Amino Acids (2008) 35: 83–88
DOI 10.1007/s00726-007-0626-9
Printed in The Netherlands

Amino Acids

Synthesis of C_3-symmetric and C_4-symmetric amino acid derivatives via Suzuki–Miyaura cross-coupling reaction

S. Kotha and **V. R. Shah**

Department of Chemistry, Indian Institute of Technology-Bombay, Powai, Mumbai, India

Received September 3, 2007
Accepted October 15, 2007

Summary. Various non-natural C_3- and C_4-symmetric α-amino acid derivatives have been synthesized via Suzuki–Miyaura cross-coupling reaction between aromatic iodides or bromide and a suitably protected DL-4-boronophenylalanine derivative.

Keywords: C_3-Symmetric amino acids – C_4-Symmetric amino acid – Carbon–carbon bond – Non-natural α-amino acid derivatives – Suzuki–Miyaura cross-coupling reaction

Introduction

C_3-Symmetric 1,3,5-triphenylbenzene and 2,4,6-trisubstituted 1,3,5-triazine derivatives have been utilized as a central core unit for the design and synthesis of a wide variety of dendrimeric type of compounds which posses interesting properties and found diverse applications in material science. Some of them are used as fluorescent probes in electronic devices, organic light emitting diodes and liquid crystalline materials etc. (Shirota, 2000). Moreover, 2,4,6-trisubstituted 1,3,5-triazine derivatives have found applications in coordination chemistry and crystal engineering (Thallapally et al., 2000, 2001, 2004; Hoz et al., 2001; Lee and Yamamoto, 2001). Shirota and co-workers have reported the synthesis of new class of fluorecent amorphous molecular materials like 1,3,5-tris(9,9-dimethylfluoren-2-yl)benzene **1** which acts as hole blocker (Okumoto and Shirota, 2003). Pei and co-workers have synthesized a nano-sized polycyclic aromatic compound such as **2** with 1,3,5-triphenylbenzene and fluorene units by $TiCl_4$-catalyzed cyclotrimerization reaction (Zhan et al., 2005). Also, Tour et al. (2001) have synthesized symmetrical conjugated oligo(phenylene ethynylene)s used for various three dimensional molecular wires and devices, and the symmetrical 1,3,5-triphenylbenzene core has also been used in synthesis of dendritic chromophores (Palomero et al., 2002; Mongin et al., 2003) and hyperbranched conjugated molecules (He et al., 2003). In another event, Wang and co-workers have synthesized a series of neutral π-conjugated star shaped organic molecules containing 1,3,5-triazine units and pyridylamino derivative **3** and studied their photo luminescent properties by complexing with palladium and zinc metal ions (Liu et al., 2003). Sun and co-workers reported nano-sized tripodal ligand, (2,4,6-tris[4-imidazol-ylmethyl)phenyl]-1,3,5-triazine **4** which forms a complex with $Pb(NO)_3$ resulting into poly-catenane 2D networks that are useful in material chemistry (Wan et al., 2002). Our group has also reported the synthesis of functionalized nano-sized C_3-symmetric molecules by trimerization and subsequent coupling with various boronic acids under Suzuki–Miyaura cross-coupling conditions to generate oligoaryl/-heteroaryl C_3-symmetric furan- and thiophene-containing star-shaped molecules (Kotha et al., 1999a, 2004).

Synthesis of non-natural and unusual α-amino acid derivatives is an active area of research (Kotha, 2003). However, C_3- and C_4-symmetric α-amino acid derivatives have attracted less attention and are relatively less explored. However, Frejd and co-workers (Ritzén et al., 1998) synthesized optically pure unusual C_3-symmetric amino acid derivatives **5** and **6**, named as phenyltrisalanine, using the Heck coupling and Horner-Wadsworth-Emmons (HWE) olefination followed by asymmetric hydrogenation in the presence of Rh-catalyst. Whereas, Beck's group reported the synthesis of alkyne bridged phenylalanine based C_3-symmetric amino acid derivatives **7** via the Pd-mediated

