DOI: 10.1002/adsc.201300373

Enantioselective Organocatalytic Addition of Nitroalkanes to Oxindolylideneindolenines for the Construction of Chiral 3,3-Disubstituted Oxindoles

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Received: April 30, 2013; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300373.

Abstract: An enantioselective organocatalytic addition of nitroalkanes to oxindolylideneindolenines in the presence of bifunctional organocatalysts has been established to provide an efficient entry to 3,3-disubstituted oxindole derivatives in high yields and with excellent enantioselectivities. The transformation has been applied to the preparation of the key intermediate for a formal total synthesis of (+)-gliocladin C.

Keywords: arylsulfonyloxindoles; asymmetric synthesis; 3,3-disubstituted oxindoles; nitroalkanes; organocatalysis; quaternary stereogenic centers

The 3,3-disubstituted oxindole skeleton, containing all-carbon quaternary stereogenic centers, is prevalent in a wide array of biologically and pharmacologically relevant natural products (Figure 1).[1] Of particular interest are 3-functionalized 3-indolyloxindole skeletons **I**, which are commonly existing in alkaloids.[1f–h] Furthermore, these building blocks have been extensively used as key intermediates in the total synthesis of natural products.[1f,2] Due to the importance of the structural motif and the challenge in the construction of all-carbon quaternary stereogenic centers,[3] various methodologies leading to the preparation of 3,3-disubstituted oxindoles in an asymmetric fashion have been developed in recent decades.[4,5]

In terms of synthetic efficiency in the production of 3-functionalized 3-indolyloxindoles **IV**, structurally similar to **I**, the enantioselective substitution with **II** *via* a 3-(3*H*-indol-3-ylidene)indolin-2-one intermediate of type **III** represents the most straightforward approach (Figure 2a). Very recently, we found that the 3-hydroxy-3-indolyloxindole **V** was able to undergo

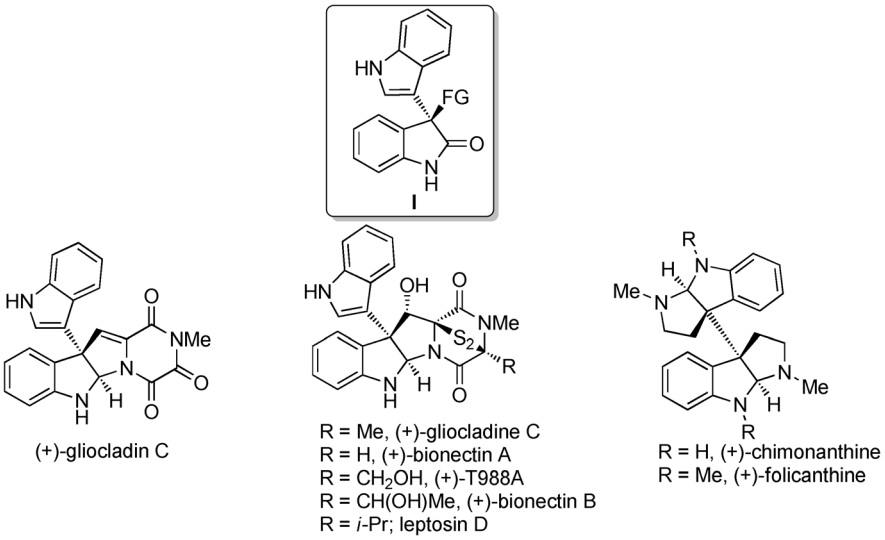


Figure 1. Natural products containing the 3,3-disubstituted oxindole scaffold.

