# COMMUNICATIONS

# Catalytic Asymmetric Intramolecular Cascade Reaction for the Construction of Functionalized Benzobicyclo[4.3.0] Skeletons. Remote Control of Enantioselectivity

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**Abstract:** A catalytic asymmetric version of the intramolecular ylide annulation has been developed which affords high *ee* values and diastereoselectivities and which further shows that spirobiindane-based chiral phosphines can be excellent organocatalysts. Both optically active benzobicyclo[4.3.0] compounds **2** and **2′** with three continuous stereogenic centers could be obtained as major products selectively under neutral and mild conditions just by a choice of an additive.

**Keywords:** annulation; asymmetric catalysis; enantioselectivity; intramolecular reactions; phosphines; ylides



**2/2′** = 90/10 – 94/6, 95 – 99% yield (1)

The development of a new method for the efficient construction of highly functionalized carbocycles and heterocycles is of significant importance in organic synthesis.[1] Nucleophilic phosphine-catalyzed annulations have emerged as a versatile method for the preparation of cyclic and heterocyclic compounds.[2–4] Of the annulations developed, however, only few asymmetric version has been reported with a few examples being related to chiral phosphine-initiated formal cycloaddition of allenes.[4] In a previous study on ylide chemistry,[5] we reported that the cyclization precursor allylic bromides **1** underwent readily a formal [3+2] cycloaddition at 80°C, affording benzobicyclo[4.3.0] compounds with excellent diastereoselectivities in good to excellent yields in the presence of 20 mol% of PPh$_3$ [Eq. (1)].[6] On the basis of these findings, recently, we found that when using
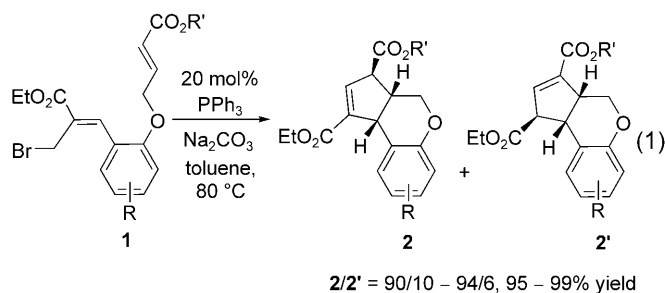
*tert*-butyl carbonate substrates **3** instead of bromides **1** the same reaction could proceed smoothly at room temperature to give the corresponding benzobicyclo-[4.3.0] compounds [Eq. (2)].[7]



**2/2′** = 93/7 – 98/2, 75 – 99% yield (2)
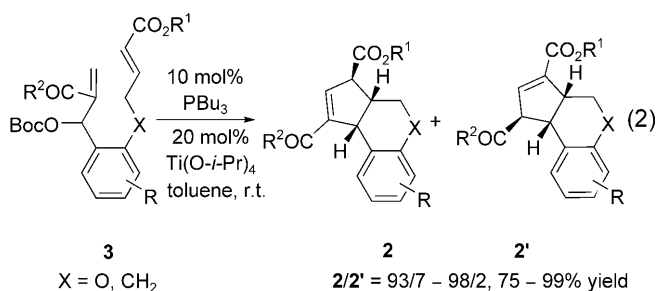
This result encouraged us to develop an asymmetric version by employing a chiral phosphine although it proved to be very difficult since the reaction involves remote control of enantioselectivity (Scheme 1), which usually leads to low enantioselectivity.[8] Very recently, we found that 10 mol% of a spirobiindane-based chiral phosphine (Scheme 2) could promote the
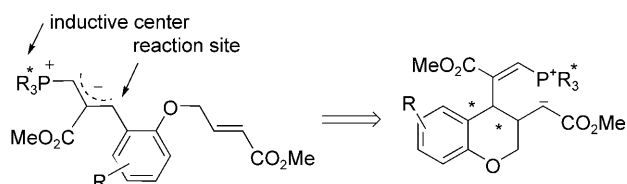
**Scheme 1.** Remote control for asymmetric induction.
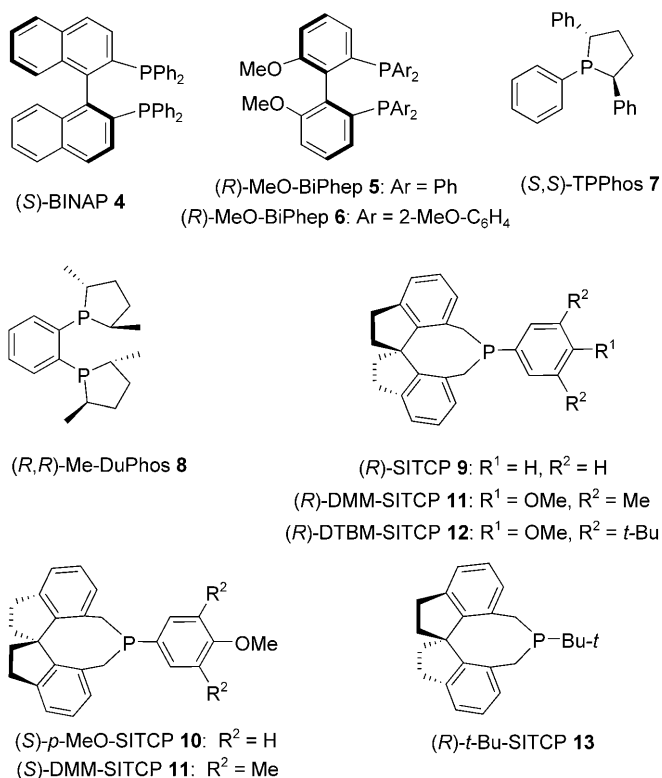


