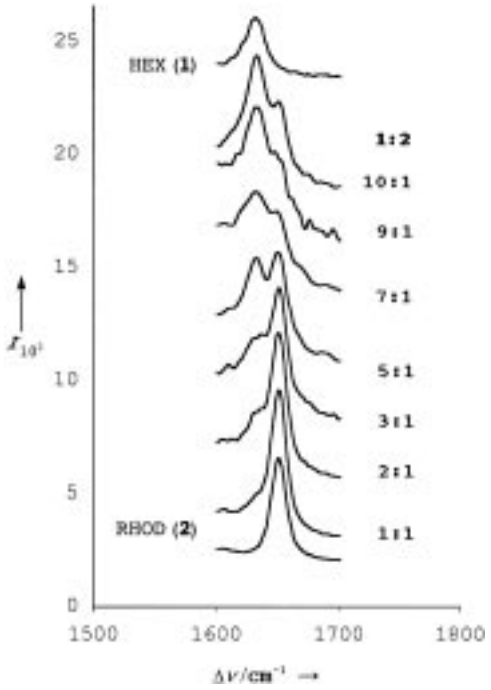

Figure 2. The signal corresponding to the quadrant aromatic stretches of the labeled oligonucleotides, as two single samples and in a mixture.

separation and in varying proportions. In addition, these initial experiments indicate that oligonucleotide probe design is crucial and there is considerable potential for further development particularly as both nonfluorescent and fluorescent chromophores can be used as SERRS labels. The modified oligonucleotide probes can also still be used as substrates for polymerases, therefore demonstrating that they remain biologically active. These results prove that, by considering the chemistry involved, SERRS can feature in the development of more effective DNA assays allowing the development of assay formats not possible by conventional methods.

Experimental Section

A solution of modified oligonucleotide (20 μL, 4×10^{-8} M) was premixed on ice with an aliquot of spermine tetrahydrochloride (20 μL, 8×10^{-2} M). Water (500 μL) and citrate-reduced silver colloid (500 μL) were added to this solution. Analysis used a Renishaw 2000 Raman Microprobe with excitation provided by a Spectra-Physics Model 2020 argon-ion laser (100 mW, $\lambda = 514.5$ nm). The detector was a charge-coupled device (CCD). Samples were analysed over 1 s in a plastic micro-titre plate using a X10 objective with the grating centred at 1400 cm^{-1}.

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[1] L. J. McBride, M. D. Oneill, *Am. Lab.* (*Boston*) **1991**, *23*, 52, and references therein.
[2] A. Castro, J. G. K. Williams, *Anal. Chem.* **1997**, *69*, 3915.
[3] B. K. Nunnally, H. He, L. C. Li, S. A. Tucker, L. B. McGown, *Anal. Chem.* **1997**, *69*, 2392.
[4] U. Lieberwirth, J. Arden-Jacob, K. H. Drexhage, D. P. Herten, R. Müller, M. Neumann, A. Schulz, S. Siebert, G. Sagner, S. Klingel, M. Sauer, J. Wolfrum, *Anal. Chem.* **1998**, *70*, 4771.
[5] A. M. Stacy, R. P. Vanduyne, *Chem. Phys. Lett.* **1983**, *102*, 365.
[6] P. Hildebrandt, M. Stockburger, *J. Phys. Chem.* **1984**, *88*, 5935.
[7] D. A. Weitz, M. Moskovits, J. A. Creighton in *Chemistry and Structures at Interfaces*, *New Laser and Optical Techniques* (Eds.: R. B. Hall, A. B. Ellis), VCH, Deerfield Beach, FL, **1986**, p. 197.
[8] A. Otto, I. Mrozek, H. Grabhorn, W. Akemann, *J. Phys. Condens. Matter* **1992**, *4*, 1143.
[9] K. Kneipp, Y. Wang, R. R. Dasari, M. S. Feld, *Appl. Spectrosc.* **1995**, *49*, 780.
[10] C. Rodger, W. E. Smith, G. Dent, M. Edmondson, *J. Chem. Soc. Dalton Trans.* **1996**, 791.
[11] D. Graham, W. E. Smith, A. M. T. Linacre, C. H. Munro, N. D. Watson, P. C. White, *Anal. Chem.* **1997**, *69*, 4703.

