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Stereoselectivity of the Petasis reaction with various chiral amines and styrenylboronic acids*

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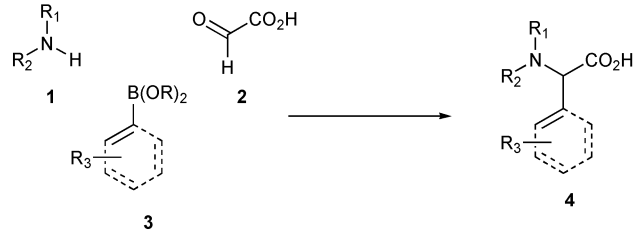
Abstract: Several chiral amines were investigated for the stereoselective preparation of homophenylalanine derivatives using the Petasis reaction. Chiral secondary amines such as *N*,α-dimethylbenzylamine and *N*-benzylphenylglycinol gave the best results in terms of both yield and diastereoselectivity. The use of *N*-benzylphenylglycinol leads directly to 3-alkenyl-4-benzyl-5-phenyloxazin-2-one products. Intriguing variation was observed in the stereoselectivity of reactions employing *para*-substituted styrenylboronic acid substrates, where presumably only electronic factors are involved.

Keywords: amino acids; Petasis reaction; boronic acids; stereoselective; multicomponent coupling.

INTRODUCTION

The Petasis reaction, or boronic acid Mannich reaction, involves the three-component coupling of an amine, aldehyde, and organoboronic acid [1–3]. One of the most important uses of the Petasis reaction is the synthesis of α-amino acids using glyoxylic acid **2** as the aldehyde component [4,5]. A range of aryl- and vinyl-boronic acids **3** have been employed in such reactions, allowing the production of a wide variety of arylglycine and vinylglycine derivatives **4** [6–20] (Scheme 1). The use of chiral amines allows the stereoselective production of α-amino acid derivatives.



Scheme 1

*Paper based on a presentation at the 21st International Congress for Heterocyclic Chemistry (ICHC 21), 15–20 July 2007, Sydney, Australia. Other presentations are published in this issue, pp. 669–805.

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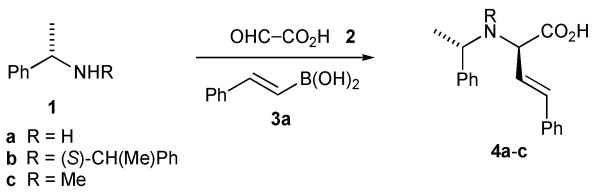
Petasis originally reported the use of the chiral amines α-methylbenzylamine and phenylglycinol in the preparation of homophenylalanine and phenylglycine derivatives [4,5]. While the use of α-methylbenzylamine gave only poor to moderate diastereoselectivities, phenylglycinol reportedly gave high (>99 %) diastereoselectivity. Various research groups have used other chiral benzylic and pyrrolidine-based amines in Petasis reactions with widely varying degrees of diastereoselectivity obtained [6,8,14]. Given the enormous potential of the Petasis reaction as a general tool for the synthesis of α-amino acids, we have investigated the effects of the nature and chirality of the amine and organoboron species on the stereochemical outcome of the Petasis reaction.

RESULTS AND DISCUSSION

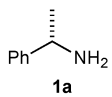
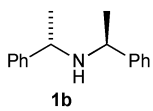
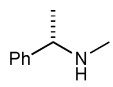
α-Methylbenzylamine-based auxiliaries

We have previously reported a study on the use of α-methylbenzylamine derivatives in the Petasis reaction [14]. The reaction of (*S*)-α-methylbenzylamine **1a** with styrenylboronic acid **3a** yielded the Petasis reaction product **4a** in high yield, as previously demonstrated by Petasis and coworkers [5]. The use of the chiral secondary amine bis-(α-methylbenzyl)amine **1b** gave the product **4b** in moderate yield but with very high stereoselectivity (Scheme 2, Table 1). Only one diastereomer was observed by ^{1}H NMR spectroscopy, indicating the product **4b** was formed in >95:5 diastereomeric ratio. The low yield from the reaction of amine **1b** is consistent with the results of other α,α-branched secondary amines, such as diisopropylamine.