**Scheme 2.** Chiral phosphines investigated.

afore-mentioned formal [3+2] cycloaddition with high enantioselectivity in good to excellent yields. Herein, we wish to report our efforts on this asymmetric cyclization.

As shown in Table 1, the chiral phosphine strongly influences the enantioselection of this reaction. Using **3a** as a model substrate, (S)-BINAP[9a,b] could not catalyze the [3+2] reaction even if the reaction was performed at 70°C (entry 1, Table 1). (R)-MeO-BiPhep **5** and (R)-MeO-BiPhep **6**[9c,d] furnished products **2a** and **2a′** at 70°C with low ee values (entries 2 and 3, Table 1). In view of the stronger nucleophilicity of alkylphosphines than triarylphosphines, we tested chiral alkylphosphines. It was found that 10 mol% of (S,S)-TPPhos **7** and (R,R)-Me-DuPhos **8** could promote this reaction to give the desired annulation products in excellent yields at 10°C with 46% ee and 51% ee respectively (entries 4 and 5, Table 1). Gratifyingly, high enantioselectivities and excellent yields could be

achieved when spirobiindane-based chiral phosphines were employed (entries 6–12, Table 1).[10] (R)-SITCP **9** gave 83% ee and (S)-p-MeO-SITCP **10** furnished 82% ee. The enantioselectivity was slightly improved when (S)-DMM-SITCP **11** was employed (entry 8, Table 1). The reaction temperature proved also to influence the enantioselection. Lowering the temperature from 10°C to −5°C increased slightly the ee values to 85% and 89%, respectively, when (S)-p-MeO-SITCP **10** and (S)-DMM-SITCP **11** were used as catalysts (entry 7 vs. 9, 8 vs. 10, Table 1). Compared with (S)-DMM-SITCP **11**, (R)-DTBM-SITCP **12** resulted in very similar yield and ee but with a longer reaction time (entry 11, Table 1). (R)-t-Bu-SITCP **13** afforded the desired product with 92% ee in moderate conversion after 7 days (entry 12, Table 1). Solvent effects were also examined and toluene was the optimal (entries 10, 13 and 14, Table 1).

