

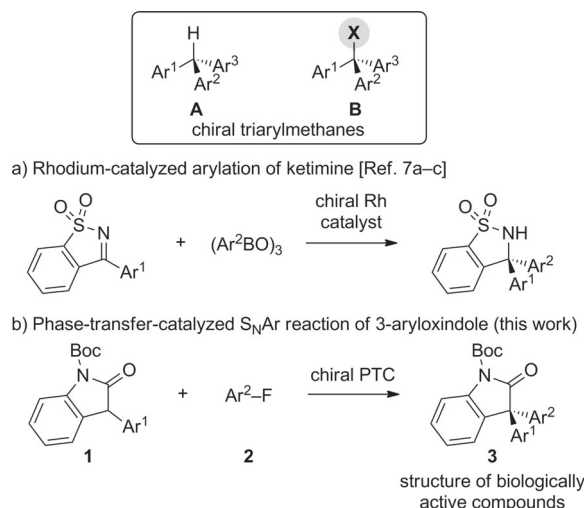
Catalytic Asymmetric Synthesis of 3,3'-Diaryloxindoles as Triarylmethanes with a Chiral All-Carbon Quaternary Center: Phase-Transfer-Catalyzed S_NAr Reaction**

Seiji Shirakawa, Kenta Koga, Takashi Tokuda, Kenichiro Yamamoto, and Keiji Maruoka*

Abstract: Catalytic asymmetric synthesis of unsymmetrical triarylmethanes with a chiral all-carbon quaternary center was achieved by using a chiral bifunctional quaternary phosphonium bromide catalyst in the S_NAr reaction of 3-aryloxindoles under phase-transfer conditions. The presence of a urea moiety in the chiral phase-transfer catalyst was important for obtaining high enantioselectivity in this reaction.

The development of efficient synthetic methods for triarylmethanes is an important task for organic chemistry because of the utility of these compounds in materials science^[1] and medicinal chemistry,^[2,3] and a number of methods have been reported to date.^[4,5] In particular, research in catalytic asymmetric methods for the synthesis of chiral, unsymmetrical triarylmethanes has attracted much attention in recent years.^[6,7] Although several catalytic asymmetric methods for the synthesis of chiral triarylmethanes of type **A** with a tertiary carbon center have been reported (Scheme 1),^[6] only one general method for the synthesis of compounds of type **B**, possessing a quaternary carbon center, has been developed and involves a rhodium-catalyzed asymmetric addition of arylboroxines to diaryl ketimines to produce chiral (triaryl)-methylamines (Scheme 1a).^[7a-c] In this context, we are interested in the development of a new approach to the synthesis of chiral triarylmethanes of type **B**. Herein we report a valuable example of the catalytic asymmetric synthesis of triarylmethanes, possessing a chiral all-carbon quaternary center, by phase-transfer-catalyzed S_NAr reaction of 3-aryloxindoles (**1**),^[8-10] and it results in chiral 3,3'-diaryloxindoles (**3**) which are biologically interesting compounds (Scheme 1b).^[3]

We first examined the screening of chiral bifunctional quaternary phosphonium bromides [(*S*)-**4–6**] as phase-transfer catalysts,^[11,12] which were developed recently by our group,^[13] for the asymmetric S_NAr reaction of the 3-phenyloxindole **1a** (Table 1). Attempted reaction of **1a** and 2,4-dinitrofluorobenzene (**2a**) with solid $KHCO_3$ in toluene



Scheme 1. Catalytic asymmetric synthesis of triarylmethanes with a quaternary carbon center. Boc = *tert*-butoxycarbonyl, PTC = phase-transfer-catalyst.