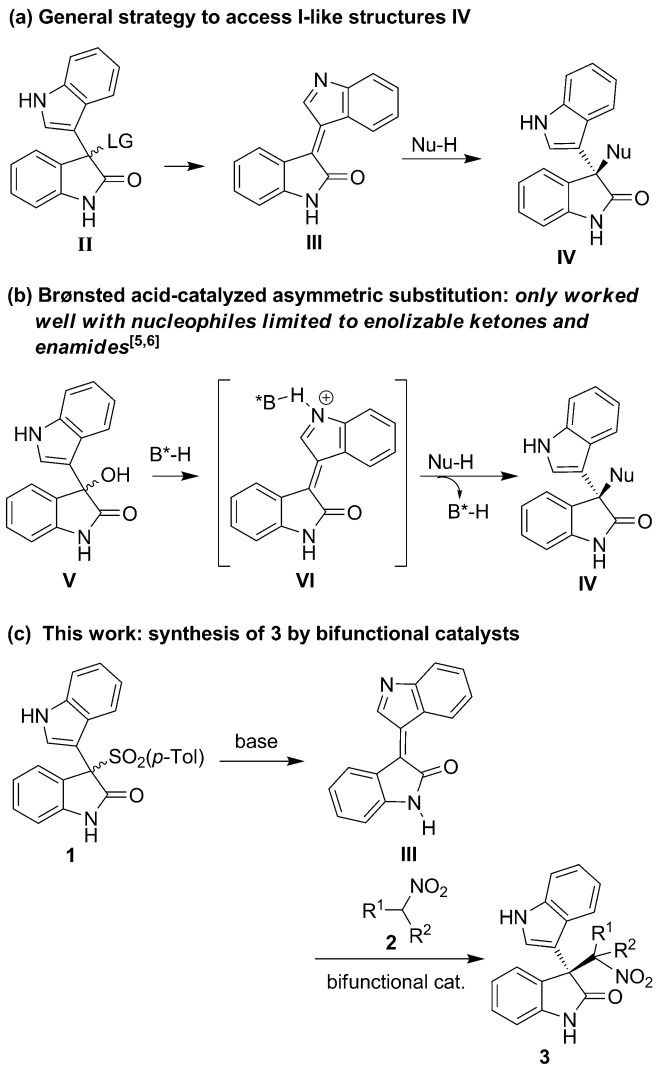


Figure 2. Alkylideneindolenine intermediates and their precursors.

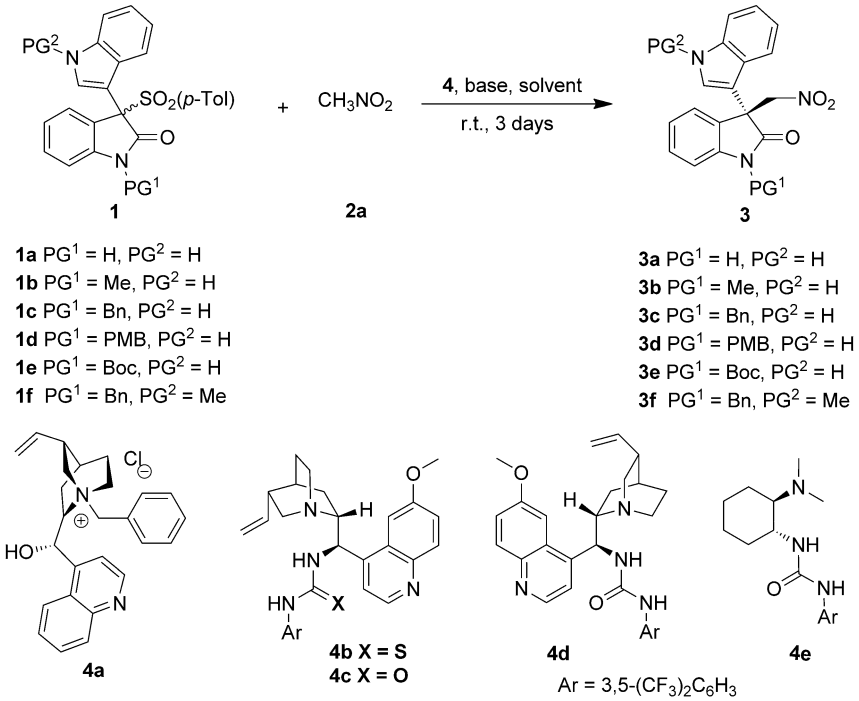
asymmetric substitution *via* sequential dehydration and enantioselective conjugate addition in the presence of chiral Brønsted acids (Figure 2b).[5] Independently, Guo and Peng established an enantioselective alkylation of ketones with 3-hydroxyoxindole *via* the intermediate **VI** catalyzed by chiral phosphoric acids (Figure 2b).[6] However, these two Brønsted acid-catalyzed asymmetric protocols only worked well with enolizable ketones or enamides. This inherent limitation to some degree inhibits their synthetic application. Thus, alternative enantioselective reactions based on the intermediate **III** are undoubtedly a valuable desire.[5,6]