Under the optimal conditions, the generality of the current catalytic asymmetric reaction was evaluated by employing a variety of α,β-unsaturated carbonyl compounds **3a–3h**. As shown in Table 2, various α,β-unsaturated carbonyl compounds are good substrates for this reaction to give the desired optically active benzobicyclo[4.3.0] compounds with high enantioselectivities (77–95% ee) in excellent yields by employing 10 mol% of (S)-DMM-SITCP **11** as catalyst. As expected, the same tandem cyclization was carried out using 10 mol% of (R)-DMM-SITCP **11** as the catalyst to give the opposite enantioselectivity with 89% ee (entries 1 and 2, Table 2). Thus, both enantiomers could be obtained easily by the choice of the phosphine catalyst. Ester groups proved to influence the enantioselectivity. For example, methyl ester **3a** gave a better ee value than ethyl ester **3b** (entries 2 and 3, Table 2). Substituents on the benzene ring had also a slight effect on the enantioselection (entries 2–6, Table 2). Substrate **3d** with no substituent on the benzene ring gave the highest ee (95% ee, entry 5, Table 2). Carbon-linked substrate **3f** furnished the thermodynamic product **2f** as the major product with 83% ee (entry 7, Table 2). Ketones **3g** and **3h** are also suitable substrates for this annulation. In these cases, α,β-unsaturated ketones were obtained as the major products and the enantioselecivities decreased slightly (entries 8 and 9, Table 2). In addition, optically pure products (>99% ee) could be obtained through a simple recrystallization. For instance, **2e** with higher than 99% ee could be collected via a recrystallization from the mixture of ethyl acetate and petroleum ether (v/v, 1/10, entry 6, Table 2, recovered yield: 76%). In all cases examined, the diastereoselectivity of the current annulation was excellent and only one diastereomer was observed (determined by ^{1}H NMR and confirmed by chiral HPLC).

In our previous study, we found that by addition of Ti(O-i-Pr)$_4$ as an additive, the isomerization of prod-

**Table 1.** Effect of chiral phosphines on the catalytic asymmetric formal [3+2] cycloaddition.[a]
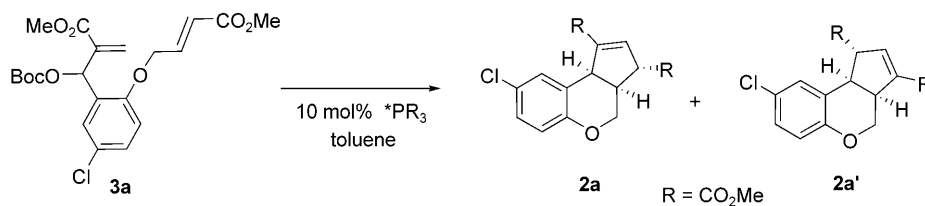


| Entry | *PR$_3$ | T [°C] | 2a/2a′[b] | Yield [%][c] | ee [%][d] |
|---|---|---|---|---|---|
| 1 | (S)-BINAP **4** | 70 | – | trace | – |
| 2 | (R)-MeO-BiPhep **5** | 70 | 19/81 | 88 | <3 |
| 3 | (R)-MeO-BiPhep **6** | 70 | 19/81 | 93 | 7 |
| 4 | (S,S)-TPPhos **7** | 10 | 88/12 | 93 | 46 |
| 5 | (R,R)-Me-DuPhos **8** | 10 | 25/75 | 90 | 51 |
| 6 | (R)-SITCP **9** | 10 | 67/33 | 98 | 83 |
| 7 | (S)-p-MeO-SITCP **10** | 10 | 20/80 | 84 | 82 |
| 8 | (S)-DMM-SITCP **11** | 10 | 20/80 | 97 | 85 |
| 9 | (S)-p-MeO-SITCP **10** | −5 | 22/78 | 90 | 85 |
| 10 | (S)-DMM-SITCP **11** | −5 | 20/80 | 90 | 89 |
| 11 | (R)-DTBM-SITCP **12** | −5 | 24/76 | 87 | 88 |
| 12 | (R)-t-Bu-SITCP **13** | −5 | 20/80 | 48[e] | 92 |
| 13[f] | (S)-DMM-SITCP **11** | −5 | 20/80 | 91 | 87 |
| 14[g] | (S)-DMM-SITCP **11** | −5 | 20/80 | 78 | 84 |

[a] *Reaction conditions:* PR$_3$ (10 mol%), **3a** (44 mg, 0.10 mmol) in toluene (0.1 M), 8–96 h.
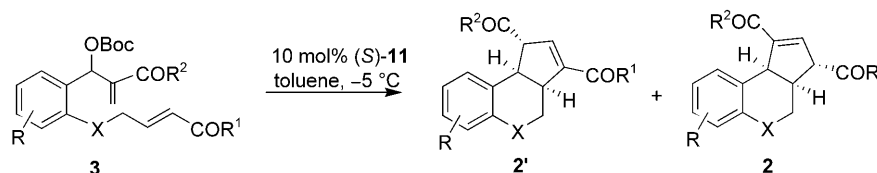[b] Determined by 300 MHz $^1$H NMR.
[c] Isolated yield for **2a+2a′**.
[d] The ee value is for the major product.
[e] Conversion by $^1$H NMR.
[f] CF$_3$C$_6$H$_5$ as the solvent.
[g] DCE as the solvent.