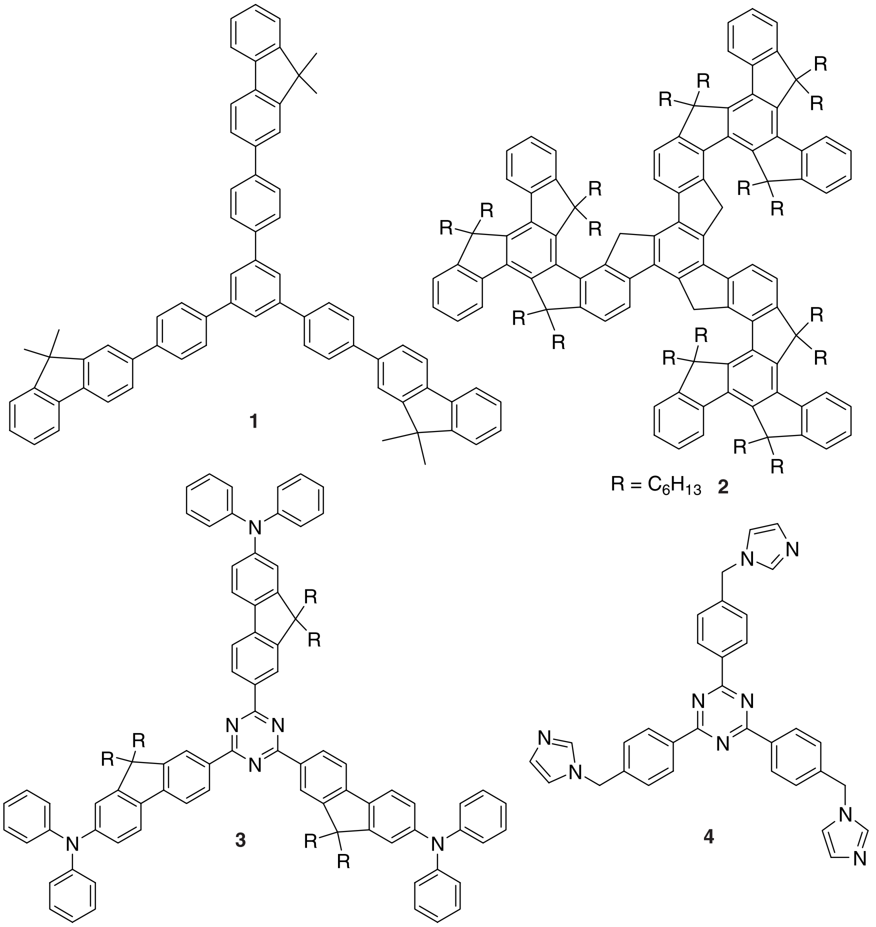

Fig. 1. Examples with 1,3,5-trisubstituted benzene and 1,3,5-triazine as core structural unit

cross-coupling reaction of suitably protected iodo-phenylalanine derivatives with alkyne (Kayser et al., 1997). Also, Nilsson and co-workers synthesized C_3-symmetric macrocycles with alternating sugar amino acid and tyrosine residues starting from the sugar amino acid precursor derived from D-glucosamine (Billing and Nilsson, 2005). Herein, we report the synthesis of C_3-symmetric and tetraphenylmethane based amino acid derivatives via the SM (Miyaura and Suzuki, 1995; Kotha et al., 2002b) cross-coupling as a key step.

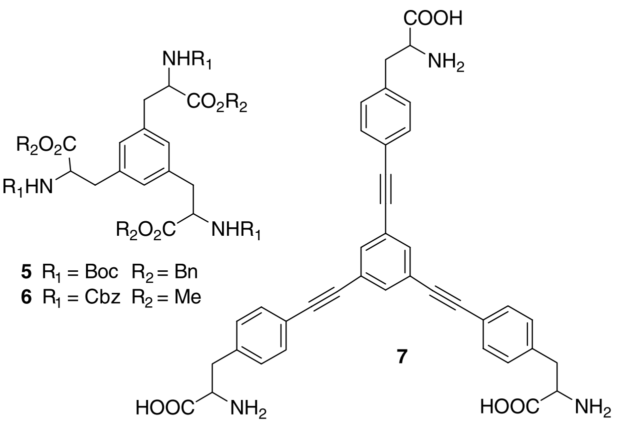

Fig. 2. C_3-symmetric amino acid derivatives

Materials and methods

General remarks

Analytical TLC was performed on (10 × 5 cm) glass plates coated with silica gel G or GF 254 (containing 13% $CaSO_4$ as a binder). Visualization of the spots was achieved either by exposure to I_2 vapor or UV light. Flash chromatography was performed using silica gel (100–200 mesh) and usually eluted with EtOAc and petroleum ether (bp 60–80 °C) mixtures. Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectral data were recorded on Varian VXR 300 or Varian VXR 400 spectrometers using TMS as internal standard and $CDCl_3$ or DMSO-d_6 as solvent. The coupling constants (J) are given in Hertz (Hz). High Resolution mass spectral data were recorded on a QToF micromass machine.