Scheme 2

Table 1 Comparison of Petasis reaction yields and stereoselectivities from Scheme 2.

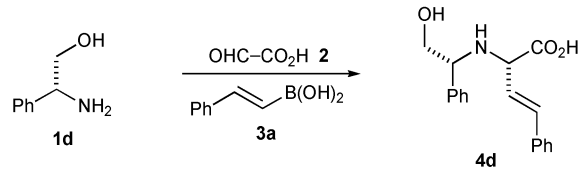
Amine substrate	Yield	d.r.
 **1a**	81	3.3:1
 **1b**	38	>95:5
 **1c**	89	>95:5

Despite the poor yields obtained from amine **1b**, the high degree of stereoselectivity obtained prompted the investigation of a chiral secondary amine with a reduced degree of branching. Accordingly, reaction with (*S*)-*N*,α-dimethylbenzylamine **1c** was conducted. Reaction of amine **1c** with styrenylboronic acid **3a** and glyoxylic acid **2** gave the corresponding amino acid product **4c** in good

yield (89 %) and high stereoselectivity (>95:5 d.r.) (Table 1). Similar results with chiral secondary amines have been observed by Nanda et al. [8] in which the three-component coupling of phenylboronic acid, glyoxylic acid, and various chiral 2-substituted pyrrolidines were studied. In all cases, the products were obtained in good yield and >95:5 diastereomeric ratio. The use of 2,5-dimethylpyrrolidine, however, resulted in no reaction, in agreement with our observations with doubly branched secondary amines. In general, it is apparent that chiral secondary amines give Petasis reaction products in much greater stereoselectivity than reactions of related chiral primary amines. However, secondary amines containing two chiral alkyl substituents by definition have a high degree of branching, which leads to low yields. Nevertheless, we have shown that only one chiral alkyl substituent is required for a high degree of stereoselectivity. Chiral secondary amines such as **1c**, containing one chiral alkyl substituent and one achiral (i.e., unbranched) substituent are the optimal reagents for Petasis reactions as they give rise to both high yields and high diastereoselectivities.

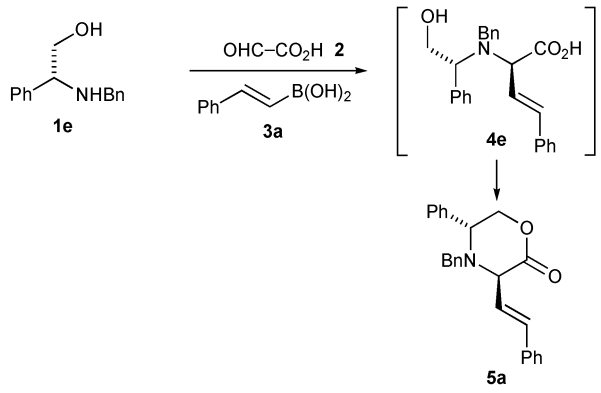
Phenylglycinol-based auxiliaries

Petasis reports the reaction of styrenylboronic acid **3a** with phenylglycinol **1d**, and glyoxylic acid **2** gives the amino acid product **4d** in 78 % yield and >99 % diastereoselectivity [5] (Scheme 3), but these results were not reproducible in our laboratories. We consistently observe formation of the product in a 3:1 ratio, similar to that observed from α-methylbenzylamine. It should be noted that in order to obtain accurate and reproducible diastereomeric ratios, reaction mixtures were evaporated and the crude product analyzed by ^{1}H NMR spectroscopy. On a preparative scale, the zwitterionic amino acid product precipitates from solution and is isolated by filtration. However, material obtained in this manner was found to be of variable diastereomeric ratio, from as low as 3:1 to as high as >95:5, presumably due to differing degrees of fractional crystallization. This may explain the discrepancy between our results and those reported by Petasis. Nevertheless, our results with phenylglycinol were consistent with our observation that primary amines give moderate levels of diastereoselectivity.