under the influence of the bifunctional catalyst (*S*)-**4**, which possesses a hydroxy group, at room temperature for 24 hours afforded the arylation product **3a** in high yield with low enantioselectivity (entry 1). Switching the catalyst to the benzamide-substituted (*S*)-**5** slightly improved the enantioselectivity (entry 2), and the benzenesulfonamide-substituted catalyst (*S*)-**6** gave the product **3a** in low yield with low enantioselectivity (entry 3). To further improve the enantioselectivity of this reaction, we next examined the newly designed bifunctional phosphonium bromides (*S*)-**7**, which possess a urea group.^[14] It was expected that the urea moiety of (*S*)-**7** interacts with the nitroarene **2** through two hydrogen bonds, thus giving rise to a well-organized transition state which provides high stereocontrol (Figure 1).^[15] Based on this hypothesis, (*S*)-**7a** was utilized in this reaction, and to our delight, **3a** was obtained in moderate enantioselectivity (entry 4). Further tuning of the catalyst structure of led to

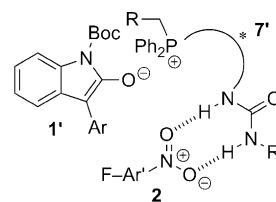
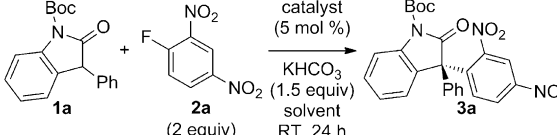


Figure 1. Proposed working model on the asymmetric arylation of 3-aryloxindole with bifunctional catalyst (*S*)-**7**.

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Table 1: Optimization of the reaction conditions.^[a]


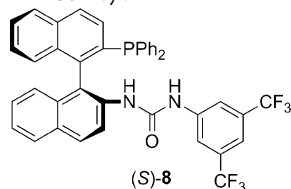
(S)-4: X = OH
 (S)-5: X = NHBz
 (S)-6: X = NHSO₂Ph
 (S)-7a: Ar = Ph, Ar' = Ph
 (S)-7b: Ar = Ph, Ar' = 3,5-(CF₃)₂-C₆H₃
 (S)-7c: Ar = Ph, Ar' = 3,5-(MeO)₂-C₆H₃
 (S)-7d: Ar = 3,5-(CF₃)₂-C₆H₃, Ar' = 3,5-(CF₃)₂-C₆H₃
 (S)-7e: Ar = 3,5-(tBu)₂-C₆H₃, Ar' = 3,5-(CF₃)₂-C₆H₃
 (S)-7f: Ar = 3,5-(tBu)₂-C₆H₃, Ar' = 3,5-(MeO)₂-C₆H₃

Entry	Catalyst	Solvent	Yield [%] ^[b]	ee [%] ^[c]
1	(S)-4	toluene	98	-17
2	(S)-5	toluene	89	35
3	(S)-6	toluene	36	3
4	(S)-7a	toluene	46	64
5	(S)-7b	toluene	42	79
6	(S)-7c	toluene	49	76
7	(S)-7d	toluene	30	76
8	(S)-7e	toluene	50	87
9	(S)-7f	toluene	85	84
10	(S)-7e	CCl ₄	80	87
11	(S)-7e	Et ₂ O	88	88
12	(S)-7e	iPr ₂ O	90	88
13	(S)-7f	iPr ₂ O	97	85
14 ^[d]	(S)-7e	iPr ₂ O	99	91

[a] Reaction conditions: **1a** (0.050 mmol), **2a** (0.10 mmol), and K₂CO₃ (0.075 mmol) in the presence of the chiral phase-transfer catalyst (5 mol %) in solvent (1.0 mL) at room temperature (25 °C) for 24 h.