General procedure for the SM cross-coupling reaction

In a three-necked RB flask equipped with reflux condenser and nitrogen inlet-outlet, aromatic halides (1 equiv.), boronic acid **8** (2 equiv. for each halogen atom of aromatic halide), Na_2CO_3 (2 equiv. for each halogen atom of aromatic halide) in H_2O (1 ml) and THF/toluene (1:1, 4 ml) were charged. The resulting mixture was stirred and degassed for 20 min. To the above mixture, $Pd(PPh_3)_4$ (5 mol% for each halogen atom of aromatic halide) was added The resulting mixture was refluxed at 80 °C and reaction was monitored with the aid of TLC. When the reaction was complete water was added and the mixture was extracted with DCM (3 × 25 ml). Combined organic layers were washed with water and brine. Solvent was removed under reduced pressure and the crude product obtained was purified by the silica-gel column chromatography. Elution of column with ethyl acetate/petroleum ether mixture gave the desired products.

*Preparation of C_3-symmetric compound **11***

In a three-necked RB flask attached with reflux condenser and nitrogen inlet-outlet, triiodo compound **9** (40 mg, 0.06 mmol), boronic acid **8** (115 mg, 0.36 mmol), Na_2CO_3 (37.3 mg, 0.35 mmol) in H_2O (1 ml) and THF/toluene (1:1, 4 ml) and $Pd(PPh_3)_4$ (13.4 mg, 0.0116 mmol) were treated as described in general procedure. When the reaction was complete (TLC analysis), the mixture was quenched with water and usual work-up procedure gave crude product which was purified by column chromatogaphy. Elution of the column with petroleum ether gave starting material (11 mg, 27.5%). Further elution with 35% ethyl acetate/petroleum ether mixture gave the product **11** (20 mg, 32%, based on starting material recovered) as liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.43$ (s, 27H), 3.07–3.23 (m, 6H), 3.75 (s, 9H), 4.65 (d, 3H), 5.05 (d, 3H), 7.24 (d, 6H, $J = 8.1$ Hz), 7.61 (d, 6H, $J = 8.1$ Hz), 7.71 (d, 6H, $J = 8.4$ Hz), 7.80 (d, 6H, $J = 8.4$ Hz), 7.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 28.3$, 38.1, 52.4, 54.5, 80.1, 125.1, 127.3, 127.5, 127.8, 129.9, 135.4, 139.4, 140.1, 142.0, 155.2, 172.4.

*Preparation of triazine-based C_3-symmetric amino acid derivative **12***

Tribromo derivative **10** (50 mg, 0.09 mmol), boronic acid derivative **8** (177 mg, 0.54 mmol), Na_2CO_3 (46 mg, 0.43 mmol), $Pd(PPh_3)_4$ (13.0 mg, 15 mol%) were treated as described in the general procedure for the SM cross-coupling reaction. Elution of the column with 25% ethyl acetate/petroleum ether mixture gave desired product **12** (27.2 mg, 26%) as a thick liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.44$ (s, 27H), 3.12–3.22 (m, 6H), 3.77 (s, 9H), 4.64–4.66 (m, 3H), 5.06 (d, 3H, $J = 8.0$ Hz), 7.27 (d, 6H, $J = 7.6$ Hz), 7.66 (d, 6H, $J = 8.4$ Hz), 8.80 (d, 6H, $J = 8.4$ Hz), 8.86 (d, 6H, $J = 8.4$ Hz); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 28.5$, 38.2, 52.6, 54.5, 80.2, 127.4, 127.6, 129.7, 130.1, 135.4, 136.1, 139.3, 144.9, 155.3, 172.5. HRMS (QToF): Cald. for $C_{66}H_{73}N_6O_{12}$ $[M + H]^+$: 1141.5286; Found: 1141.5297.