α-Oxymethyl Ketone Enolates for the Asymmetric Mannich Reaction. From Acetylene and *N*-Alkoxycarbonylimines to *β*-Amino Acids**

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The reactions of enolizable carbonyl compounds with azomethine functions, usually referred to as Mannich-type reactions (also termed aza–aldol reactions), result in the formation of *β*-amino acids, ketones, or aldehydes.[1] These reactions are conceptually equivalent to the aldol reactions, but, in sharp contrast, they have been substantially less developed.[2, 3, 4] There are two reasons that can justify this situation: firstly, the poorer electrophilicity of the azomethine function relative to that of the carbonyl function, and secondly, the preference of enolizable azomethines to undergo *α*-deprotonation rather than addition.[5] To date, there are two main ways to approach these problems. One strategy lies in the use of activated forms of azomethines,[1, 2] and the other in the use of trialkylsilylenol ethers or *O*-(trialkylsilyl)ketene acetals as nucleophiles.[3, 6] The later strategy has led to outstanding advances in enantioselective Mannich reactions[7] catalyzed by chiral ruthenium,[8a–b] palladium,[8c–e] and copper[8e–g] complexes. Some highly diastereoselective methods involving chiral azomethines are also known,[6, 9] but in most

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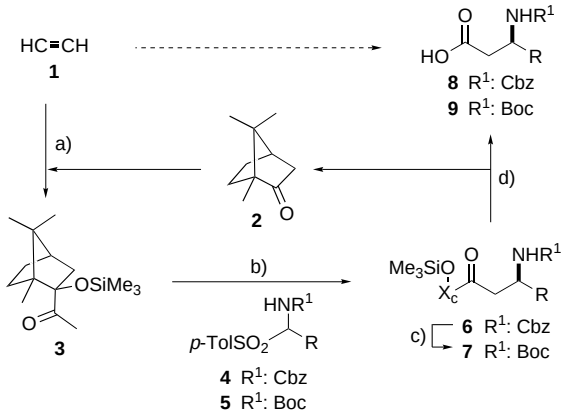
instances, the chiral auxiliary is often difficult to recover. Despite these achievements, however, there are very few known diastereoselective methods involving chiral enolates,[1] which are almost paramount in the parent aldol reactions. Most importantly, the stereoselectivity attained with the hitherto known α-unsubstituted chiral enolates is still rather inadequate.[10, 11] We report here on a new diastereoselective Mannich-type reaction that helps to solve the above problems.

The lithium enolate of the methyl ketone **3**, the latter being readily prepared from acetylene (**1**) and (1*R*)-(+)-camphor (**2**),[12] reacted, in the presence of an excess of LDA, with the carbamates **4** or **5**[13, 14] to afford the corresponding adducts **6**/**7** in good yields[15] and, in both cases, with diastereomeric ratios greater than 96:4 (Scheme 1). In general carbamates **5** provided the adducts **7** essentially as single diastereomers



Scheme 1. Asymmetric Mannich-type synthesis of β-amino acids. a) ref. [12]; b) LDA (3.5 equiv), THF, $-78\,^{\circ}C$, 1 h then **4** or **5** (2 equiv), THF, $-78\,^{\circ}C$, 15 min; c) H_2 (1 atm), Pd/C, EtOAc, RT, $(Boc)_2O$; d) $(NH_4)_2Ce(NO_3)_6$ (3 equiv), CH_3CN/H_2O, $0\,^{\circ}C$, 16 h. Boc = *tert*-butoxycarbonyl, Cbz = benzyloxycarbonyl, LDA = lithium diisopropylamide, Tol = tolyl.

(Table 1), while the carbamates **4** led to slightly lower reaction diastereoselectivities, typically 98:2 for carbamates with linear side chains, and 96:4 for those bearing branched side chains. For stereochemical correlation purposes the adducts **6** were converted into the *N*-Boc derivatives **7** in a one-pot procedure.[16] The assigned configuration for the adducts was established by a single-crystal X-ray structure analysis of the β-amino ketones **7a** and **7j**.[17] The configuration for the other adducts was assigned by analogy.

