Indian Journal of Chemistry
Vol. 45B, December 2006, pp. 2684-2689

Rapid Communication

Preparation of functionalised tetraphenylmethane derivatives *via* the Suzuki-Miyaura cross-coupling reaction

Sambasivarao Kotha* & Manoranjan Behera
Department of Chemistry, Indian Institute of Technology,
Bombay, Powai, Mumbai 400 076, India
E-mail: srk@chem.iitb.ac.in

Received 3 January 2006; accepted (revised) 14 September 2006

A general methodology for the synthesis of various symmetrical and unsymmetrical tetraphenylmethane (TPM) derivatives is reported using the Suzuki-Miyaura (SM) cross-coupling reaction as a key step. The formation of an interesting self-coupling product **14** during the SM cross-coupling reaction of mono-iodo tetraphenylmethane derivative **5** is also observed.

Keywords: SuzukiMiyaura coupling, carbon-rich compounds, palladium, nanostructures, boron, tetraphenylmethane

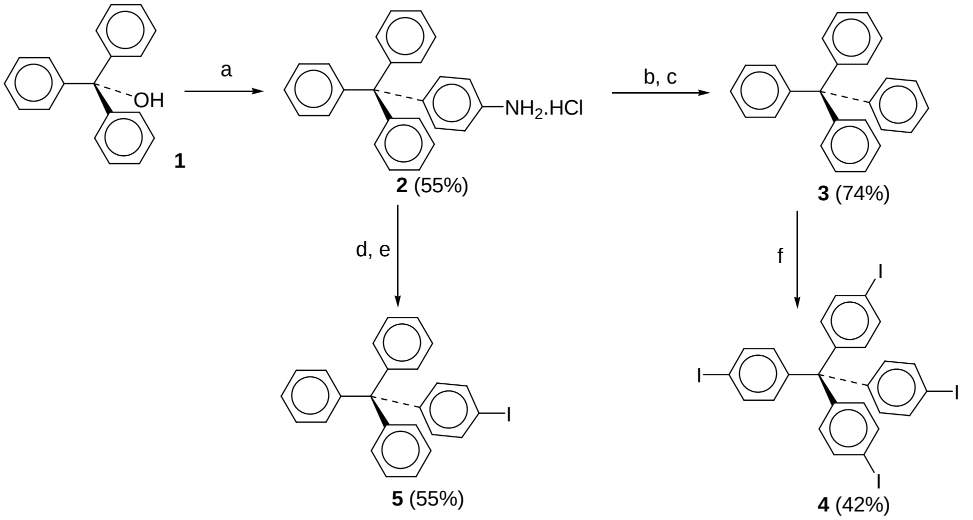
IPC Code: Int.Cl.^{8} C07C

The synthesis of topologically interesting all-carbon networks has gained momentum in recent years[1]. Although several researchers studied linear and planar networks, limited efforts were directed for the construction of centrally based three dimensional carbon frameworks, perhaps due to difficulties in synthesis of the tetrahedral building blocks necessary for such study. Current interest in the synthesis of centrally tetrahedral molecular structures (*e.g.* TPM derivatives) is due to their potential applications in different areas of material science[2-6]. A tetrahedral core with suitable functionality at its vertices is an attractive starting point for the construction of nanomaterials[7] and dendrimer with spherical topologies[8]. The tetrahedral geometry of this type of molecules offers numerous opportunities for the design of interesting molecular entities. For example, fabrication of organic crystals with tailor-made crystallinity and improved solid-state properties such as organic glasses, organic light-emitting diodes (OLEDs), has become an important issue[9]. Among structural motifs with tetrahedral symmetry, tetraarylmethanes are of particular interest[10,11]. The sp^3-hybridized center links four substituents with extended π-systems in a close proximity and the four substituents are in homoconjugation resulting in simultaneous mutual orthogonality[12]. Few functionalized tetraarylmethanes derivatives with different substitution at their peripheries are available in the literature[13]. However, polyaromatics linked directly to the sp^3-hybridized center has so far not studied extensively. In this communication, we would like to report a useful method for the preparation of various TPM derivatives using SM cross-coupling reaction as a key step.