*Preparation of C_3-symmetric amino acid derivative **14***

1,3,5-Triiodo benzene **13** (40 mg, 0.08 mmol), boronic acid derivative **8** (170 mg, 0.48 mmol), Na_2CO_3 (56 mg, 0.48 mmol), $Pd(PPh_3)_4$ (15.0 mg, 15 mol%) were treated as described in the general procedure for the SM cross-coupling reaction. At the conclusion of the reaction (TLC monitoring), the reaction mixture was worked-up as described in the general procedure. Elution of the column with 20% ethyl acetate/petroleum ether mixture gave the desired product **14** (62 mg, 78%) as a thick liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.44$ (s, 27H), 3.10-3.22 (m, 6H), 3.75 (s, 9H), 4.64-4.66 (m, 3H), 5.06 (d, 3H, $J = 8.0$ Hz), 7.24 (d, 6H, $J = 8.0$ Hz), 7.62 (d, 6H, $J = 8.0$ Hz), 7.73 (s, 3H). ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 28.4$, 38.1, 52.4, 54.5, 80.1, 124.9, 127.5, 129.9, 135.5, 139.8, 141.9, 155.2, 172.4.

*Preparation of 4-(triphenylmethyl)-N-Boc- DL-phenylalanine methyl ester **17***

Monoiodo TPM **15** (50 mg, 0.1121 mmol), boronic acid **8** (157 mg, 0.4861 mmol), Na_2CO_3 (47.5 mg, 0.4481 mmol) in H_2O (1 ml) and THF/Toluene (1:1, 6 ml) and $Pd(PPh_3)_4$ (13.0 mg, 10 mol%) were treated as described in the general procedure for SM cross-coupling. When the reaction was complete (TLC analysis), the reaction mixture was worked-up as described in general procedure and crude product was charged on silica gel column. Elution with 8% ethyl acetate/petroleum ether mixture gave the product **17** (23 mg, 34%) as a white solid. Mp: 182–186 °C. ^{1}H-NMR (300 MHz, $CDCl_3$):$\delta = 1.41$ (s, 9H), 3.03–3.18 (m, 2H), 3.72 (s, 3H), 4.61 (d, 1H), 4.99 (d, 1H), 7.16–7.29 (m, 19H), 7.46 (d, 2H, $J = 8.1$ Hz), 7.52 (d, 2H, $J = 8.1$ Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 28.5$, 38.2, 52.4, 54.5, 80.2, 126.0, 126.1, 127.2, 127.7, 129.9, 131.1, 131.3, 131.7, 135.1, 138.1, 139.4, 146.1, 146.9, 155.3, 172.6.

*Preparation of tetra-armed amino acid derivative **18***

In a three-necked RB flask attached with reflux condenser and nitrogen inlet-outlet, tetraiodo TPM **16** (40 mg, 0.05 mmol), boronic acid **8** (146 mg, 0.40 mmol), Na_2CO_3 (42 mg, 0.40 mmol) in H_2O (1 ml) and THF/toluene (1:1, 6 ml) $Pd(PPh_3)_4$ (11.0 mg, 20 mol%) were treated as described in the general procedure for SM cross-coupling When the reaction was complete (TLC analysis), the mixture was worked-up as described by general procedure and crude product was charged on a silica gel column. Elution of column with 40% ethyl acetate/petroleum ether mixture gave **18** (12 mg, 20%) as a thick liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.42$ (s, 36H), 3.02–3.16 (m, 8H), 3.72 (s, 12H), 4.61 (q, 4H), 4.99 (d, 4H), 7.18 (d, 8H, $J = 6.9$ Hz), 7.36–7.41 (m, 8H), 7.50–7.56 (m, 16H).

Results and discussion

As a part of an ongoing project aimed at the synthesis of unusual α-amino acid derivatives (Kotha and Brahmachary, 1997, 2000; Kotha et al., 1998, 1999b, 2000a, b, 2001, 2002a; Kotha and Sreenivasachary, 2000a, b, 2001; Kotha and Lahiri, 2001), we were interested to synthesize C_2-, C_3- and C_4-symmetric amino acid derivatives via the Suzuki–Miyaura (SM) cross-coupling reaction as a key step. Recently, we have reported the synthesis of linear as well as angular bis-armed amino acid derivatives via the application of SM cross-coupling between the 4-borono phenylalanine derivative **8** and aromatic dihalides (Kotha et al., 2007a). Also, we have synthesized and studied the fluorescence properties of anthracene based bis-armed amino acid derivative and found that it showed very high quantum yield independent of polarity of the solvents (Kotha et al., 2007b).

