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Asymmetric synthesis of binaphthyls through photocatalytic cross-coupling and organocatalytic kinetic resolution

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By capitalizing on the capability of photoredox catalysis to generate reactive radical intermediate under mild conditions, we established a photocatalytic cross-coupling protocol that could deliver both derivatives from 1-bromo-2-naphthols in combination with 2-naphthols or 2-naphthylamines. This distinct activation mode could overcome structural or electronic limitation associated with conventional coupling pathways. Additionally, a novel kinetic resolution protocol of unprotected BINOLs has been established with azodicarboxylates via chiral phosphoric acid (CPA) catalysis. Selectivity factor of up to 175 could be achieved and delivered to both enantiomers in atropisomerically enriched form after a simple work-up.

1,1′-bi-2-naphthols, 2-amino-2′-hydroxy-1,1′-binaphthyls, chiral phosphoric acid, kinetic resolution, photocatalysis

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1 Introduction

Aside from being privileged structures in chiral ligands or catalysts [1], binaphthyl backbones exist in many natural products [2], biologically active molecules [3] and functional materials [4]. As the most representative members, numerous ligands and catalysts built on 1,1′-bi-2-naphthol (BINOL), 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) and 1,1′-binaphthyl-2,2′-diamine (BINAM) saw successful applications in asymmetric synthesis [1,5]. Their syntheses are therefore longstanding aspiration of synthetic chemists which yielded methodologies that proceed by way of arylation reaction [5–8], arene formation [5,9] and enantioselective functionalization of preformed biaryl scaffolds [5,10,11].

Among these pathways, aryl-aryl coupling represents the most retrosynthetically straightforward route. Indeed, direct oxidative synthesis of BINOLs with stereoselective protocols based on copper [7b–e], vanadium [7f–h], iron [7i] and ruthenium [7j] catalysts is well-established. Despite the notable challenge in translating this reactivity paradigm to construct C_1-symmetric BINOL and NOBIN analogues due to homo-coupling reactivity, Katsuki [8a], Pappo [8b], Tu [8c,d] and Uchida [8e] have cleverly achieved good cross-selectivity by the judicious introduction of substituents or by modulating the substrate electronics (Scheme 1a). While applying differentiated arene substrates under transition metal catalytic cross-coupling conditions (such as aryl halides and boronic acids in Suzuki coupling) could, in principle, circumvent the homo-coupling issue and provide a general route to BINOLs and NOBINs, undesired side re-

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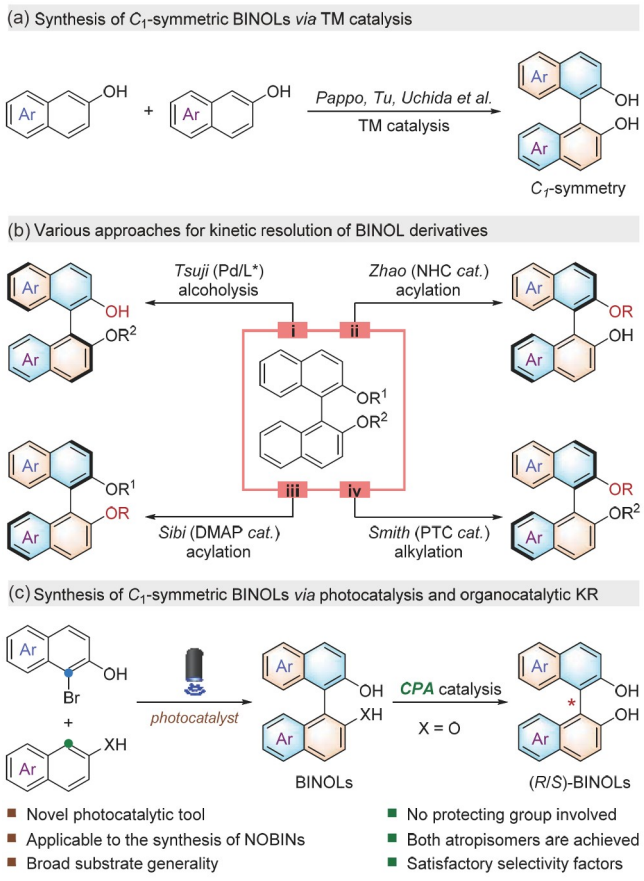