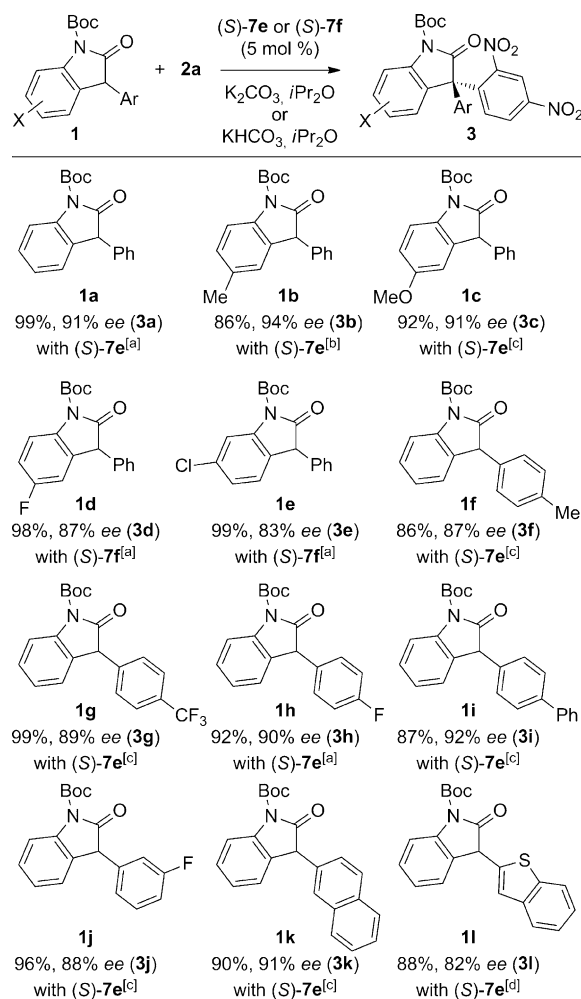
[b] Enantiomeric excess (ee) was determined by HPLC analysis using a chiral stationary phase. [c] Yield of isolated product. [d] The reaction was performed at -20 °C with K₂CO₃ (0.038 mmol) as a base.

Bz = benzoyl.



improved enantioselectivity (entries 5–9), and the arylation product **3a** was obtained with good enantioselectivity by using the catalysts (S)-7e and (S)-7f (entries 8 and 9). The screening of solvents led to improved yields (entries 10–13), and the highest yield and enantioselectivity were obtained at a lower temperature (-20 °C) with K₂CO₃ in diisopropylether in the presence of (S)-7e (entry 14). Notably, the reaction with the triarylphosphine catalyst (S)-8 gave the product **3a** with low enantioselectivity (< 5 % ee), that is, the quaternary phosphonium bromide moiety of (S)-7e was essential to obtaining high enantioselectivity.

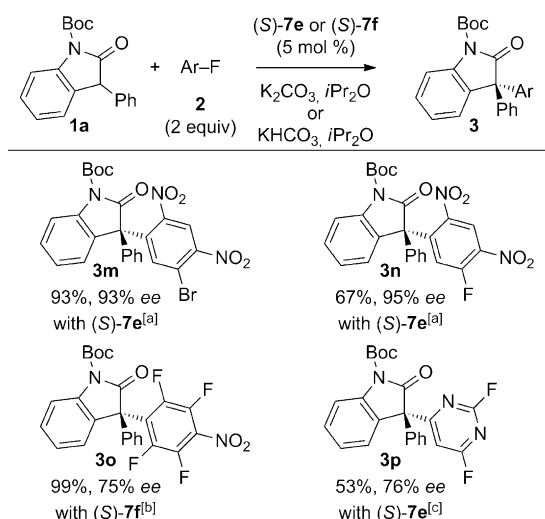
With the effective chiral bifunctional quaternary phosphonium bromides (S)-7e and (S)-7f in hand, we studied the substrate generality of the asymmetric arylation of various 3-



Scheme 2. Asymmetric arylation of the 3-aryloxindoles **1** with 2,4-dinitrofluorobenzene (**2a**). [a] Run with K₂CO₃ (0.75 equiv) at -20 °C for 24 h. [b] Run with K₂CO₃ (0.75 equiv) at -20 °C for 48 h. [c] Run with K₂CO₃ (1.5 equiv) at RT for 24 h. [d] Run with K₂CO₃ (1.5 equiv) at 0 °C for 48 h.