Petrini and co-workers found that the reactive indolenine intermediates could be readily generated by the elimination of the leaving group from 3-(1-arylsulfonylalkyl)indoles under basic conditions,[7] allowing the realization of a large variety of nucleophilic substitution reactions to produce functionalized indole derivatives.[8] Johnston established an enantioselective Brønsted base-catalyzed alkylation of nitroalkanes with arylsulfonylindoles, which proceeded *via* the conjugate addition to the eneindolenine, in high yields and with fairly good enantiomeric excesses.[9] Petrini, Bernardi and co-workers found that the *Cinchona* alkaloids-derived bifunctional catalysts showed excellent catalytic activity and provided high levels of enantioselectivity for the similar reaction under solvent-free conditions.[10] Very recently, Arai established an enantioselective addition of indoles to isatin-derived nitroalkenes for the synthesis of 3-nitromethyl 3-indolyloxindoles.[4l] Inspired by these fundamental achievements, we proposed that in the presence of a bifunctional catalyst, 3-(1*H*-indol-3-yl)-3-tosylindolin-2-ones of type **1** would be converted into oxindolylideneindolenine intermediate **III**, which might participate in an enantioselective conjugate addition with nitroalkanes, to furnish 3-alkyl-3-indolyloxindole **3** (Figure 2c). Herein, we report our efforts directed toward this reaction and its application to a catalytic enantioselective formal total synthesis of (+)-gliocladin C.

A variety of structurally different chiral organocatalysts **4** were first investigated in the reaction between nitromethane **2a** and the 3-(1*H*-indol-3-yl)-3-tosylindolin-2-one **1a** in the presence of K_3PO_4 as an inorganic base in dichloromethane (Table 1, entries 1–5). Chiral ammonium salt **4a**[11] and bifunctional thiourea **4b**[12a] were able to catalyze the alkylation reaction but in lower yield and with moderate *ee* (entries 1 and 2). In comparison with the thiourea, bifunctional urea-based organocatalysts **4c–4e**[12,13] proved to be much more enantioselective (entries 3–5). In particular, the organocatalyst **4c** afforded the product with the highest level of enantioselectivity (entries 1–5). Subsequently, different solvents were also surveyed for the reaction catalyzed by **4c** and it was found that toluene was the most suitable medium (entries 3, 6–8). The variation of bases exerted a considerable impact on the reaction (entries 9–13). In addition, the N-substituents in the oxindole moieties had salutary effects on both the yield and enantioselectivity (entries 14–17). Notably, the introduction of a benzyl group gave a much higher yield (90%) and excellent enantioselectivity (95%) (entry 15). However, no reaction occurred when the nitrogen of the indole ring was methylated, as shown for **1f** (entry 18), suggesting that reaction proceeds *via* the proposed pathway rather than the indol-2-one (Figure 2). Notably, a scale-up procedure also afforded the product in good yield with retained enantiomeric excess (entry 19).

The optimized reaction conditions were then utilized to the substitution reaction of nitroalkanes with a variety of substituted 3-(arylsulfonylalkyl)oxindoles (Table 2). Either the indole or oxindole moiety substi-

Table 1. Catalysts screening and optimization of the reaction conditions.[a]