Scheme 1 Conventional methods for synthesizing C_1-symmetric BINOLs and their kinetic resolution as well as our design (color online).

actions or competitive substrate coordination due to the presence of free amine or hydroxyl functionality could detract from this otherwise appealing approach [12].

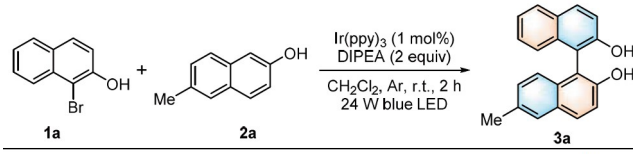
This synthetic constraint motivates our pursuit of a general cross-coupling strategy to streamline unified access to both C_1-symmetric BINOLs and NOBINs. To avert the substrate specificity and harsh reaction conditions associated with conventional aryl-aryl cross-coupling reactions, we conjectured that identifying a suitable 2-naphthol coupling partner which could selectively convert into a reactive species under mild conditions would be a key design consideration. When contemplating the intermediacy of α-carbonyl carbon radical (naphthoxyl radical) commonly implicated in conventional radical-radical or radical-anion couplings [8a–c], we were particularly intrigued by the facile tautomerization of 1-bromo-2-naphthols to 1-bromonaphthalen-2(1*H*)-ones under basic conditions. In particular, the generation of α-carbonyl carbon-centered radical from α-bromo carbonyl compounds under photocatalytic conditions has been utilized in designing a variety of chemical transformations [13]. In the present scenario, the formation of this reactive radical species from 1-bromonaphthalen-2(1*H*)-ones should occur readily under photocatalytic conditions and its addition to a naphthylamine or naphthol partner [14] would achieve the direct forging of aryl-aryl linkage. This overall strategy represents an ideal blueprint to target both BINOLs and NOBINs with expanded substrate scope as substituent or electronic requirements for cross-selectivity would be bypassed.

On the other hand, kinetic resolution (KR) represents one robust method to obtain enantioenriched C_1-symmetric binaphthyls [11]. Early in 2005, Tsuji and co-workers [11e] successfully developed KR of BINOL derivatives through palladium-catalyzed alcoholysis of vinyl ethers with high enantioselectivities and selectivity factor (s) of up to 36 (Scheme 1b-i). In 2014, Zhao's group [11f] devised an NHC-catalyzed enantioselective acylation of BINOL derivatives (Scheme 1b-ii), whereas Sibi and co-workers [11g] achieved a chiral DMAP-catalyzed *O*-acylation process to afford C_1-symmetric BINOL derivatives (Scheme 1b-iii). Later in 2019, Smith and co-workers [11h] demonstrated a chiral ammonium ion-catalyzed KR of C_1- and C_2-symmetric BINOLs *via* *O*-alkylation with s up to 46 (Scheme 1b-iv). While KR establishes a reliable avenue to BINOLs, most developed methods require judiciously protected substrates to control reactivity and stereoselectivity. Herein, we report on the successful implementation of a distinctive radical reaction mode that permits the efficient cross-coupling of 1-bromo-2-naphthols with 2-naphthol or 2-naphthylamine derivatives. Both coupling partners could bear similar electronic properties or small structural differences at a position distal from coupling sites. Moreover, to efficiently access both enantiomers of BINOLs in atropisomerically enriched form, a chiral phosphoric acid (CPA)-catalyzed KR with high selectivity factor (s) was established. The present method constitutes an alternative protecting group-free protocol and is amenable to both C_1- and C_2-symmetric BINOLs (Scheme 1c).