Scheme 3

We therefore sought to extend the findings with chiral secondary amines to phenylglycinol derivatives, and chose *N*-benzylphenylglycinol **1e** as a suitable chiral secondary amine. Use of *N*-benzylphenylglycinol **1e** in place of phenylglycinol **1d** gave the corresponding products with much higher diastereoselectivity. In these reactions, the initial Petasis reaction product **4** cyclizes to give the corresponding oxazinone **5**. Use of styrenylboronic acid **3a** gave the oxazinone **5a** in excellent yield and 20:1 diastereomeric ratio, with the *trans*-oxazinone obtained in 80 % isolated yield after recrystallization (Scheme 4 and Table 2). The stereochemistry of oxazinone **5a** was determined by X-ray crystallography (Fig. 1) [21].



Scheme 4

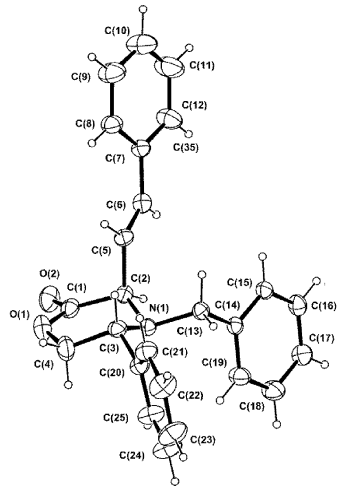
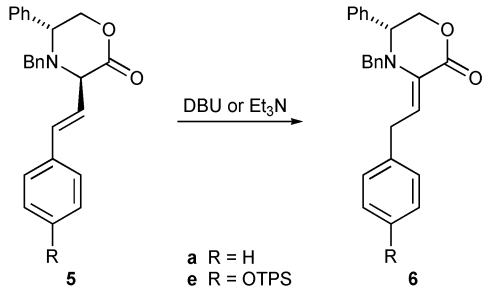


Fig. 1 ORTEP diagram of oxazinone **5a**.

Table 2 Comparison of Petasis reaction yields and stereoselectivities from Scheme 6.

Product	R	Yield (%)	d.r.
5a	H	89	20:1
5b	NO_2	–	–
5c	CH_3	92	1.3:1
5d	OAc	82	1.2:1
5e	OTPS	90	1:1

This reaction is closely related to the system described by Jiang and Xu [6]. In their case, treatment of styrenylboronic acid **3a**, glyoxylic acid **2**, and *N*-propargylphenylglycinol gave the corresponding *N*-propargyloxazinone in a 1.5:1 diastereomeric ratio, with the *cis*-isomer being the major product. Equilibration of the diastereomeric mixture in the presence of base gave the *cis*-isomer only. Perplexingly, our attempts to convert our closely related *N*-benzyl-*trans*-oxazinone **5a** to the corresponding *cis*-isomer under similar conditions resulted only in isomerization of the double bond into conjugation to give **6a** (Scheme 5).

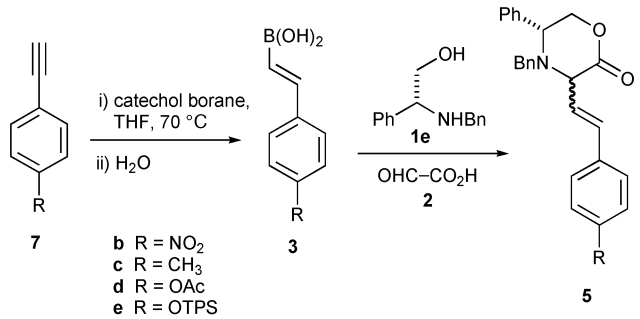


Scheme 5

As stated above, these results show that the use of chiral secondary amines containing only one branched substituent give optimal yields and diastereoselectivities, though the related observations of Jiang and Xu show that there are always exceptions to the rule and we are still a long way from a complete understanding of the Petasis reaction.

Substituted styrenylboronic acids

Given the successful preparation of dehydrohomophenylalanine derivative **5a** through the Petasis reaction with *N*-benzylphenylglycinol **1e**, we were keen to investigate the use of substituted styrenylboronic acids to give functionalized homophenylalanine derivatives. Accordingly, a range of 4-substituted styrenylboronic acids **3** was prepared by hydroboration of the corresponding phenylacetylenes **7** (Scheme 6) (which were prepared from the corresponding iodobenzenes through Sonagashira coupling) [22].