The excellent diastereoselectivity attained with *N*-[1-arylsulfonyl)alkyl]carbamates derived from either nonenolizable or enolizable aldehydes is of particular interest in that it provides, through oxidative cleavage of the acyloin moiety, β-alkyl-β-amino acids.[18] For example, the β-amino acid **8a**, the *N*-Cbz β-homovaline **8d**, and the *N*-Boc-β-homophenylglycine **9j** were formed in yields of 81, 86, and 80%, respectively, by prolonged exposure of the adducts **6a**, **6d**, and **7j** to a threefold excess of ammonium cerium nitrate (CAN) in acetonitrile/water. Thus, β-amino acids appropriately protected at the amino function are obtained in an enantiomerically pure form,[19] along with the recovery of the starting (1*R*)-(+)-camphor.[20] This result is also particularly important because it makes it economically viable to use the more expensive

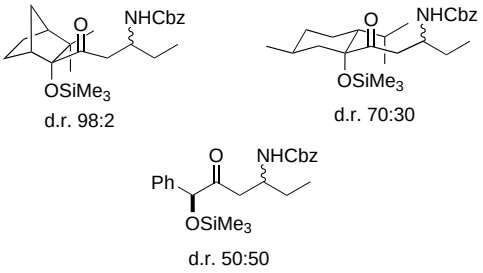
Table 1. Mannich-type synthesis of β-amino ketones **6** and **7**.[a]

			Product **6**/**7**		
	R	R^1	d.r.[b]	yield[%][c]	m.p. [°C]
a	CH_3CH_2	Cbz	98:2	94	98–99
		Boc	>98:2[d]	71	120
b	$CH_3(CH_2)_2$	Cbz	98:2	66	82–84
		Boc	>99:1	60	61–62
c	$CH_3(CH_2)_3$	Cbz	>98:2[d]	80	104–105
d	$(CH_3)_2CH$	Cbz	98:2	82	87–88
		Boc	>99:1	60	77–78
e	$PhCH_2CH_2$	Cbz	98:2	90	92–94
f	$(CH_3)_2CHCH_2$	Cbz	96:4	65	86–89
g	$BnOCH_2CH_2$	Cbz	97:3	55	oil
h	c-C_6H_{11}	Cbz	98:2	81	103–105
i	c-$C_6H_{11}CH_2$	Cbz	96:4	54	133–136
j	Ph	Boc	>99:1	72	105–106
k	4-Cl-C_6H_4	Cbz	>98:2[d]	60	104–105

[a] Reactions carried out on a 4 mmol scale. [b] Diastereomeric ratios determined by HPLC analysis, using a LiChrospher 100 RP-18 column and mixtures of CH_3CN/H_2O as eluant ($T = 40\,^{\circ}C$). [c] Yields of **6** and **7** after purification of the crude product by column chromatography and/or crystallization from *n*-hexane. [d] Determined by ^{13}C NMR spectroscopy.

(1*S*)-(−)-camphor isomer, which would lead to the corresponding enantiomeric β-amino acids. Both (*R*)- and (*S*)-β-amino acids are found in natural products[18b] and are also very interesting as potential building blocks for β-lactam antibiotics[21] and for β-peptides.[22]

To gain further insight into the importance of the present enolate model, three representative chiral α-oxymethyl ketones were also examined. Scheme 2 illustrates that of



Scheme 2. Mannich-type adducts from some selected α-silyloxymethyl ketones and carbamate **4a**. The configuration at the newly created stereogenic center was not determined. The diastereomeric ratios were determined by HPLC.

these ketones only that derived from (1*R*)-(−)-camphenilone was comparable in terms of efficiency to **3**. Therefore, owing to the advantageous preparation and low cost of the methyl ketone **3** it should be, from a practical standpoint, the reagent of choice for highly diastereoselective "acetate" aza–aldol reactions. In this respect, the example of double asymmetric induction[23] depicted in Scheme 3 demonstrates the potential scope of **3**. Carbamate **10**, which shows essentially no diastereofacial selectivity against the lithium enolate of methyl acetate, reacted with the lithium enolate of **3** to produce **11**, essentially as the sole isomer, in 70% yield. This result was also consistently reproducible when mixtures of **10** with different epimeric compositions were employed.[24] In addition, desilylation of **11** and subsequent oxidative cleavage of the acyloin moiety in the resulting intermediate afforded