2 Results and discussion

As a starting point, we selected 1-bromo-2-naphthol (**1a**) and 6-methyl-2-naphthol (**2a**) as the model cross-coupling partners for our envisioned approach to assembling C_1-symmetric BINOL derivative. As shown in Table 1, the desired binaphthyl product **3a** was achieved in 71% isolated yield in the presence of $Ir(ppy)_3$ as photocatalyst ($E_{1/2}^{IV/*III}$ = −1.73 V *vs.* SCE, $E_{1/2}^{III/II}$ = −2.19 V *vs.* SCE) [13a], DIPEA as additive and CH_2Cl_2 as solvent under irradiation of 24 W blue LED at room temperature. Control experiments indicated that the reaction did not work in the absence of DIPEA, photocatalyst or light source (entries 2–4), validating a visible-light-induced reaction process. Applying $Ir(ppy)_2(dtbbpy)PF_6$ as the photocatalyst instead has affected the yield in a negative manner (entry 5, 64% yield). There was

Table 1 Optimization for reaction conditions[a] (color online)



1a 2a 3a

Entry	deviations from standard conditions	Yield[b](%)
1	none	77 (71)[c]
2	without $Ir(ppy)_3$	N.R.
3	without light source	N.R.
4	without DIPEA	N.R
5	$Ir(ppy)_2(dtbbpy)PF_6$ as PC	64[d]
6	$Ru(phen)_3(PF_6)_2$ as PC	N.R.
7	Eosin Y as PC	N.R
8	PhF instead of CH_2Cl_2	75
9	$PhCF_3$ instead of CH_2Cl_2	76
10	1,4-dioxane instead of CH_2Cl_2	trace
11	TMEDA instead of DIPEA	60
12	*N*,*N*-dimethylaniline instead of DIPEA	75[d]

a) Conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Ir(ppy)_3$ (1 mol%), DIPEA (0.2 mmol), CH_2Cl_2 (2 mL), Ar, r.t., 24 W blue LED, 2 h; N.R. = no reaction. b) Yields were determined through ^{1}H NMR crude spectrum using $CHPh_3$ as internal standard. c) Yield in parentheses is isolated yield. d) 12 h.

no sign of product **3a** when other metal-complex- and organo-photocatalysts, such as $Ru(phen)_3(PF_6)_2$ and Eosin Y, were employed (entries 6, 7, see Table S1 for more PC options, Supporting Information online). The choice of solvent could impact reaction outcome: PhF or $PhCF_3$ caused only 1%–2% decrease in yield compared to CH_2Cl_2 (entries 8, 9) while the variation to 1,4-dioxane resulted in trace amount of product (entry 10). When TMEDA and *N*,*N*-dimethylaniline were applied as additives, **3a** was furnished in 60% and 75% yield, respectively (entries 11, 12). In addition, 24 W blue LED was the optimal choice through examination of different light sources (see Table S4 for more details).