Scheme 6

Attempted Petasis reaction of *p*-nitrostyrenylboronic acid **3b** with *N*-benzylphenylglycinol **1e** and glyoxylic acid **2** gave none of the oxazinone product, with unreacted boronic acid recovered. Use of *p*-methylstyrenylboronic acid **3c** gave the oxazinone **5c** in good yield, but with low diastereoselectivity (1.3:1 diastereomeric ratio). Similarly, use of *p*-acetoxystyrenylboronic acid **3d** gave oxazinone **5d** in 82 % yield and 1.2:1 diastereomeric ratio, while the *p*-OTPS-styrenylboronic acid **3e** gave oxazinone **5e** in 90 % yield and 1:1 diastereomeric ratio (Table 2). To check that the mixture of isomers was not arising through equilibration, oxazinone **5e** was subject to the conditions described by Jiang and Xu [6], as described for **5a**, but again only double bond isomerization to give the α,β-unsaturated system **6e** was observed (Scheme 5). From these results, it is apparent that the electronic nature of the substituent is influencing both the rate and diastereoselectivity of the reactions. The lack of reactivity exhibited through introduction of the strongly electron-withdrawing nitro-group is consistent with decreased

nucleophilicity of the corresponding boronate intermediate. There is also a possible trend with a decrease in diastereoselectivity as more electron-donating substituents are incorporated in the styrenylboronic acid substrate. While substituent electronic effects have been observed to greatly influence diastereoselectivity in related systems [23,24], the significantly greater selectivity observed in the unsubstituted system compared with that for the substituted systems does seem surprising, and no apparent rationale is evident. Accordingly, further studies to fully elucidate the factors effecting the stereoselectivity of these reactions are underway.

In summary, we have shown that the Petasis reaction employing chiral secondary amines such as *N*,α-dimethylbenzylamine and *N*-benzylphenylglycinol is an efficient and stereoselective method for the preparation of homophenylalanine and homotyrosine derivatives.

Experimental

*General procedure for preparation of N-benzyl-5-phenyloxazin-2-ones **5***

Glyoxylic acid **2** (0.405 g, 4.4 mmol) and (*R*)-*N*-benzylphenylglycinol **1e** (1.00 g, 4.4 mmol) were stirred in CH_2Cl_2 (20 mL) at room temperature for 10 min. *trans*-2-Arylethenyl boronic acid **3** (4.4 mmol) was added and the reaction stirred for 48 h at room temperature. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica to give the product as a white solid.

5a: Recrystallization from hexane/ethyl acetate yielded the product as a single diastereomer as colorless crystals (1.30 g, 80 %). M.p.: 157–158 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44–7.27 (m, 15H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.42 (dd, *J* = 7.8 Hz, 15.8 Hz, 1H), 4.62 (dd, *J* = 4.5 Hz, 11.3 Hz, 1H), 4.54 (dd, *J* = 8.1 Hz, 11.3 Hz, 1H), 4.33 (d, *J* = 8.1 Hz, 1H), 4.32 (d, *J* = 7.8 Hz, 1H), 3.71 (d, *J* = 13.7 Hz, 1H), 3.49 (d, *J* = 13.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.1, 137.1, 137.0, 136.7, 135.9, 129.0, 128.6, 128.5, 128.3, 128.1, 127.4, 126.7, 121.4, 72.6, 62.5, 56.9, 52.7. IR (NaCl disc): 3028, 1740, 968, 700 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{23}NO_2$: *m/z* 369.1729; found *m/z* 369.1729. Calcd for $C_{25}H_{23}NO_2$: C: 81.3, H: 6.3, N: 3.8 %, found C: 81.3, H: 6.3, N: 3.8 %.