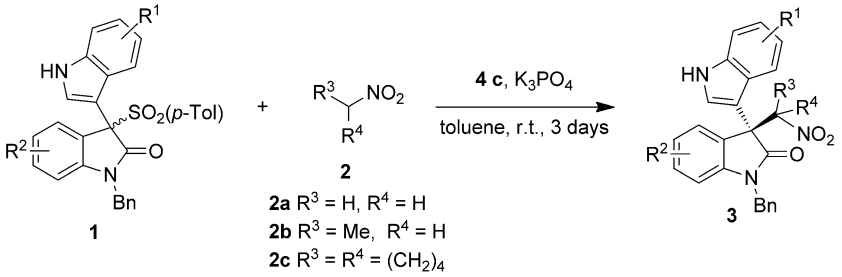
Entry	4	1	Base	Solvent	Yield [%][b]	*ee* [%][c]
1	**4a**	**1a**	K_3PO_4	CH_2Cl_2	15	55
2	**4b**	**1a**	K_3PO_4	CH_2Cl_2	16	36
3	**4c**	**1a**	K_3PO_4	CH_2Cl_2	22	56
4	**4d**	**1a**	K_3PO_4	CH_2Cl_2	25	52
5	**4e**	**1a**	K_3PO_4	CH_2Cl_2	5	52
6	**4c**	**1a**	K_3PO_4	$CHCl_3$	19	58
7	**4c**	**1a**	K_3PO_4	DCE	23	66
8	**4c**	**1a**	K_3PO_4	toluene	24	82
9	**4c**	**1a**	Et_3N	toluene	–	–
10	**4c**	**1a**	$KHCO_3$	toluene	–	–
11	**4c**	**1a**	K_2HPO_4	toluene	–	–
12	**4c**	**1a**	K_2CO_3	toluene	78	32
13	**4c**	**1a**	Cs_2CO_3	toluene	63	30
14	**4c**	**1b**	K_3PO_4	toluene	77	94
15	**4c**	**1c**	K_3PO_4	toluene	90	95
16	**4c**	**1d**	K_3PO_4	toluene	95	92
17	**4c**	**1e**	K_3PO_4	toluene	79	95[d]
18	**4c**	**1f**	K_3PO_4	toluene	–	–
19	**4c**	**1e**	K_3PO_4	toluene	64	95[e]

[a] *Reaction conditions:* **1** (0.1 mmol), **2a** (0.5 mmol), base(0.101 mmol), 10 mol% catalyst **4**, with 1 mL solvent.
[b] Isolated yield.
[c] The *ee* value was determined by HPLC analysis using a chiral stationary phase.
[d] The reaction was carried out under argon in the presence of 50 mg Na_2SO_4.
[e] 0.5 g of **1** was used.

tuted with either electron-donating or electron-withdrawing substituents was well tolerated and afforded products in good to excellent yields (79–98%) and with excellent enantioselectivities (89–98% *ee*) (entries 1–16). Notably, the α-branched nitroalkanes **2b** and **2c** were also able to participate in the substitution reaction and, respectively, furnished the corresponding products **3w** and **3x** in good yields (83% and 78%, respectively) and high levels of enantioselectivity (entries 17 and 18).

More significantly, the reaction conditions were also amenable to asymmetric substitution reactions with acidic methylene nucleophiles. For example, the dibenzyl malonate **2d** smoothly underwent a highly

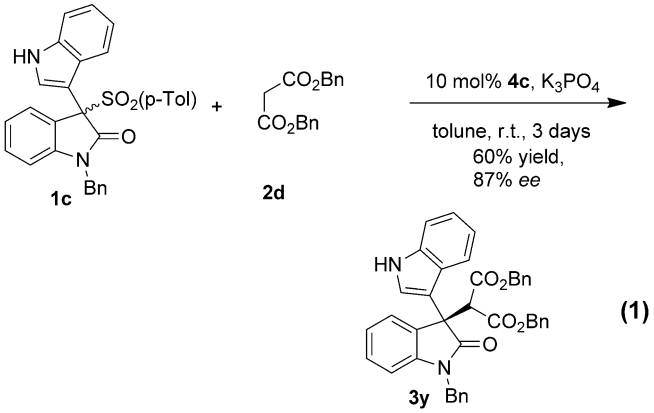
Table 2. The scope of 3-(1-arylsulfonylalkyl)oxindoles.[a]



Entry	**1** (R^1, R^2)	**2**	**3**	Yield [%][b]	*ee* [%][c]
1	**1g** (5-Cl, H)	**2a**	**3g**	80	89
2	**1h** (5-Br, H)	**2a**	**3h**	98	90
3	**1i** (5-Me, H)	**2a**	**3i**	97	97
4	**1j** (5-OMe, H)	**2a**	**3j**	85	92
5	**1k** (6-F, H)	**2a**	**3k**	90	93
6	**1l** (6-Cl, H)	**2a**	**3l**	77	92
7	**1m** (7-Me, H)	**2a**	**3m**	95	94
8	**1n** (2-Me, H)	**2a**	**3n**	97	90
9	**1o** (H, 5-F)	**2a**	**3o**	76	93
10	**1p** (H, 5-Cl)	**2a**	**3p**	97	99
11	**1q** (H, 5-Br)	**2a**	**3q**	92	93
12	**1r** (H, 5-Me)	**2a**	**3r**	96	98
13	**1s** (H, 5-OMe)	**2a**	**3s**	84	90
14	**1t** (H, 6-Br)	**2a**	**3t**	95	95
15	**1u** (H, 7-Br)	**2a**	**3u**	79	96
16	**1v** (H, 7-CF_3)	**2a**	**3v**	88	93
17	**1p** (H, 5-Cl)	**2b**	**3w**	83	92[d]
18	**1c** (H, H)	**2c**	**3x**	78	78

