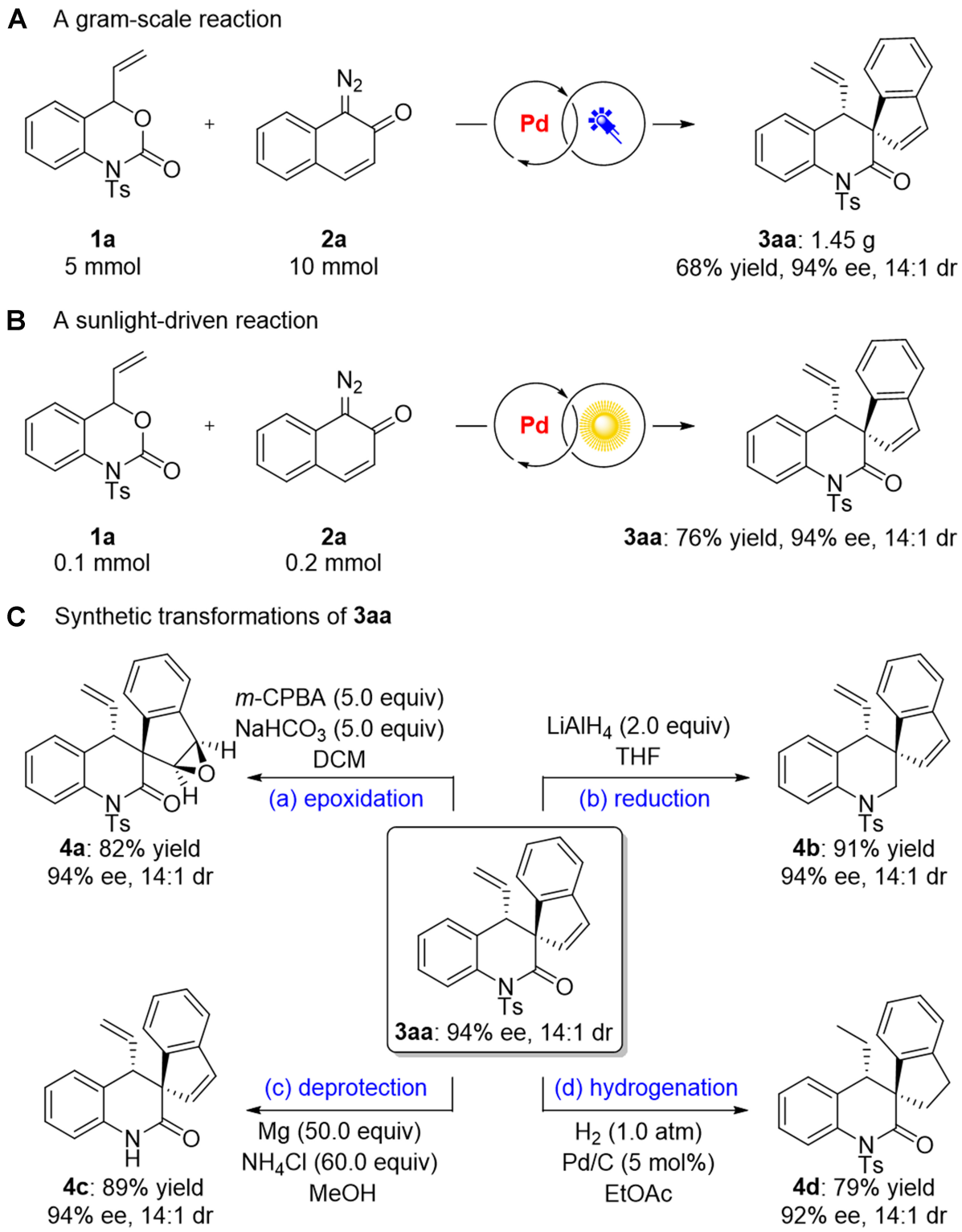


Figure 5. Demonstration of the synthetic utility of methodology. ee: Enantiomer excess; dr: diastereoisomer ratio; DCM: dichloromethane; THF: tetrahydrofuran.