5c: 1.3:1 mixture of diastereomers (92 %). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 7.61 (d, *J* = 7.4 Hz, 2H), 7.51–7.16 (m, 12H), 6.65 (d, *J* = 15.8 Hz, 1H), 6.43 (dd, *J* = 7.8 Hz, 15.8 Hz, 1H), 4.65 (dd, *J* = 4.5, 11.4 Hz, 1H), 4.56 (dd, *J* = 11.4, 8.4, Hz, 1H), 4.43–4.35 (m, 3H), 3.75 (d, *J* = 13.7 Hz, 1H), 3.54 (d, *J* = 13.7 Hz, 1H), 2.39 (s, 3H); (minor diastereomer) δ 7.61 (d, *J* = 7.4 Hz, 2H), 7.51–7.16 (m, 12H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 5.2 Hz, 16.0 Hz, 1H), 4.43–4.35 (m, 3H), 4.21 (br d, *J* = 11.6 Hz, 1H), 4.10 (br d, *J* = 11.6, 1H), 3.90 (d, *J* = 13.8 Hz, 1H), 3.72 (d, *J* = 13.8 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.3, 169.5, 138.5, 138.2, 138.1, 137.50, 137.45, 137.0, 136.8, 133.7, 133.5, 132.6, 129.71, 129.68, 129.6, 129.5, 129.3, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.9, 127.7, 126.9, 126.8, 126.7, 120.5, 77.6, 77.3, 77.1, 72.9, 71.2, 63.7, 63.2, 62.9, 62.8, 58.0, 57.3, 53.1, 30.0, 21.53, 21.49. IR: 3028, 2922, 1741, 1455, 907, 697 cm^{-1}.

5d: 1.2:1 mixture of diastereomers (82 %). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.44–7.22 (m, 12H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.39 (dd, *J* = 7.8, 15.8 Hz, 1H), 4.62 (dd, *J* = 4.5, 11.4 Hz, 1H), 4.53 (dd, *J* = 8.2, 11.4 Hz, 1H), 4.35–4.32 (m, 3H), 3.72 (d, *J* = 13.7 Hz, 1H), 3.49 (d, *J* = 13.7 Hz, 1H), 2.32 (s, 3H); (minor diastereomer) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.44–7.22 (m, 12H), 6.73 (dd, *J* = 16.0, 1.8 Hz, 1H), 6.15 (dd, *J* = 5.6, 16.0 Hz, 1H), 4.39 (dd, *J* = 1.8, 5.3 Hz, 1H), 4.35–4.32 (m, 3H), 4.20 (dd, *J* = 3.5, 11.4 Hz, 1H), 4.08 (dd, *J* = 3.5, 11.4 Hz, 1H), 3.89 (d, *J* = 13.8 Hz, 1H), 3.67 (d, *J* = 13.8 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.6, 169.3, 150.9, 150.6, 137.9, 137.31, 137.28, 136.7, 136.0, 134.2, 134.0, 131.8, 129.73, 129.69, 129.40, 129.37, 129.3, 129.01, 128.99, 128.97, 128.92, 128.89, 128.84, 128.79, 128.78, 128.74, 128.65, 128.4, 128.2, 128.1, 128.0, 127.92, 127.85, 127.7, 127.66, 122.2, 122.1, 122.04, 121.97, 77.6, 77.3, 77.1, 72.9, 71.2, 63.7, 63.2, 62.8, 58.0, 57.3, 53.1, 21.4. IR: 3031, 1742, 1506, 1190, 907, 697 cm^{-1}. MS *m/z* 428 $[M+H]^+$.