**Table 2.** Synthesis of functionalized benzobicyclo[4.3.0] compounds **2′** through catalytic asymmetric formal [3+2] cycloaddition.[a]



| Entry | 3 | R | R$^1$ | R$^2$ | X | 2′/2[b] | Yield [%][c] | ee [%][d] |
|---|---|---|---|---|---|---|---|---|
| 1 | **3a** | 4-Cl | OMe | OMe | O | 80/20 | 91 | 86 |
| 2[e] | **3a** | 4-Cl | OMe | OMe | O | 80/20 | 90 | 89 |
| 3[e] | **3b** | 4-Cl | OEt | OEt | O | 81/19 | 91 | 82 |
| 4 | **3c** | 4-Br | OMe | OMe | O | 80/20 | 98 | 87 |
| 5[f] | **3d** | H | OMe | OMe | O | 80/20 | 92 | 95 |
| 6[f] | **3e** | 2-OMe | OMe | OMe | O | 81/19 | 93 | 92 (>99) |
| 7[g] | **3f** | H | OMe | OMe | C | 10/90 | 81 | 83 |
| 8 | **3g** | 4-Br | OMe | Me | O | 25/75 | 83 | 84 |
| 9[g] | **3h** | H | Me | OMe | C | >95/5 | 76 | 77 |

[a] *Reaction conditions:* (S)-**11** (10 mol%), **3** (0.20 mmol) in toluene (0.1 M), −5 °C.[11]
[b] Determined by 300 MHz $^1$H NMR.
[c] Isolated yield for **2′+2**.
[d] The ee value is for the main product.
[e] 10 mol% (R)-**11** as the catalyst.
[f] After the reaction was complete, Cs$_2$CO$_3$ (14 mg, 0.2 equiv.) was added and stirred for another 10 h.
[g] Room temperature, 20 mol% (S)-**11** as the catalyst.

uct **2a** could be slowed down successfully and **2a** was isolated with high selectivity.[7] Using 10 mol% of (*S*)-DMM-SITCP **11** as the catalyst, under similar reaction conditions, we were pleased to find that the isomerization could also be blocked and optically active **2a** was isolated as the major product with the enantioselectivity almost maintained [entry 1 in Table 2 *vs.* Eq. (3)].



99% yield, 86% *ee*, **2a/2a'** = 93/7

$$(3)$$
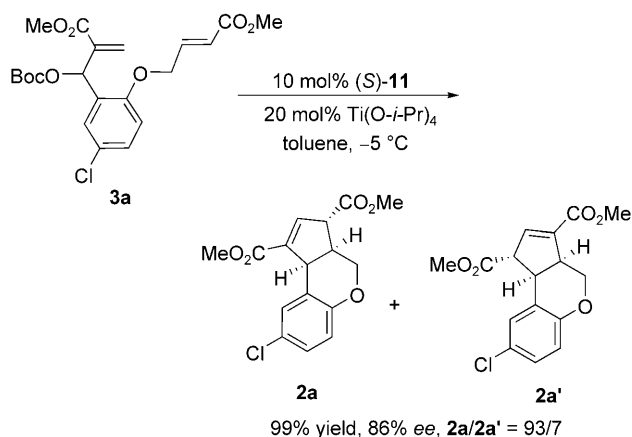
Using 20 mol% Ti(O-*i*-Pr)$_4$ as an additive, benzobicyclo[4.3.0] compounds **2a–2g** could also be synthesized as major products with high enantioselectivities (77–92% *ee*) in excellent yields by employing 10 mol% of (*S*)-DMM-SITCP **11** as the catalyst, as

shown in Table 3. Ketones **3h** also worked well but the thermodynamic product **2h'** was obtained as the major product with 77% *ee* (entry 9, Table 3). Notably, the *ee* values of both **2** and **2'** were almost identical with the addition of Ti(O-*i*-Pr)$_4$ or not (Table 2 vs. Table 3). These results further supported our previous supposed mechanism that products **2'** were isomerized from **2**.[7]

Thus, the present reaction provided a facile and an efficient method for the synthesis of optically active functionalized benzobicyclo[4.3.0] compounds in a high-yielding and stereocontrolled manner.