An acidic mixture of triphenylmethanol **1** and aniline on heating gave the intermediate anilinium salt **2**. Then, the anilinium salt was treated with isoamyl nitrite and hypophosphorus acid to give TPM **3**. In the later part of our study, TPM was also prepared using diazotisation of 4-tritylanilium chloride in presence of $NaNO_2$ (**Scheme I**)[14].

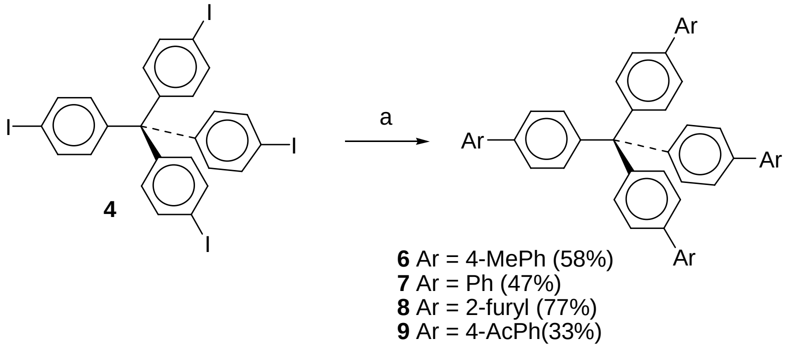
Having prepared TPM, the iodination reaction was attempted with various reagents[15]. Using I_2, HNO_3 and H_2SO_4; H_5IO_6, I_2, H_2SO_4 and AcOH conditions, the iodination product[16-18] was not obtained successfully. Monitoring the progress of the reaction is a major problem with TPM derivatives. After considerable experimentation a suitable solvent system (CCl_4) was found to monitor the reaction by TLC technique. Using [(bistrifluroacetoxy)iodo] benzene and iodine in CCl_4 conditions, the tetraiodo derivative **4** was isolated in good yield (42%) (**Scheme I**)[19,20]. Having prepared the tetraiodo derivative **4**, we attempted the SM coupling reaction[21] of **4** with 4-methylphenylboronic acid (**Scheme II**).

In a typical experimental procedure, a mixture of tetraiodo derivative **4** (1 equiv.), 4-methylphenylboronic acid (8 equiv.), Na_2CO_3 (6 equiv.), $Pd(PPh_3)_4$ (5 mole %) in THF/ toluene (1:1) was heated at 80°C for 12 h. Usual work up followed by column chromatography gave the compound **6** (58% yield). ^{1}H NMR spectra of the compound shows a singlet at δ 2.38 corresponding to methyl group. Further, ^{13}C NMR showed peaks at δ 21.3 and 64.3 due to methyl carbon and tertiary carbon atoms respectively which support the formation of the cross-coupling product **6**. The presence of molecular ion peak at m/z M^+ 680 ($C_{53}H_{44}$) in the mass spectrum gave additional support for its formation. Later on, the SM cross-coupling reaction was attempted with other



Reagents and conditions: (a) aniline, HCl, AcOH, reflux, 48 h; (b) $NaNO_2$, EtOH, H_2SO_4, 30 min; (c) H_3PO_2, reflux, 12 h; (d) HCl, $NaNO_2$, H_2O, 0°C, 30 min; (e) KI, H_2O, reflux, 7 h; (f) [(bistrifluroacetoxy)iodo]benzene, I_2, CCl_4, 12 h.

Scheme I



Reagents and conditions: (a) $ArB(OH)_2$, $Pd(PPh_3)_4$, THF/toluene, H_2O, Na_2CO_3, 12 h.

Scheme II

aryl boronic acids such as 2-furylboronic acid, 4-acetylphenylboronic acid and phenylboronic acid and the results are included in **Scheme II**. Typically 33-77% yields of the coupling products were obtained. We have observed that boronic acid containing electron withdrawing group gave low yield of the coupling products.