5e: 1:1 mixture of diastereomers (90 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72–7.69 (m, 4H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.42–7.13 (m, 16H), 7.08 (d, *J* = 8.6 Hz, 1H), 6.71 (m, 2H), 6.60 (dd, *J* = 1.6, 15.9 Hz, 0.5H), 6.50 (d, *J* = 15.8 Hz, 0.5H), 6.20 (dd, *J* = 7.9, 15.8 Hz, 0.5H), 5.98 (dd, *J* = 5.8, 15.9 Hz, 0.5H), 4.57 (dd, *J* = 4.5, 11.4 Hz, 0.5H), 4.48 (dd, *J* = 8.1, 11.3 Hz, 0.5H), 4.35–4.30 (m, 1H), 4.27–4.22 (m, 1H), 4.15 (dd, *J* = 3.5, 11.3 Hz, 0.5H), 4.03 (dd, *J* = 3.5, 10.7 Hz, 0.5H), 3.83 (d, *J* = 13.9 Hz, 0.5H), 3.67 (d, *J* = 11.1 Hz, 0.5H), 3.64 (d, *J* = 11.3 Hz, 0.5H), 3.44 (d, *J* = 13.6 Hz, 0.5H), 1.21 (s, 4.5H), 1.20 (s, 4.5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 137.1, 135.4, 132.7, 131.9, 129.9, 129.4, 129.0, 128.5, 128.4, 127.8, 127.6, 119.8, 62.5, 56.9, 26.5, 19.4. IR (NaCl disc): 2932, 2858, 1732, 822 cm^{-1}. HRMS (EI) calcd for $C_{41}H_{41}NO_3Si$; 623.2856: found *m/z* 623.2854. Calcd for $C_{41}H_{41}NO_3Si$; C: 78.9, H: 6.6, N: 2.3 %, found C: 78.6, H: 6.8, N: 2.3 %.

*General procedure for preparation of (E)-2-arylethenylboronic acids **3***

The 4-substituted phenylacetylene **7** [22] (2.0 mmol) was added to a solution of catechol borane (1 M in THF, 3 mL) and the mixture was stirred under nitrogen at 75 °C for 16 h. The reaction was cooled to room temperature and water (10 mL) was added. The precipitate was isolated by filtration and washed with water. The product was purified by chromatography on silica to yield the boronic acid (with varying amounts of boroxine) as a white solid.

3b: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 18.4 Hz, 1H), 7.53 (d, J = 8.7 Hz, 2H), 6.47 (d, *J* = 18.4 Hz, 1H).

3c: (80 %). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75 (d, *J* = 18.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.28 (d, *J* = 18.2 Hz, 1H), 2.40 (s, 3H). MS (ESI$^-$) *m/z* 305 [2M–H_2O–H$^+$], 161 [M–H$^+$].

3d: (62 %). ^{1}H NMR (CD_3OD, 500 MHz) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 18.1 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.34 (d, *J* = 18.1 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (CD_3OD, 125 MHz) δ 171.18, 152.68, 148.48, 137.10, 129.13, 123.08, 21.07. MS (ESI$^-$) *m/z* 205 [M–H$^+$].

3e: (75 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73–7.69 (m, 4H), 7.60 (d, *J* = 18.1 Hz, 1H), 7.46–7.14 (m, 8H), 6.77–6.73 (m, 2H), 6.03 (d, *J* = 18.1 Hz, 1H), 1.04 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.7, 130.2, 129.9, 128.8, 128.3, 128.0, 119.6, 26.7, 19.6. IR (NaCl disc): 1360, 1115, 822, 812 cm^{-1}.

*General procedure for isomerization of 3-(2-arylethenyl)-oxazinones **5** to 3-(2-arylethylidene)-oxazinones **6***

Triethylamine (28.0 μL, 0.2 mmol) was added to a solution of the 3-(2-arylethenyl)-oxazinone **5** (0.1 mmol) in $CDCl_3$ (1 mL), and the mixture was stirred for 3 days. The solvent was removed under reduced pressure, and the product was purified by column chromatography on silica to yield a clear, colorless oil.

6a: (92 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36–7.04 (m, 15H) 6.27 (dd, *J* = 5.8, 9.1 Hz, 1H), 4.34 (d, *J* = 14.9 Hz, 1H), 4.15 (m, 1H), 4.00 (m, 1H), 3.87–3.78 (m, 1H), 3.81 (d, *J* = 14.9 Hz, 1H), 3.59 (dd, *J* = 5.8, 16.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 139.1, 136.8, 135.5, 136.2, 128.8, 128.6, 128.3, 127.7, 127.4, 126.4, 123.0, 69.4, 58.5, 55.6, 34.2. IR (NaCl disc): 2959, 1734, 1265, 739 cm^{-1}. MS (EI) *m/z* 369.1 (M$^{+\bullet}$, 71 %).