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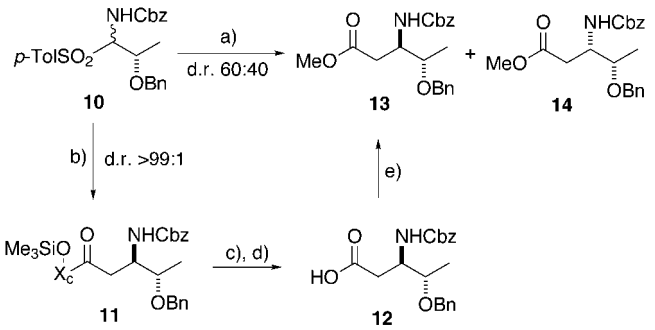


Scheme 3. Diastereoselective synthesis of β-homo-*allo*-threonine **12**. a) CH_3CO_2Me, LDA (3.5 equiv), THF, $-78\,^{\circ}C$, 1 h then **10**, 15 min; b) **3**, LDA (3.5 equiv), THF, $-78\,^{\circ}C$, 1 h then **10**, 15 min; c) TBAF, THF, RT, 5 min; d) $(NH_4)_2Ce(NO_3)_6$ (3 equiv), CH_3CN-H_2O, $0\,^{\circ}C$, 1 min; e) Me_3SiCHN_2, MeOH/C_6H_6. TBAF = tetrabutylammonium fluoride.

the *N*-Cbz-*O*-benzyl-β-homo-*allo*-threonine **12** in 75% yield. The diastereomeric purity of this compound was established by both ^{13}C NMR and HPLC analyses of the corresponding methyl ester **13**, and comparison with the chromatograms from the mixture of **13**/**14**. The determination of isomeric ratios, the preparation procedures, and the analytical data for compounds **6a–j**, **7a–b**, **7j**, **8a**, **8d, 9j**, **11**, and **12** can be found in the Supporting Information.

In summary, an asymmetric Mannich-type reaction that involves the use of acetylene and α-sulfonyl carbamates as the consumable organic materials is described for the first time.

Received: July 23, 1999 [Z13773]

[1] For a recent review, see M. Arend, B. Westermann, N. Risch, *Angew. Chem.* **1998**, *110*, 1096; *Angew. Chem. Int. Ed.* **1998**, *37*, 1044.

[2] a) *Stereoselective Synthesis* (*Houben-Weyl*), *Vol. E21/3* (Eds.: G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann), Thieme, Stuttgart, **1996**; b) *Comprehensive Organic Synthesis*, *Vol. 2* (Eds.: B. M. Trost, I. Fleming), 1st ed., Pergamon, Oxford, **1991**; c) *Enantioselective Synthesis of β-Amino Acids* (Ed.: E. Juaristi), Wiley-VCH, New York, **1997**.

[3] a) N. Risch, M. Arend in ref. [2a], p. 1908; b) C. Gennari in ref. [2b], p. 629; c) C. Gennari, A. Vulpetti in ref. [2c], p. 151; d) E. F. Kleinman in ref. [2b], p. 893; e) M. R. Sardi, A. Heydari, J. Ipaktschi, *Chem. Ber.* **1994**, *127*, 1761.

[4] The exception is the reaction of metal ester enolates with non-enolizable Schiff bases, which generally affords β-lactams. For pertinent information, see a) D. J. Hart, D. C. Ha, *Chem. Rev.* **1989**, *89*, 1447; b) M. J. Brown, *Heterocycles* **1989**, *29*, 2225.

[5] For pertinent information on these problems, see N. Risch, M. Arend in ref. [2a], p, 1833; b) S. E. Denmark, O. J. C. Nicaise, *Chem. Commun.* **1996**, 999.