[a] *Reaction conditions:* **1** (0.1 mmol), **2** (0.5 mmol), K_3PO_4 (0.101 mmol), 10 mol% catalyst **4c**, with 1 mL toluene.
[b] Isolated yield.
[c] The *ee* value was determined by HPLC analysis using a chiral stationary phase.
[d] The values refer to the main diastereoisomer's *ee*; the other diastereoisomer's *ee* = 90%; *dr* = 1.2/1, determined by ^{1}H NMR spectroscopy.

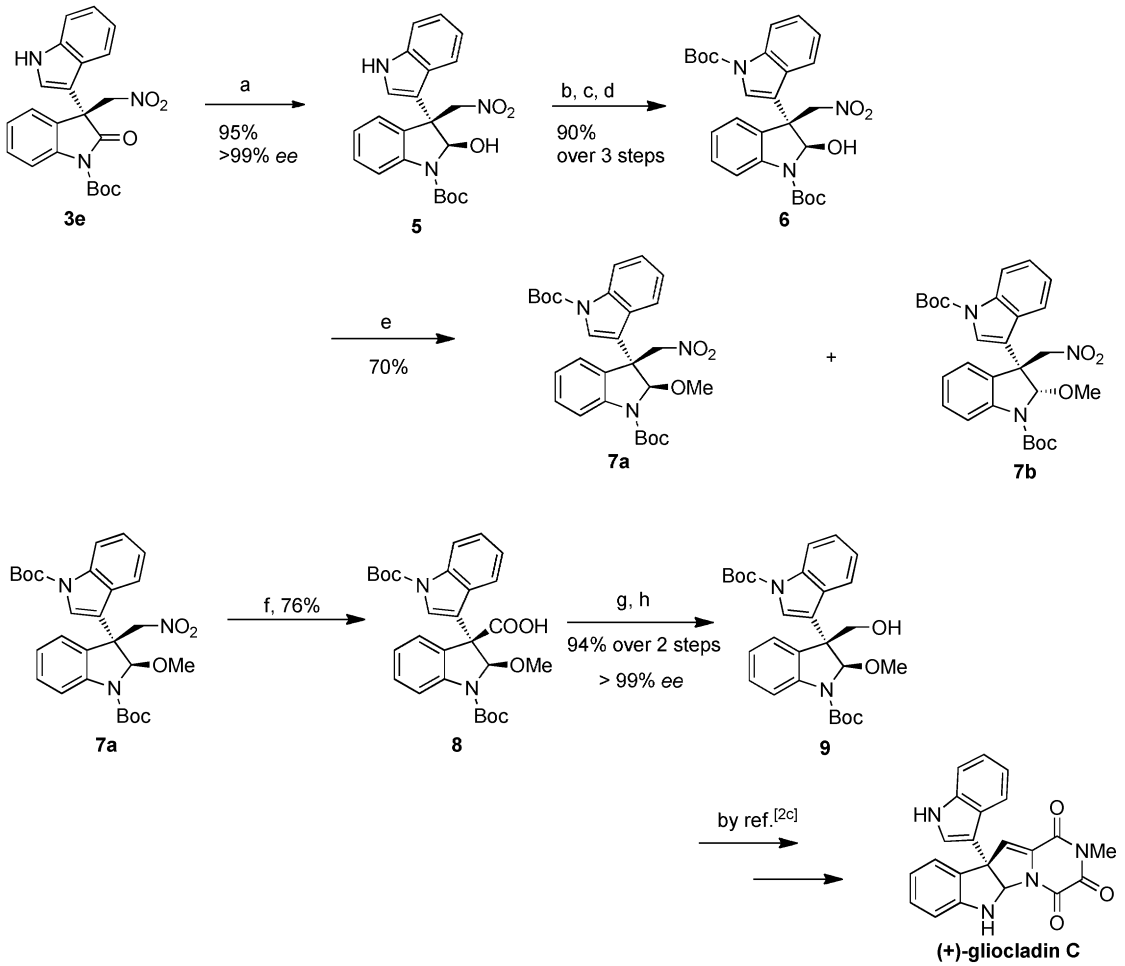
enantioselective substitution reaction with **1c**, to produce **3y** in 60% yield and with 87% *ee* under the optimized conditions [Eq. (1)].