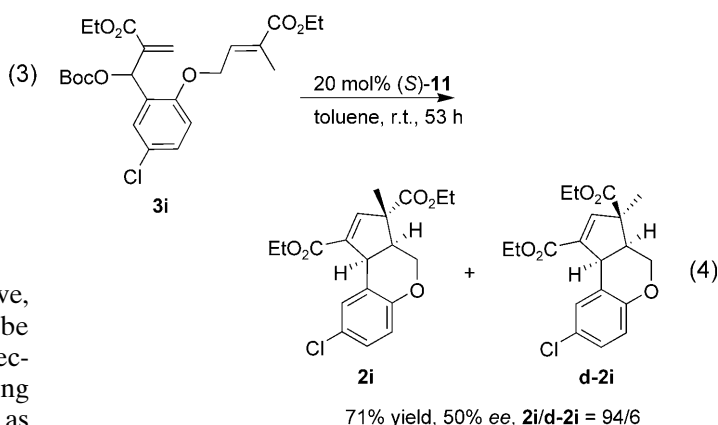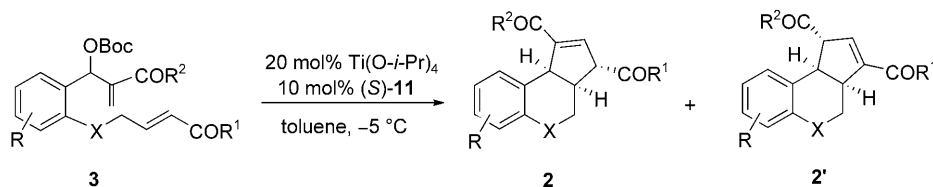In addition, α-methyl α,β-unsaturated ester **3i** also gave optically active benzobicyclo[4.3.0] compounds



$$(4)$$

71% yield, 50% *ee*, **2i/d-2i** = 94/6

**Table 3.** Synthesis of functionalized benzobicyclo[4.3.0] compounds **2** through catalytic asymmetric formal [3+2] cycloaddition.[a]



| Entry | 3 | R | R[1] | R[2] | X | 2/2'[b] | Yield [%][c] | *ee* [%][d] |
|---|---|---|---|---|---|---|---|---|
| 1 | **3a** | 4-Cl | OMe | OMe | O | 93/7 | 99 | 86 |
| 2[e] | **3a** | 4-Cl | OMe | OMe | O | 94/6 | 90 | 90 |
| 3[e] | **3b** | 4-Cl | OEt | OEt | O | 94/6 | 92 | 84 |
| 4 | **3c** | 4-Br | OMe | OMe | O | 93/7 | 90 | 77 |
| 5 | **3d** | H | OMe | OMe | O | 92/8 | 86 | 92 |
| 6 | **3e** | 2-OMe | OMe | OMe | O | 90/10 | 76 | 90 |
| 7[f] | **3f** | H | OMe | OMe | C | >95/5 | 78 | 83 |
| 8 | **3g** | 4-Br | OMe | Me | O | >95/5 | 92 | 85 |
| 9[f] | **3h** | H | Me | OMe | C | <5/95 | 75 | 77 |