[6] For recent examples on diastereoselective trialkylsilylketene acetal–chiral azomethine additions, see a) H. Kunz, A. Burgard, D. Schanzenbach, *Angew. Chem.* **1997**, *109*, 394; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 386; b) F. Guenoun, T. Zair, F. Lamaty, M. Pierrot, R. Lazaro, P. Viallefont, *Tetrahedron Lett.* **1997**, *38*, 1563; c) K. Higashiyama, H. Kyo, H. Takahashi, *Synlett* **1998**, 489; d) K. Ishihara, K. Hattori, H. Yamamoto in ref. [2c], p. 159; e) H. Kunz, M. Weymann, A. Burgard in ref. [2c], p. 407; f) R. Muller, H. Goesmann, H. Waldmann, *Angew. Chem.* **1999**, *111*, 166; *Angew. Chem. Int. Ed.* **1999**, *38*, 184.

[7] S. Kobayashi, H. Ishitani, *Chem. Rev.* **1999**, *99*, 1069.

[8] a) H. Ishitani, M. Ueno, S. Kobayashi, *J. Am. Chem. Soc.* **1997**, *119*, 7153; b) S. Kobayashi, H. Ishitani, M. Ueno, *J. Am. Chem. Soc.* **1998**, *120*, 431; c) E. Hagiwara, A. Fujii, M. Sodeoka, *J. Am. Chem. Soc.* **1998**, *120*, 2474; d) A. Fujii, E. Hagiwara, M. Sodeoka, *J. Am. Chem. Soc.* **1999**, *121*, 5450; e) D. Ferraris, B. Young, T. Dudding, T. Lectka, *J. Am. Chem. Soc.* **1998**, *120*, 4548; f) D. Ferraris, B. Young, C. Cox, W. J. Drury, III, T. Dudding, T. Lectka, *J. Org. Chem.* **1998**, *63*, 6090; g) D. Ferraris, T. Dudding, B. Young, W. J. Drury, III, T. Lectka, *J. Org. Chem.* **1999**, *64*, 2168.

[9] For recent examples on diastereoselective metal ester enolate–chiral azomethine additions, see a) F. A. Davis, P. Zhou, B. Chen, *Chem. Soc. Rev.* **1998**, *27*, 13; b) T. Fujisawa, Y. Kooriyama, M. Shimizu, *Tetrahedron Lett.* **1996**, *37*, 3881; c) T. P. Tang, J. A. Ellman, *J. Org. Chem.* **1999**, *64*, 12; d) F. A. Davis, R. E. Reddy, J. M. Szewczyk, *J. Org. Chem.* **1995**, *60*, 7037.

[10] a) K. Broadley, S. G. Davies, *Tetrahedron Lett.* **1984**, *25*, 1743; b) L. S. Liebeskind, M. E. Welker, R. W. Fengl, *J. Am. Chem. Soc.* **1986**, *108*, 6328; c) T. Shono, N. Kise, F. Sanda, S. Ohi, K. Tsubata, *Tetrahedron Lett.* **1988**, *29*, 231; d) M. Shimizu, Y. Kooriyama, T. Fujisawa, *Chem. Lett.* **1994**, 2419.

[11] For reviews dealing with the stereochemical problem of α-unsubstituted enolates, see a) M. Braun in ref. [2a], p. 133; b) M. Braun, *Angew. Chem.* **1987**, *99*, 24, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 24; c) M. Braun, H. Sacha, *J. Prakt. Chem.* **1993**, *335*, 653.

[12] For the preparation and aldol reactions of **3**, see a) C. Palomo, A. González, J. M. García, C. Landa, M. Oiarbide, S. Rodríguez, A. Linden, *Angew. Chem.* **1998**, *110*, 190; *Angew. Chem. Int. Ed.* **1998**, *37*, 180; b) C. Palomo, M. Oiarbide, J. M. Aizpurua, A. González, J. M. García, C. Landa, I. Odriozola, A. Linden, *J. Org. Chem.* **1999**, *64*, 8193.

[13] For the preparation of α-sulfonylalkyl carbamates, see W. H. Pearson, A. C. Lindbeck, J. W. Kampf, *J. Am. Chem. Soc.* **1993**, *115*, 2622, and references therein.