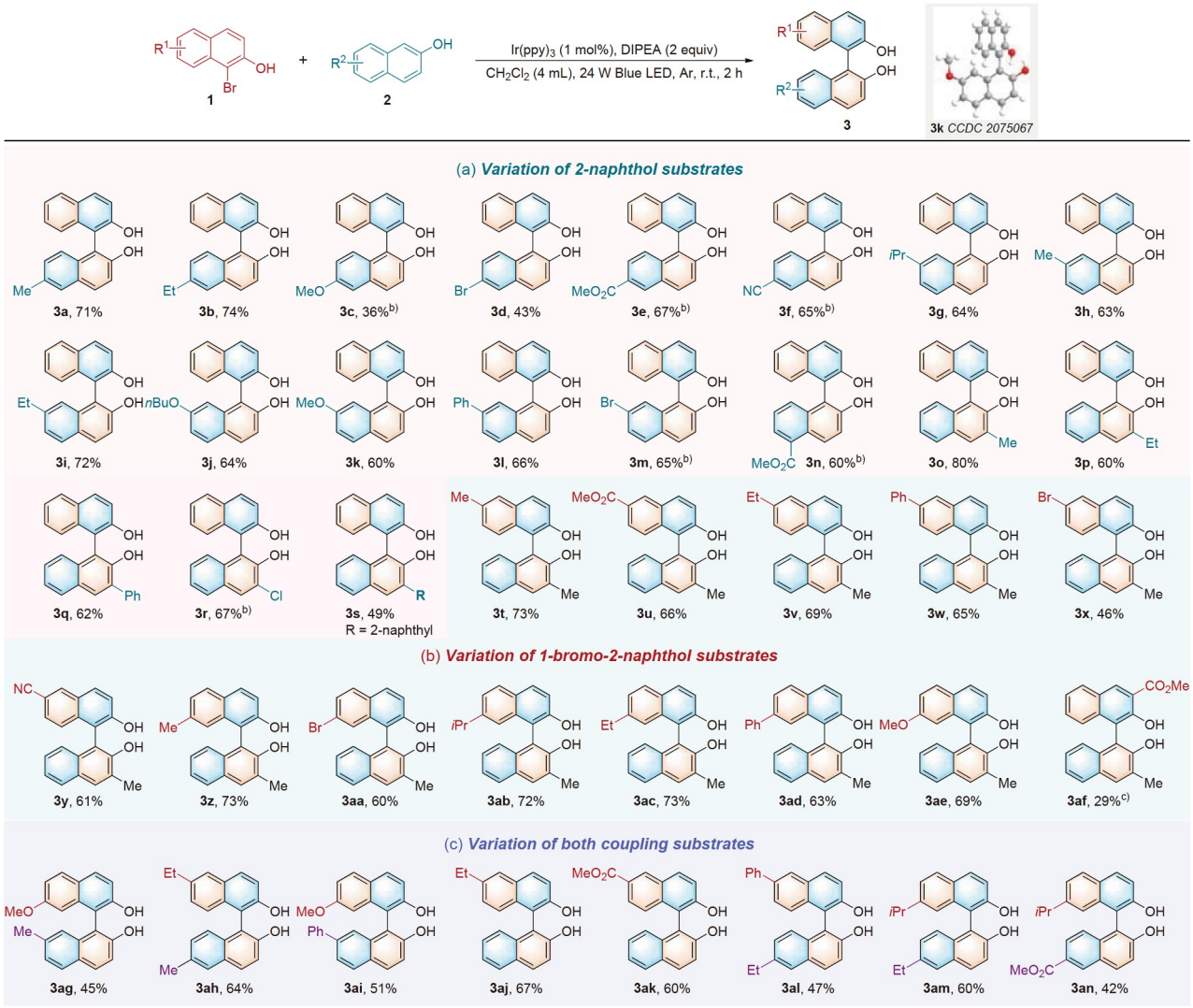
Having identified the viable reaction conditions, we sought to explore the generality of this set of conditions with regards to substituted 2-naphthols (Table 2a). Various electron-donating entities, including alkyl and alkoxy groups installed at C6 or C7 position of naphthyl ring were well tolerated, forming products in moderate to good yields (**3a**–**3c** & **3g**–**3k**). With electron-withdrawing substituent at C6 or C7 position, products were delivered in 43%–67% yield (**3d**–**3f** & **3m**). We were encouraged to observe selective reaction with retention of other bromide functionality after the photocatalytic process (**3d**, **3m**), implying the possibility of further synthetic applications. A moderate yield was achieved when the electron-withdrawing ester group was appended at C5 position of naphthyl ring (**3n**, 60%). Furthermore, substrates bearing the aryl group (phenyl or 2-naphthyl) were amenable to give products in moderate to good yields under standard conditions (**3l**, **3q**, **3s**). Notably, 2-naphthol with C3-methyl group gave the best yield (**3o**, 80%).