aryloxindoles (**1**) with **2a** (Scheme 2). The introduction of electron-donating and electron-withdrawing substituents on both the oxindole core and the 3-aryl group uniformly gave the products (**3a–k**) in good to high enantioselectivities (83–94 % ee). 3-Heteroaryl-substituted oxindole could also be used in this reaction, thus providing the product **3l** with good enantioselectivity (82 % ee).^[16]

Other electron-deficient aryl fluorides could also be employed in the S_NAr reaction (Scheme 3). The asymmetric arylation of **1a** with 1-bromo-5-fluoro-2,4-dinitrobenzene and 1,5-difluoro-2,4-dinitrobenzene in the presence of (S)-7e gave the corresponding arylation products **3m** and **3n**, respectively, with high enantioselectivities. Pentafluoronitrobenzene was also used in the reaction, thus giving the product **3o** as a single regioisomer with good enantioselectivity. The reaction with 2,4,6-trifluoropyrimidine as a heteroaryl fluoride was also promoted by (S)-7e to afford the product **3p** as a single regioisomer with good enantioselectivity.^[17] The absolute configuration of the arylation products **3** was determined by X-ray diffraction analysis of **3m** (Figure 2).^[18]



Scheme 3. Asymmetric arylation of 3-phenyloxindole (**1a**). [a] Run with K_2CO_3 (0.75 equiv) at $-20^\circ C$ for 24 h. [b] Run with $KHCO_3$ (1.5 equiv) at RT for 24 h. [c] Run with $KHCO_3$ (1.5 equiv) at RT for 48 h.

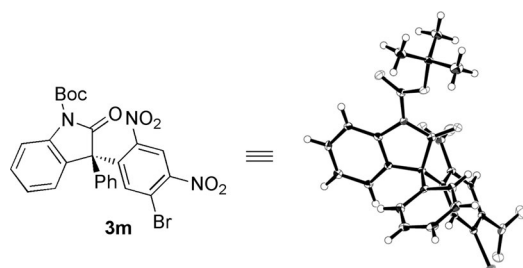
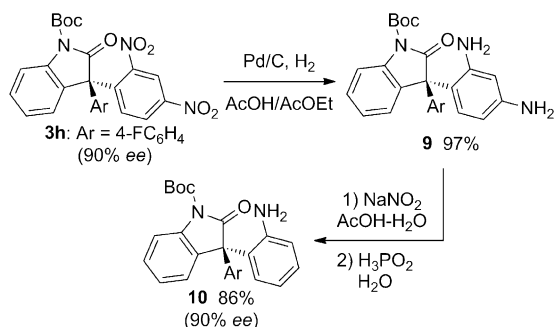


Figure 2. X-ray crystal structure of **3m**. Thermal ellipsoids shown at 50% probability.



Scheme 4. Transformation of the product **3h**.

The nitro groups in the products **3** can be readily transformed into other functionalities (Scheme 4). For example, the nitro groups of **3h** were reduced to amino groups by hydrogenation in the presence of Pd/C to give the compound **9**. The regioselective removal of an amino group at the *para*-position of **9** was performed via the formation of the corresponding diazonium salt and subsequent treatment with H_3PO_2 to give the *ortho*-amino compound **10** in good yield without any loss of stereoinformation.

In summary, we have successfully developed an efficient method for the synthesis of chiral triarylmethanes possessing an all-carbon quaternary center by S_NAr reaction of 3-aryloxindoles under phase-transfer conditions. The reactions were efficiently promoted by newly-designed chiral bifunctional quaternary phosphonium bromides possessing a urea moiety to give chiral triarylmethanes with good to high enantioselectivities. Further studies will be directed toward expansion of the reaction scope.

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- [16] The *tert*-butoxycarbonyl group on the nitrogen atom of the 3-aryloxindoles **1** was important for promoting the reaction efficiently.
- [17] In the case of reaction with 2,4,6-trifluoropyrimidine, the urea moiety of catalyst (*S*)-**7e** may interact with basic nitrogen atoms in the pyrimidine heterocycle.
- [18] CCDC 985318 (**3m**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.