[14] For leading references on reactions involving α-sulfonyl carbamates, see a) ref. [13]; b) A. M. Kanazawa, J.-N. Denis, A. E. Greene, *J. Org. Chem.* **1994**, *59*, 1238; c) R. Ballini, M. Petrini, *Tetrahedron Lett.* **1999**, *40*, 4449.

[15] In some instances, small amounts of the starting methyl ketone were isolated from the reaction mixture.

[16] J. S. Bajwa, *Tetrahedron Lett.* **1992**, *33*, 2955.

[17] Crystallographic data (excluding structure factors) for the structures **7a** and **7j** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-130261 and 130262, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[18] For reviews on β-amino acids, see a) D. C. Cole, *Tetrahedron* **1994**, *50*, 9517; b) G. Cardillo, C. Tomassini, *Chem. Soc. Rev.* **1996**, 117; c) E. Juaristi, D. Quintana, J. Escalante, *Aldrichimica Acta* **1994**, *27*, 3; d) ref. [2c]; e) M. B. Smith, *Methods of Non-α-Amino Acid Synthesis*, Dekker, New York, **1995**.

[19] The enantiomeric purity of the final β-amino acids was determined by HPLC analyses of their methyl ester derivatives, using a chiralcel OD column and mixtures of *n*-hexane/isopropanol as the eluent. Comparison of these chromatograms with those corresponding to the racemic β-amino acid esters, the latter prepared by the reaction of the lithium enolate of methyl acetate and the corresponding *N*-1[*p*-(tolylsulfonyl)alkyl] carbamate, revealed an $ee \geq 99\%$ for the cases studied.

[20] (+)-Camphor was typically recovered, after filtration of the crude material through a Sep-pak cartridge and evaporation of the solvent, in 75–80% yield, and showed an optical rotation value of $[\alpha]_D^{25}$ (EtOH, $c = 1.0$) = +41.5 ($[\alpha]_D^{25}$ (EtOH, $c = 1.0$) = +42.2 for the starting camphor, purchased from Aldrich).

[21] R. Southgate, C. Branch, S. Coultton, E. Hunt in *Recent Progress in the Chemical Synthesis of Antibiotics and Related Microbial Products*, *Vol. 2* (Ed.: G. Lukacs), Springer, Berlin, **1993**, p. 621.

[22] For reviews, see a) D. Seebach, J. L. Matthews, *Chem Commun.* **1997**, 2015; b) U. Koert, *Angew. Chem.* **1997**, *109*, 1922; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1836; c) S. H. Gellman, *Acc. Chem. Res.* **1998**, *31*, 173.

[23] For an example of double asymmetric induction in aza–aldol reactions, see K. Ishihara, M. Miyata, K. Hattori, T. Tada, H. Yamamoto, *J. Am. Chem. Soc.* **1994**, *116*, 10520.

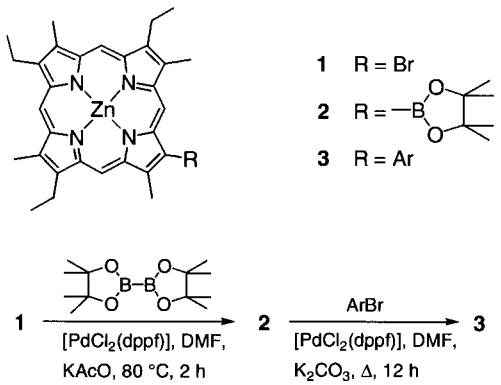
[24] Apparently, these results indicate that the present Mannich-type reaction proceeds through prior formation of the corresponding *N*-alkoxycarbonylimine.