6e: (98 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, *J* = 6.9 Hz, 4H), 7.44–7.27 (m, 14H), 7.08–7.05 (m, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.22 (dd, *J* = 5.6, 9.1 Hz, 1H), 4.33 (d, *J* = 15.0 Hz, 1H), 4.22–4.13 (m, 2H), 4.01 (dd, *J* = 11.1, 11.7 Hz, 1H), 3.81 (d, *J* = 15.0 Hz, 1H), 3.74 (dd, *J* = 9.1, 16.6 Hz, 1H), 3.48 (dd, *J* = 5.6, 16.6 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz)) δ 167.1, 154.2, 136.7, 135.5, 133.0, 129.9, 129.2, 129.0, 128.8, 128.7, 128.6, 127.9, 127.8, 127.7, 127.6, 127.3, 123.9, 119.9, 69.6, 58.6, 55.8, 33.6, 26.5, 19.5. IR (NaCl disc): 2932, 1740, 822 cm^{-1}. MS (EI) *m/z* 623 (M$^{+\bullet}$, 21 %).

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REFERENCES

1. N. A. Petasis, I. Akritopoulou. *Tetrahedron Lett.* **34**, 583 (1993).
2. G. S. Currie, M. G. B. Drew, L. M. Harwood, D. J. Hughes, R. W. A. Luke, R. J. Vickers. *J. Chem. Soc., Perkin Trans. 1* 2982 (2000).
3. L. M. Harwood, G. S. Currie, M. G. B. Drew, R. W. A. Luke. *Chem. Commun.* 1953 (1996).
4. N. A. Petasis, A. Goodman, I. A. Zavialov. *Tetrahedron* **53**, 16463 (1997).
5. N. A. Petasis, I. A. Zavialov. *J. Am. Chem. Soc.* **119**, 445 (1997).
6. B. Jiang, M. Xu. *Org. Lett.* **4**, 4077 (2002).
7. B. Jiang, C.-G. Yang, X.-H. Gu. *Tetrahedron Lett.* **42**, 2545 (2001).
8. K. K. Nanda, B. W. Trotter. *Tetrahedron Lett.* **46**, 2025 (2005).
9. N. A. Petasis, S. Boral. *Tetrahedron Lett.* **42**, 539 (2001).
10. N. A. Petasis, Z. D. Patel. *Tetrahedron Lett.* **41**, 9607 (2000).
11. N. A. Petasis, I. A. Zavialov. *J. Am. Chem. Soc.* **120**, 11798 (1998).
12. G. K. S. Prakash, M. Mandal, S. Schweizer, N. A. Petasis, G. A. Olah. *Org. Lett.* **2**, 3173 (2000).
13. G. K. S. Prakash, M. Mandal, S. Schweizer, N. A. Petasis, G. A. Olah. *J. Org. Chem.* **67**, 3718 (2002).
14. T. J. Southwood, M. C. Curry, C. A. Hutton. *Tetrahedron* **62**, 236 (2006).
15. A. Golebiowski, S. R. Klopfenstein, J. J. Chen, X. Shao. *Tetrahedron Lett.* **41**, 4841 (2000).
16. S. R. Klopfenstein, J. J. Chen, A. Golebiowski, M. Li, S. X. Peng, X. Shao. *Tetrahedron Lett.* **41**, 4835 (2000).
17. N. Kumagai, G. Muncipinto, S. L. Schreiber. *Angew. Chem., Int. Ed.* **45**, 3635 (2006).
18. N. J. McLean, H. Tye, M. Whittaker. *Tetrahedron Lett.* **45**, 993 (2004).
19. D. Naskar, A. Roy, W. L. Seibel, L. West, D. E. Portlock. *Tetrahedron Lett.* **44**, 6297 (2003).
20. D. E. Portlock, R. Ostaszewski, D. Naskar, L. West. *Tetrahedron Lett.* **44**, 603 (2003).
21. CCDC 675215 contains the supplementary crystallographic data for compound **5a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <www.ccdc.cam.ac.uk/data_request/cif>.
22. E. Yashima, S. Huang, T. Matsushima, Y. Okamoto. *Macromol.* **28**, 4184 (1995).
23. C. A. Hutton. *Tetrahedron Lett.* **38**, 5899 (1997).
24. C. A. Hutton. *Org. Lett.* **1**, 295 (1999).