(1)

(+)-Gliocladin C is a typical member of the alkaloid family containing the 3-alkyl-3-indolyloxindole skeleton, exhibiting significant cytotoxic activity against the murine P388 lymphocytic leukemia cells.[1g] Thus, great efforts have been directed toward the development of synthetic approaches for the total synthesis of natural products of this family and indeed led to several elegant total synthesis.[2a–d,5,14] However, new synthetic routes to access this molecule are still of great importance.

Thus, we finally investigated the feasibility to apply the asymmetric reaction to the catalytic enantioselective formal total synthesis of (+)-gliocladin C (Scheme 1). The reduction of the compound **3e**[15] afforded the corresponding hemiaminal **5** in 95% yield with a single diastereomer. Then, the TMS group and Boc group were respectively introduced to protect the hydroxy and nitrogen atom of hemiaminal **5** in the indole ring. Afterwards, the TMS group was removed with TBAF, providing the hemiaminal **6** in a 90% yield over 3 steps. The obtained hemiaminal **6** was exposed to a solution of trimethyl orthoformate and $BF_3{\cdot}Et_2O$ at room temperature, to generate **7** as a 2/1 (**7a**/**7b**) diastereomeric mixture in 70% overall yield.



Scheme 1. Application in the synthesis of the intermediate towards (+)-gliocladin C. *Reaction conditions:* (a) $NaBH_4$, MeOH/THF, room temperature (95% *ee*, >99% *ee* after a single recrystallization); (b) TMSCl, imidazole, CH_2Cl_2, room temperature; (c) $(Boc)_2O$, DMAP, CH_2Cl_2, room temperature; (d) TBAF, THF, room temperature; (e) $BF_3{\cdot}Et_2O$, $CH(CH_3O)_3$, Et_2O, room temperature; (f) $NaNO_2$, AcOH, DMSO, 35 °C; (g) ClCOOMe, Et_3N, THF, room temperature; (h) $NaBH_4$, MeOH, room temperature.

Basically, the completion of the synthesis required conversion of the primary nitro group of **7a** to an aldehyde *via* the Nef reaction.[16] However, the aldehyde could not be generated although a variety of hydrolytic or oxidative conditions were examined. Fortunately, an acid **8** could be generated from compound **7a** by a protocol developed by Mioskowski.[17] By sequential protection and reduction, the acid **8** was transformed into an alcohol **9**, which was in agreement with the data reported by Overman. Finally, with the key intermediate **9** in hand, (+)-gliocladin C could undoubtedly be accessed by following the synthetic route developed by Overman.[2c]

In conclusion, we have developed a highly enantioselective organocatalytic addition of nitroalkanes to oxindolylideneindolenines catalyzed by a *Cinchona*-derived urea catalyst under basic reaction conditions. The protocol represents a new approach to access polyfunctionalized 3,3-disubstituted oxindoles with the generation of a quaternary all-carbon stereogenic center at C-3. More importantly, this method could be applied to the enantioselective formal total synthesis of (+)-gliocladin C.

Experimental Section

General Procedure for the Addition of Nitroalkanes to Oxindolylideneindolenines

To a solution of 3-(1-arylsulfonylalkyl)oxindole **1** (0.1 mmol) in toluene (1 mL) were added catalyst **4c** (10 mol%, 5.8 mg) and K_3PO_4 (0.101 mmol, 21.4 mg). The reaction mixture was stirred at room temperature for 15 min. Nitroalkane **2** (0.5 mmol) was then added to the mixture. The resulting suspension was stirred at room temperature for 3 days, then was diluted with EtOAc (15 mL), followed by washing with H_2O (10 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was fi-

nally purified by flash chromatography (petroleum ether:-ethyl acetate = 2: 1) on silica gel to give product **3**.

Acknowledgements

We are grateful for financial support from NSFC (20732006), MOST (973 program 2009CB825300), the Ministry of Education, and CAS.

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[15] CCDC 921642 [(*S*)-**3e**] 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. The absolute configurations of compounds **3a**–**3y** were determined by analogy to **3e**.

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