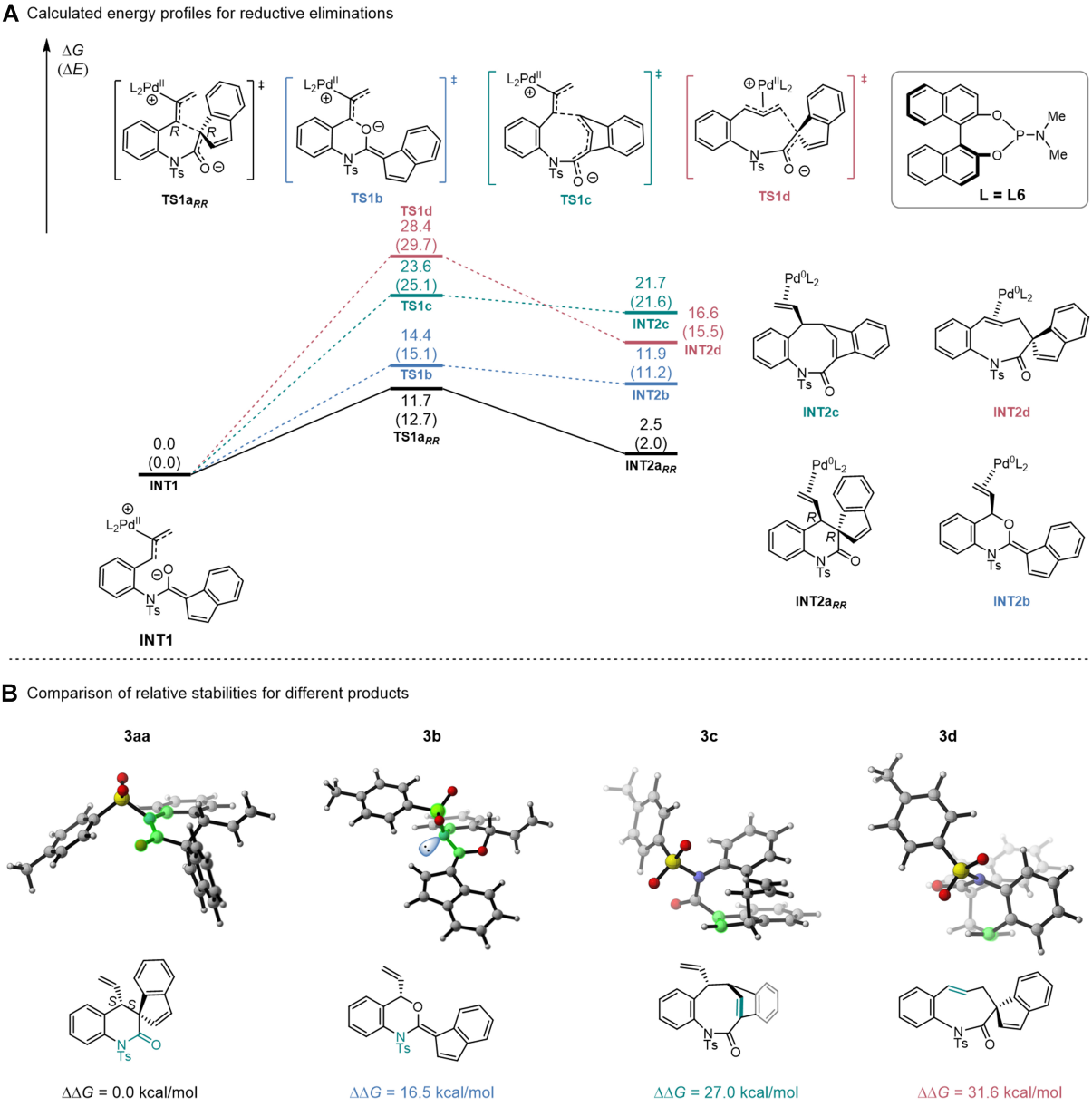


Figure 6. DFT Calculations. Energies are given in kcal/mol. DFT: density functional theory.

DECLARATIONS

Authors' contributions

Conceiving the work: He L
Designing and conducting the experiments: He L, Qu BL, Yu JQ, Yu J
DFT calculations: Xiao M, Zhang Z
Discussion and manuscript preparation: Cheng Y, Xiao WJ
Supervising and directing the research: Lu LQ

Availability of data and materials

Detailed experimental procedures and spectroscopic data can be found in Supplementary Materials. Deposition Number 2271263 (for **3aa**) contains the supplementary crystallographic data for this paper.

These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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