The range of applicable 1-bromo-2-naphthols was studied subsequently using 3-methyl-2-naphthol as the fixed coupling partner. As displayed in Table 2b, substrates bearing different substitutions (**3t**–**3af**) coupled smoothly under the photoreaction conditions, regardless of the electronic nature and the position of the substituent on the naphthyl ring. However, having an ester group at C3 position gave poor results (**3af**, 29% yield), which might be attributed to a faster hydrogen abstraction process and the ensuing homo-coupling reaction. Both bromo functional handles of naphthol partners were left unreacted (**3x** , **3aa**), again pointing to potential downstream chemical derivatization. Furthermore, substitution patterns on both naphthyl rings were assessed, which invariably afforded products in moderate to good yields (**3ag**–**3ai**, **3al**–**3an**). The undecorated 2-naphthol was also compatible and gave products in good yields (**3aj**, **3ak**).

Successful establishment of a highly efficient and selective approach to construct C_1-symmetric BINOLs drove the attempt to access NOBINs, another class of privileged functionalized binaphthyls, which would expand the applicability of current strategy. This was nonetheless projected to be a more ambitious task compared with 2-naphthol due to the conspicuously different nucleophilicity of 2-naphthylamines as well as the availability of multiple reactive sites. It was remarkable and unexpected that NOBIN **5a** was obtained when the standard conditions used to synthesize BINOLs were applied directly. For a more optimal outcome, we re-evaluated the reaction parameters (see Tables S5–S8 for details) before testing the compatibility of a range of 1-bromo-2-naphthols and 2-naphthylamines (Table 3). 1-Bromo-2-naphthols and 2-naphthylamines with diversified groups introduced at different positions of aromatic rings were well-suited to the re-optimized conditions and all of them delivered products in moderate yields (**5a**–**5j**). As with the case of BINOL products, the bromide substituent was also preserved in NOBIN **5g**. Present protocol constituted a novel protecting- and directing-group-free approach to NOBIN analogues.

To appraise the practical utility of this methodology, a gram-scale synthesis was conducted. It was notable that with photocatalyst loading reduced to 0.1 mol%, the process proceeded smoothly to give product **3o** in 75% yield (Scheme 2a), exhibiting only a slight loss compared with 0.2 mmol scale. To shed light on the mechanism, a series of experiments was carried out. First, when 2,2,6,6-tetramethylpiperidinooxy (TEMPO) was included in the arylation of 7-methoxy-2-naphthol **2k**, the photocatalytic process was nearly suppressed. The putative aryl radical intermediate was intercepted by TEMPO as adduct **6**, which was detected through high resolution mass spectroscopy (HRMS) analysis (Scheme 2b, Figure S3) of the reaction mixture. When α-methylstyrene was added to the reaction mixture, the desired product **3k** was isolated in 21% yield,

Table 2 Substrate generality for the synthesis of BINOLs *via* photocatalytic cross-coupling reaction[a] (color online)



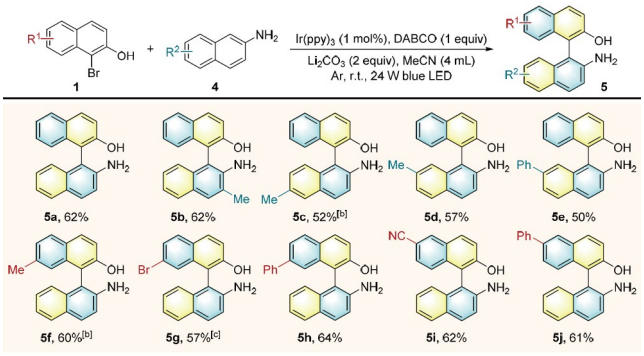
a) Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $Ir(ppy)_3$ (1 mol%), DIPEA (0.4 mmol), CH_2Cl_2 (4 mL), Ar, r.t., 24 W blue LED. b) **2** (0.6 mmol) was used for this reaction. c) DIPEA (3 equiv.) was used for this reaction.

accompanied by adducts **7** and **8** in 8% and 13% yields, respectively (Scheme 2c). Furthermore, cyclic voltammetry and Stern-Volmer quenching experiments showed that 1-bromo-2-naphthol **1a** could effectively quench the excited state of $Ir(ppy)_3$ (see Figures S4–S6 for details) [15].