Towards the goal of synthesizing C_3-symmetric α-amino acid derivatives, when the triiodo derivative **9** was coupled with the boronic acid derivative **8** under

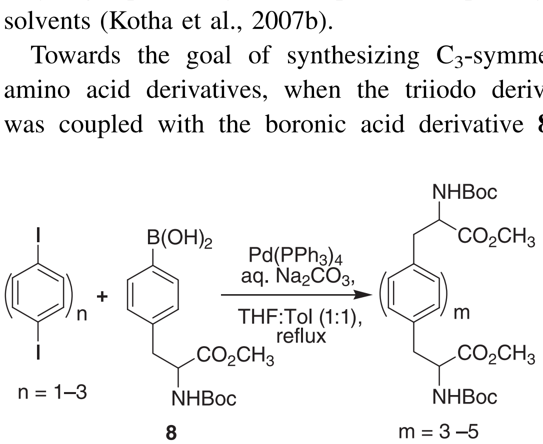

Fig. 3. Bis-armed amino acid derivatives via the SM cross-coupling

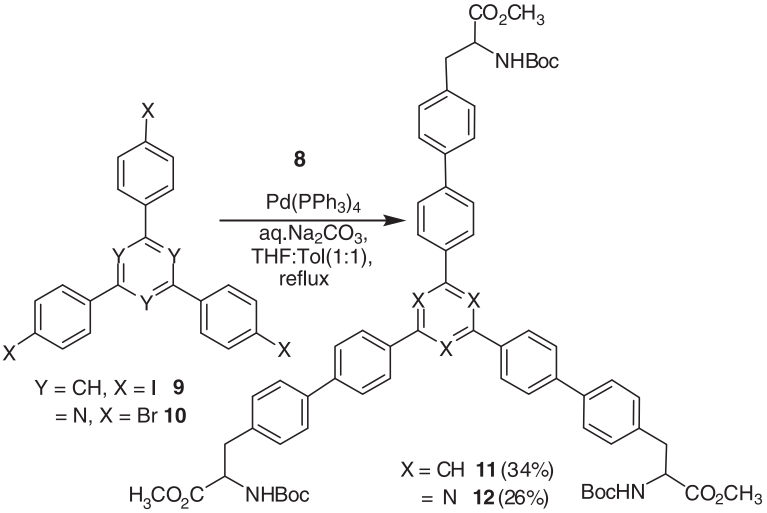

Fig. 4. SM cross-coupling approach towards the synthesis of C_3-symmetric amino acid derivatives

the SM cross-coupling conditions [Pd(PPh_3)$_4$, aq. Na_2CO_3, THF:toluene (1:1), reflux], the corresponding cross-coupling product **11** was isolated in 32% yield (based on starting material recovered) (Fig. 4). Here, the reaction was very sluggish and does not proceed to completion under refluxing conditions for 3 days. The reaction was stopped after 80 h. The product formation was confirmed from its complementary spectral data. Similarly, when triazine based C_3-symmetric tribromide **10** was subjected to the coupling conditions, the corresponding C_3-symmetric amino acid derivative **12** was isolated in 26% yield (Fig. 4). Along similar lines, the amino acid derivative **14** was isolated in 78% yield when the triiodide **13** was coupled with the boronic acid derivative **8** (Fig. 5).

Tetraphenylmethane (TPM) and tetraphenylsilane are further core structural units available for designing supramolecular studies. The organic compounds with a tetrahedral core unit in particular TPM have found applications ranging from light-emitting materials (Wilson and Griffin, 1993; Wang et al., 2000; Chan et al., 2001, 2002), electronically active materials (Zimmermann et al., 2000; Rathore et al., 2001), and also as a molecular caltrop in scanning probe microscopy (Mongin and Gossauer, 1996). Keana and co-workers (Li et al., 2002) synthesized TPM-based tetrahedral shaped nano-scale molecules via the applications of four-fold Sonogashira coupling. By contrast, Sengupta et al. (2001) synthesized dendrimers with C_3-symmetric core and ferrocene group attached to TPM at the outer periphery. Recently, he and co-workers reported the synthesis of TPM based fluorescent octa-carboxylic acid derivatives (Liu et al., 2004a) as well as TPM-based water soluble PEG linked polymers (Liu et al., 2004b). Yamamoto and co-workers reported the synthesis and properties of TPM based phenylazomethine dendrimers (Enoki et al., 2006). Recently, our group reported the synthesis of functionalized TPM derivatives via the SM cross-coupling (Kotha and Behera, 2006). However, being so useful and having numerous applications in the field of chemistry and material sciences, there are no reports mentioning the synthesis of TPM-based amino acid derivatives. We are interested to synthesis the TPM based peptide dendrimers for which TPM-based amino acid derivatives are needed. We envisioned that these derivatives can be assembled via the SM cross-coupling. Therefore, we choose the monoiodo TPM **15** and tetraiodo TPM **16** as a starting material towards the synthesis of unusual amino acid derivatives with TPM core. Monoiodo TPM (Witten and Reid, 1950; Sengupta et al., 2002) and tetraiodo TPM (Menger and Su, 1997; Grimm et al., 1986) compounds were prepared by the known literature procedure.