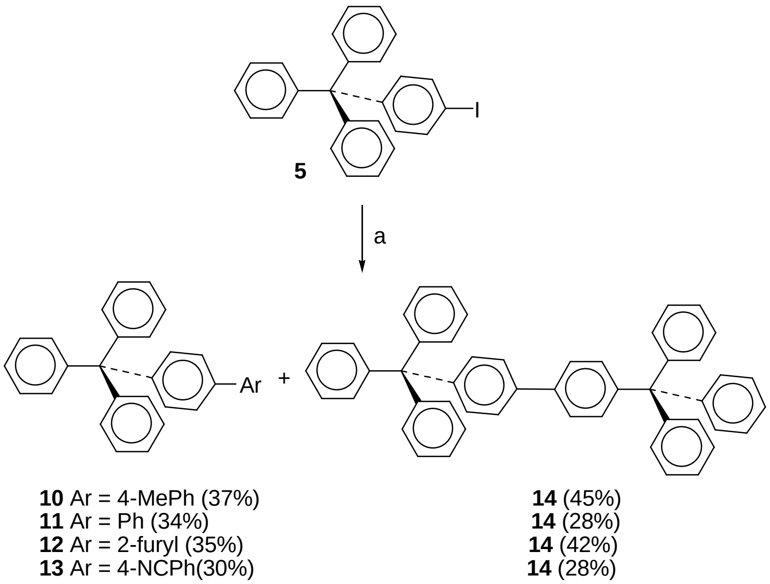
4-Tritylanilium chloride **2** was also used to prepare mono iodo TPM derivative **5**. The anilinium salt **2** underwent quantitative diazotisation in presence of $NaNO_2$ and subsequent reaction with KI gave the desired mono-iodo product **5**. Having prepared the mono-iodo derivative **5**, the attention was then focused on SM cross-coupling reaction (**Scheme III**). This compound **5** is a promising building block for preparing unsymmetrical TPM derivatives and avoids, conventional problems related to the formation of mixture of isomers[22].

Towards our goal to prepare unsymmetrical TPM derivative, the mono-iodo derivative **5** was treated with 4-methylphenylboronic acid in the presence of $Pd(PPh_3)_4$ catalyst in aqueous base and THF/ toluene solvent (**Scheme III**). An interesting side product **14** was also isolated besides the expected cross-coupling product. The product was isolated in all the instances irrespective of the substitution on the boronic acid. Its formation can be explained by self-coupling of the mono-iodo derivative under these reaction conditions[23]. It is noteworthy to mention here that the self-coupling product is a new promising building block.

In conclusion, the Suzuki-Miyaura cross-coupling reaction was successfully applied to the iodo derivatives of TPM. A family of tetrahedral molecules containing TPM moiety at the core and with different substitution pattern at the vertices have been prepared. These molecules are attractive starting point for the construction of nano material and dendrimers with spherical topologies. Synthetic yields are moderate and in reality are even better considering the multiple C–C bond formation in single operation. Synthesis of molecules of type **14** would find an interesting application in molecular engineering.

Experimental Section

Melting points were recorded on a Labhosp or Veego melting point apparatus and are uncorrected. Boiling points refer to the bath temperatures. IR spectra were recorded on a Nicolet Impact-400 FT IR spectrometer. Solid samples were recorded as KBr wafers or as $CHCl_3$ film. ^1H NMR spectra were recorded on EM-360 (60 MHz) or Varian VXR 300 (300 MHz) or Varian VXR (200 MHz) or Varian VXR (400 MHz) spectrometers. Carbon Nuclear Magnetic Resonance (^{13}C NMR) spectra were recorded on Varian VXR 300 (75.4 MHz) or Brucker 400 (100 MHz) or Varian VXR (100 MHz) or Varian VXR (50.3 MHz) spectrometer. Mass spectral measurements were carried out on GCD 1800 Hewlett-Packard GS-MS spectrometer. The high-resolution mass measurements were carried out using JEOL JMS-DX 303 GC-MS instrument. EIMS were recorded on YA 105 Waters Q-TOF Micro-Mass spectrometer. Analytical TLC were performed on (10 × 5 cm) glass plates coated with Acme's silica gel G or GF 254 (containing 13% calcium sulfate as a binder). Silica gel is coated on glass plate using 'Sandwich Technique.' In this process, two equally sized clean glass plates are immersed in uniformly stirred silica gel suspension in an organic solvent (usually ethyl acetate). Only the exposed surface of the plate is thus coated with silica gel. The solvent evaporates readily leaving a thin-layer of silica gel and then the plate is ready for the use. Visualization of the spots on TLC plates was achieved either by exposure to iodine vapors or UV light. Flash chromatography was performed using Acme's silica gel (100-200 mesh) according to method of Still (ref: Still W C; Kahn M & Mitra A, *J Org Chem*, 43, **1978**, 2923). All the reactions were monitored by employing TLC technique using appropriate solvent system for development. Reactions involving oxygen sensitive reagents or catalysts are performed in degassed solvents. Transfer of moisture sensitive materials were carried out in a glove box, using standard syringe-septum techniques and the reactions were maintained under nitrogen or argon atmosphere until the work up. Dry tetrahydrofuran (THF) and diethyl ether were freshly distilled over sodium benzophenone ketyl prior to use. Dichloromethane, carbon tetrachloride, chloroform and acetonitrile were