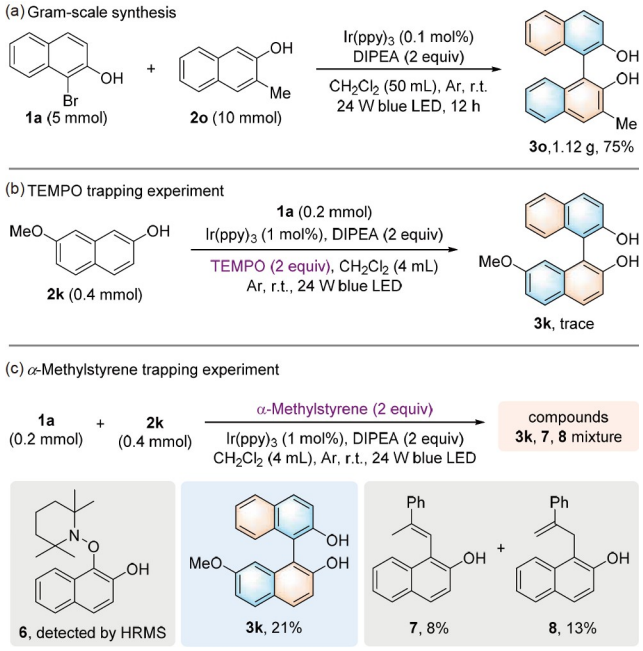
On the basis of experimental data and previous reports [16], a mechanistic proposal, as outlined in Figure 1, was made. The process initiates as the photocatalyst Ir(III) is excited to *Ir(III) under visible light irradiation. Through single electron transfer (SET), *Ir(III) is oxidatively quenched by **1′**, the tautomer of **1.** The *α*-keto carbon radical intermediate **Int-I** will be captured by 2-naphthol (**2**) or 2-naphthylamine (**4**) to forge the C–C bond in intermediate **Int-II**, which undergoes a SET process with DIPEA radical cation to yield **Int-III** and DIPEA. The coupled product (**3** or **5**) is released upon base-mediated aromatization. At the same time, the ground state Ir(III) is regenerated to complete the catalytic cycle as Ir(IV) undergoes SET with DIPEA.

To implement practical access to enantiopure BINOL derivatives, we endeavored to realize the photocatalytic asymmetric synthesis based on the current reaction conditions initially by introducing chiral catalysts, such as chiral phosphoric acids and (thio)ureas. However, the coupling products were formed with no sign of asymmetric induction. Thus, we changed our approach to the study of catalytic kinetic resolution. At the beginning of reaction optimization, it was found that the treatment of commercially available (*rac*)-BINOL **9a** with ethyl azodicarboxylate **10** in the presence of CPA (*R*)-**C1** would give rise to adduct **11a** in 85% *ee* and returned (*R*)-**9a** in minimal enantioselectivity. As seen in Table 4, catalyst **C5** performed better (s = 51) than other evaluated CPAs in this reaction to afford product **13a** (24% yield, 94% *ee*) and the recovered starting material (*R*)-**9a** (64% yield, 46% *ee*) (entries 1–5). A major improvement

Table 3 The synthesis of NOBINs[a] (color online)



a) Unless otherwise noted, reaction conditions: **1** (0.2 mmol), **4** (0.4 mmol), Ir(ppy)$_3$ (1 mol%), DABCO (1 equiv.), Li_2CO_3 (2 equiv.), MeCN (4 mL), 24 W blue LED, Ar at r.t. b) MeCN/acetone (4 mL, 1/1). c) DABCO (1.5 equiv.), Li_2CO_3 (1.5 equiv.).