[a] *Reaction conditions:* 10 mol% (*S*)-**11**, 20 mol% Ti(O-*i*-Pr)$_4$, **3** (0.20 mmol) in toluene (0.1 M), −5 °C.
[b] Determined by 300 MHz $^1$H NMR.
[c] Total yield for **2+2'**.
[d] The *ee* value is for the major product.
[e] 10 mol% (*R*)-**11** as the catalyst.
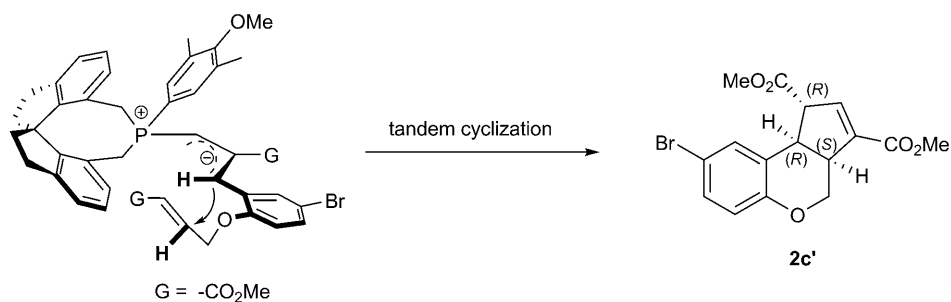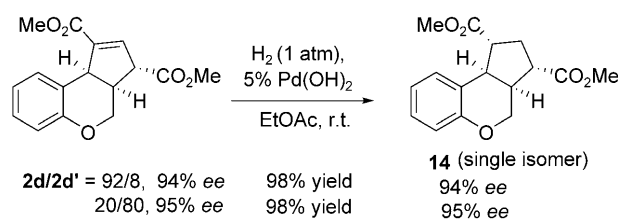[f] 20 mol% (*S*)-**11** as the catalyst, room temperature.

**Figure 1.** A possible stereochemical model.

**2i** and **d-2i** with a quaternary carbon as the products in good yield with moderate enantioselectivity using 20 mol% of (*S*)-DMM-SITCP **11** as the catalyst at room temperature [Eq. (4)].

The absolute configuration of the **2c′** was determined by X-ray analysis.[12] The stereochemical model, as shown in Figure 1, could explain the enantioselection, in which the first Michael addition occurred from the *Re* face of the Michael acceptor to deliver the product with the observed stereochemistry. The detailed mechanism requires further investigation.

The so-produced enantiomerically-enriched benzobicyclo[4.3.0] compounds can undergo several chemical transformations and are potentially useful in organic synthesis. For example, a mixture of optically active **2d** and **2d′** with a ratio of 92 to 8 or 20 to 80 was subjected to hydrogenation, affording the corresponding product **14**[12] as a single isomer that contains four contiguous stereocenters with excellent diastereoselectivity (*dr* > 99/1) (Scheme 3). Noticeably, in this chemical transformation, the enantioselectivities were well-maintained.

In summary, a catalytic asymmetric version of the intramolecular ylide annulation has been developed which affords high *ee* values and diastereoselectivities, and which further shows that spirobiindane-based chiral phosphines can be excellent organocatalysts as demonstrated by Fu very recently.[13] Both of optically active benzobicyclo[4.3.0] compounds **2** and **2′** with three continuous stereogenic centers could be obtained as major products selectively under neutral and mild conditions just by a choice of an additive. These products can undergo readily chemical transfor-

mations, providing a direct and practical access to the corresponding derivative with four contiguous stereocenters. The simple procedure, the high diastereoselectivity and enantioselectivities, excellent yields, metal-free catalyzed processes and, in particular, the facile chemical transformations make this method potentially useful in organic synthesis. Further investigations into the synthetic application of the current reaction are in progress.

## Experimental Section

### Typical Procedure for the Chiral Phosphine-Catalyzed Synthesis of Optically Active Benzo-bicyclo[4.3.0] Compounds 2′ (Examplified for the Preparation of Chiral 2a′)

To a solution of chiral phosphine (*S*)-DMM-SITCP **11** (8.2 mg, 0.020 mmol) in toluene (2.0 mL) was added substrate **3a** (88 mg, 0.20 mmol) at −5°C. The resulting mixture was stirred at −5°C for 57 h. After the reaction was complete, the mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with ethyl acetate. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 25:1) to afford the desired products **2a′** and **2a**, respectively. Total yield: 58.8 mg (91%), 86% *ee* for **2a′**. The **2a′/2a** ratio determined by ^{1}H NMR spectroscopy of the crude product is 80/20.

## Acknowledgements

**Scheme 3.** Chemical transformation of the products **2d** and **2d′**.

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[11] For detailed experimental procedures, see the Supporting Information.

[12] The structure of **14** and the absolute configuration of **2c′** were determined by X-ray analysis. CCDC 697325 (**14**) and CCDC 697326 (**2c′**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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