Facile Synthesis of β-Derivatized Porphyrins—Structural Characterization of a β–β-Bis-Porphyrin**

Yongqi Deng, C. K. Chang,* and Daniel G. Nocera*

Linked porphyrin complexes have been a popular structural motif for studies of electron and energy transfer. The ability to tune the electronic properties of porphyrins by their catenation is central to controlling the efficiencies and rates of these transfers,[1–6] engendering applications in areas ranging from the design of "molecular wires" and optoelectronic materials to the development of biomimetic models of photosynthetic reaction centers and light-harvesting antenna complexes.[7–12] Modification of porphyrins is more common at the *meso*-position than at the β-position, which confronts more lengthy syntheses and lower product yields. This is especially true for bis-porphyrins where several new emerging methodologies for direct *meso* coupling[13–16] contrast a limited set of approaches for the synthesis of β–β linked bis-porphyrins.[16b, 17] Porphyrin coupling chemistry has changed in recent years with the emergence of metal-catalyzed cross-coupling methods, which have been employed to link bis-porphyrins via phenyl and ethynyl spacers at *meso*–*meso*-, *meso*–β- and β–β-positions.[7, 8] The direct coupling of porphyrins by such methods, however, has not yet been achieved. We now show the utility of metal-mediated cross-coupling for the general synthesis of β-derivatized porphyrins, including the preparation and first structural characterization of a bis-porphyrin unit directly linked at the β-position.

Scheme 1 shows the strategy developed for the direct β–β coupling of the porphyrin rings. Air- and water-stable **2** was isolated in 76% yield by applying the method of Miyaura et al.[18] to couple the pinacol diboronate with bromoporphyrin **1**.[19] Porphyrin **2** can also be prepared according to Masuda's method where the pinacol borane is the transmetalating reagent.[20, 21] The same boronate has recently been applied to synthesize porphyrins derivatized at the *meso*-position[22] in yields similar to that reported here for β-derivatization. Cross-coupling **1** and **2** under typical Suzuki reaction conditions affords the previously reported bis-porphyrin **3a**,[17, 23] but prepared here more conveniently and in higher yield (62%).



a: Ar = (7,12,17-triethyl-3,8,13,18-tetramethylporphyrinato)zinc(II); **b:** Ar = Ph; **c:** Ar = *p*-CH_3Ph; **d:** Ar = 9-Anthryl; **e:** Ar = *p*-OHCPh

Scheme 1. Synthesis of **3a**–**e**.

The crystal structure of the porphyrin dimer **3a**[24] (Figure 1) is unique inasmuch as no porphyrin system directly linked by a carbon–carbon bond at the β-position of the rings has been heretofore structurally characterized. Connection

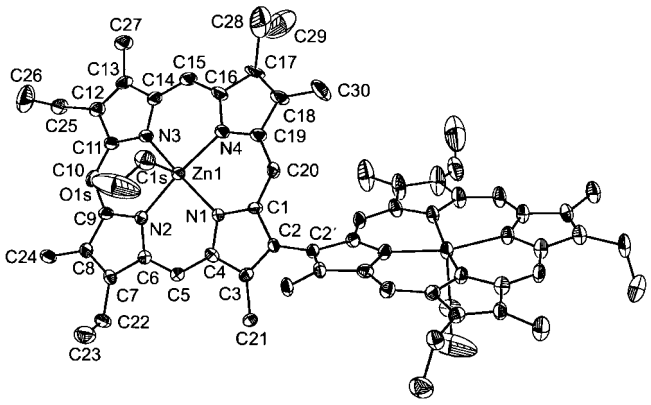


Figure 1. ORTEP representation of **3a** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

at the less sterically encumbered β-position results in a dihedral angle (51.7°) (defined by four $N_{pyrrolyl}$ atoms of each porphyrin) between the two porphyrin macrocycles that is considerably smaller than that observed between the phenyl and porphyrin rings in tetraphenylporphyrin (TPP),[25] other crystallographically characterized TPP type compounds[26, 27] and, most pertinently, than two porphyrins directly linked by a C–C bond at their *meso*-positions (dihedral angle of 65 to 84°).[14] The unique bridging C2–C2′ bond (1.46 Å) is also shorter than the C–C bond of the *meso*–*meso* coupled bis-porphyrin ($d = 1.51$ Å) and the sp^3–sp^3 distance of a recently reported β–β linked bis-chlorin ($d = 1.61$ Å), which is typical of a single bond.[28] These bond length comparisons suggest greater electronic conjugation between two porphyrin macrocycles when linked at their β-positions.

Figure 2a compares the electronic absorption spectra of the monomeric subunit (zinc(II) etio-I porphyrin) and **3a**. The

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