Scheme 2 Gram-scale synthesis and mechanistic studies (color online).

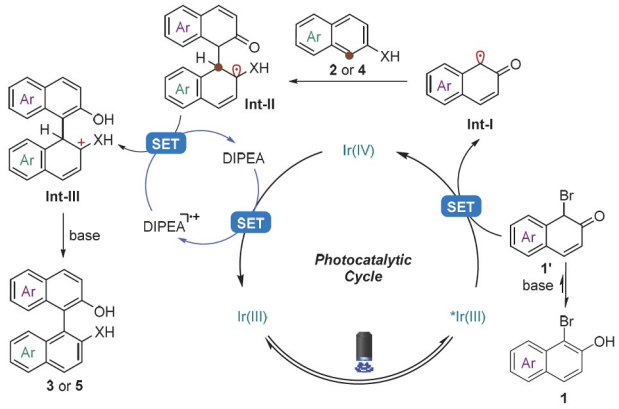
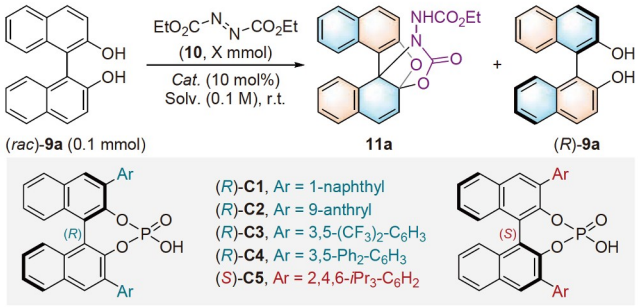


Figure 1 Proposed mechanism (color online).

Table 4 Optimization for kinetic resolution of BINOL (color online)



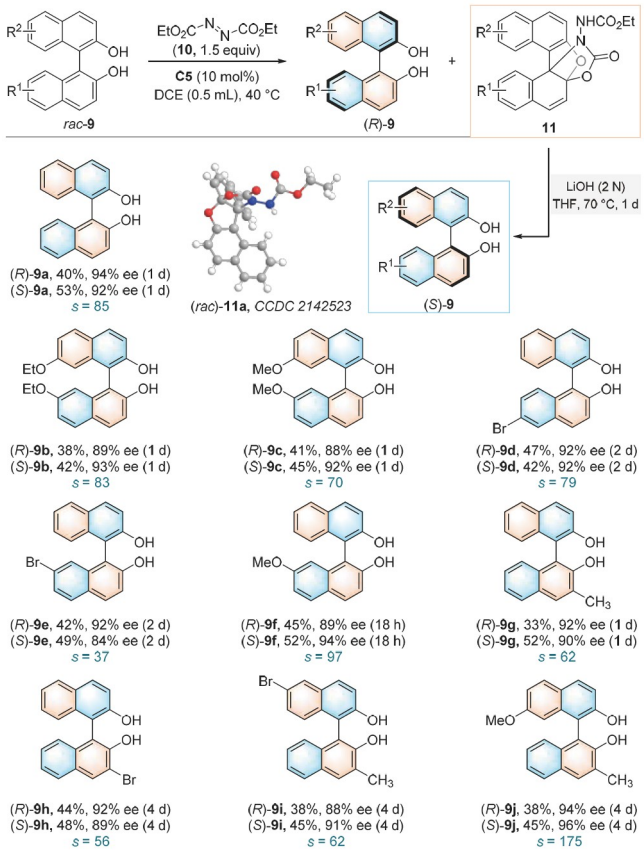
Entry	Cat.	X	Solv.	t (d)	11a yield (%)	11a *ee* (%)	(*R*)-9a yield (%)	(*R*)-9a *ee* (%)	*s*
1	**C1**	0.05	CH_2Cl_2	7	8	85	82	5	13
2	**C2**	0.05	CH_2Cl_2	7	6	90	75	5	20
3	**C3**	0.05	CH_2Cl_2	5	8	75	77	0	-
4	**C4**	0.05	CH_2Cl_2	7	13	73	76	13	7
5	**C5**	0.05	CH_2Cl_2	2.5	24	94	64	46	51
6[a]	**C5**	0.07	CH_2Cl_2	2.5	50	96	50	72	106
7[a]	**C5**	0.07	DCE	2.5	44	98	53	75	224
8[a]	**C5**	0.07	CCl_4	2.5	21	96	66	27	64
9[a]	**C5**	0.07	PhCl	2.5	45	98	53	74	221
10[a]	**C5**	0.07	$CHCl_3$	2.5	38	98	52	71	211
11[a,b]	**C5**	0.15	DCM	1	57	92	38	92	79
12[a,b]	**C5**	0.15	DCE	1	53	94	40	94	115