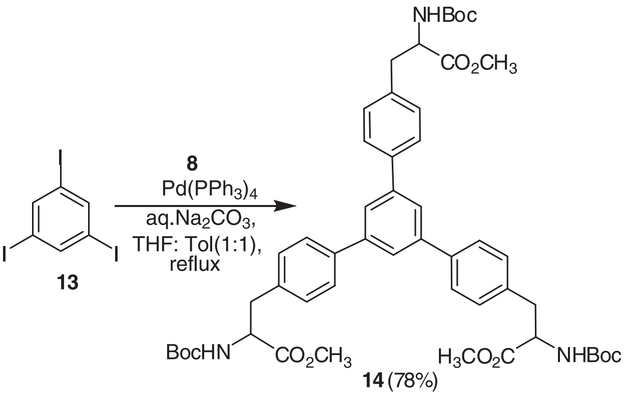

Fig. 5. C_3-Symmetric amino acid derivative

The coupling of the boronic acid **8** with the monoiodo TPM **15** provided the cross-coupled product **17** in 34% yield (Fig. 6) along with the dimer of starting iodo com-

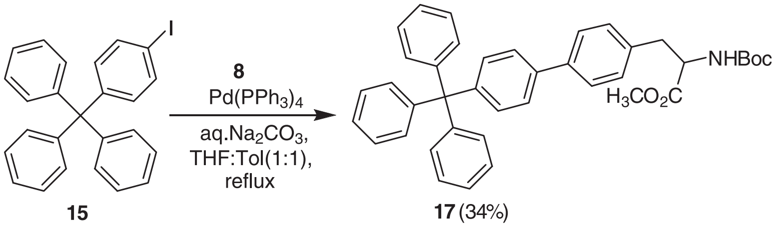

Fig. 6. SM cross-coupling of mono-iodo TPM with boronic acid derivative **8**

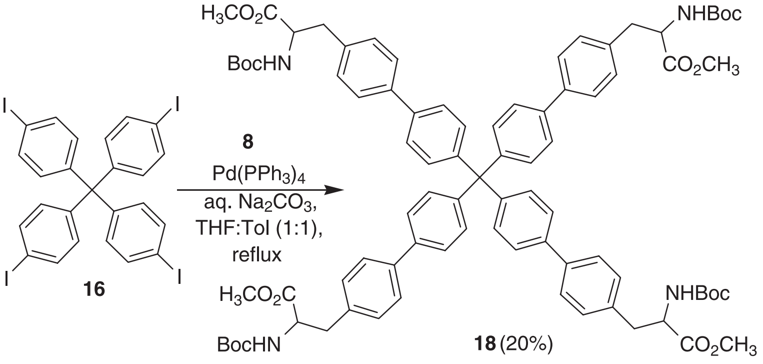

Fig. 7. Tetraphenylmethane based C_4-symmetric amino acid derivative via the SM cross-coupling

pound. The formation of the amino acid derivatives **17** was confirmed from ^{1}H NMR spectral data. Similarly, when tetraiodo-TPM derivative was subjected to SM coupling conditions with boronic acid derivative **8**, the tetrahedral, C_4-symmetric amino acid derivative **18** was isolated in 20% yield (Fig. 7).

Conclusions

We have synthesized C_3-symmetric α-amino acid derivatives via the SM cross-coupling reaction. To the best of our knowledge, we are the first to report the synthesis of TPM based amino acid derivatives. These amino acid derivatives can be useful for the synthesis of C_3-symmetric as well as TPM based peptide dendrimers and may find interesting applications and can exhibit important physical properties.

Acknowldegements

We are thankful to DST, New Delhi and CSIR, New Delhi, India for the financial support. VRS thanks CSIR, New Delhi and IRCC, IIT-Bombay for the award of Research Fellowship.

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Authors' address: Sambasivarao Kotha, Department of Chemistry, Indian Institute of Technology-Bombay, Powai, Mumbai 400 076, India, Fax: 091-22-2572 3480, E-mail: srk@chem.iitb.ac.in