a) The reaction was performed with c = 0.2 M. b) The reaction was performed at 40 °C. s = selectivity factor.

was obtained by employing a higher loading of **10** (entry 6), enhancing the yield and enantioselectivity of **11a** (50% yield, 96% *ee*) and unreacted (*R*)-**9a** (50% yield, 72% *ee*). When alternative halogenated solvents were tested, DCE appeared as a better choice (s = 224, entry 7), though PhCl and $CHCl_3$ gave similar results with slightly lower selectivity factors. On the basis of these data, a further increase of the amount of **10** and reaction temperature gave the most optimal result, providing product **11a** and (*R*)-**9a** in 94% *ee* as well as a selectivity factor of 115.

It was encouraging to find that after a brief separation *via* preparative thin layer chromatography, product **11** could be transformed into the enantiomeric (*S*)-**9** under basic conditions and after a simple work-up. Having established this conversion, we examined the applicability of this workflow to both C_2- and C_1-symmetric BINOLs (Table 5). 7,7′-Disubstituted BINOLs were well resolved under this set of conditions and yielded both enantiomers in high efficiency and good enantioselectivity (s = 83 for **9b** and 70 for **9c**). C_1-Symmetric 6- and 7-substituted BINOLs afforded recovered (*R*)-**9** and enantiomer (*S*)-**9** with high enantioselectivities (**9d**–**9f**) whereas selectivity factor of 62 and 56 was achieved for 3-methyl (**9g**) and 3-bromo-substituted (**9h**) unsymmetrical BINOLs respectively. In addition, BINOLs that bore differing substitutions on both naphthyl rings underwent the kinetic resolution to provide axially chiral C_1-symmetric BINOLs in excellent enantiopurity (**9i**, **9j**).

Table 5 Scope of KR of C_2- and C_1-symmetric BINOLs[a] (color online)



a) KR condition: (*rac*)-**9** (0.1 mmol), DEAD **10** (0.15 mmol), (*S*)-**C5** (10 mol%), DCE (0.5 mL), 40 °C. Condition of **11** transformed to (*S*)-**9**: LiOH (2 N, 7 equiv.), THF (1.0 mL), 70 °C for 1 d, then work-up with HCl (6 N, 2 mL).

3 Conclusions

In summary, the photocatalytic system described here presents an efficient arylation pathway towards C_1-symmetric BINOL derivatives and protecting-group-free NOBINs with varied substitutions under mild conditions in moderate to good efficiencies. The practicability of this protocol was demonstrated by gram-scale synthesis with 0.1 mol% of catalyst loading. We further explored an efficient kinetic resolution of C_2- and C_1-symmetric BINOLs *via* CPA catalysis with *s* up to 175, affording both enantiomers of BINOLs with high enantioselectivities after a simple work-up. The chemistry demonstrated here could serve as an inspiration to integrate new reaction mode in addressing other challenges in the synthesis of axially chiral compounds.

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Conflict of interest The authors declare no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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