10 Ar = 4-MePh (37%)
11 Ar = Ph (34%)
12 Ar = 2-furyl (35%)
13 Ar = 4-NCPh(30%)

14 (45%)
14 (28%)
14 (42%)
14 (28%)

Reagents and conditions: (a) $ArB(OH)_2$, $Pd(PPh_3)_4$, THF/toluene, H_2O, Na_2CO_3, 12 h.

Scheme III

distilled over P_2O_5. Dimethyl sulfoxide was distilled over CaH_2. Ethyl acetate was distilled over potassium carbonate. (For the purification of the solvents and reagents see: Perrin, D, D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd Edn, Pergamon Press: Oxford, **1988**). Magnesium sulfate was dried in an oven at 130°C for one day. All the solvent extracts were washed successively with water, brine (saturated sodium chloride solution) and dried over anhydrous magnesium sulfate and concentrated at reduced pressure on a Buchi R-114 rotary evaporator. Yields reported are isolated yields of the materials.

General procedure for the Suzuki-Miyaura cross-coupling reaction of tetraiodo compound 4. A mixture of tetraiodo compound **4** (1 equiv.), arylboronic acid (8 equiv.), $Pd(PPh_3)_4$ (10 to 15 mole %), Na_2CO_3 (8 equiv.) in water and solvent (THF and toluene 1:1) was heated at 80°C. Typically completion of the reaction requires 12 h. At the conclusion of the reaction (monitored by TLC), the reaction mixture was diluted with water and extracted with chloroform. The combined organic layer was washed with water, brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was charged on a silica gel column. Elution of the column with ethyl acetate-petroleum ether gave the desired cross-coupling product

Tetrakis(4´-methylbiphenyl-4-yl)methane 6. To a solution of **4** (25 mg, 0.03 mmole) in THF/toluene (1:1) mixture (4 mL), 4-methylphenylboronic acid (33 mg, 0.24 mmole), aqueous Na_2CO_3 (25 mg in 1.5 mL water) and $Pd(PPh_3)_4$ (4 mg, 11.5 mole %) were added and the resultant reaction mixture was refluxed for 12 h. At the conclusion of the reaction (monitored by TLC), the reaction mixture was worked-up according to the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with 5% ethyl acetate/petroleum ether gave the compound **6** (12 mg, Yield 58%) as a grey crystalline solid; m.p. 236-38°C; IR (KBr): 3109, 2959, 2365, 1233, 1049, 937, 779 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 12H), 7.21-7.26 (m, 8H), 7.3-7.41 (m, 8H), 7.45-7.52 (m, 16H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.3, 64.2, 126.1, 127.0, 127.8, 129.7, 131.7, 137.1, 137.9, 145.8; HRMS: m/z Calcd. for $C_{53}H_{44}$: 680.3442 (M+). Found: 680.3436.

Tetrakis(biphenyl-4-yl)methane 7. To a solution of **4** (23 mg, 0.027 mmole) in THF/toluene (1:1) mixture (4 mL), phenylboronic acid (20 mg, 0.16 mmole), aqueous Na_2CO_3 (13 mg in 1.5 mL water) and $Pd(PPh_3)_4$ (4 mg, 12.8 mole %) were added and the resultant reaction mixture was refluxed for 12 h. At the conclusion of the reaction (monitored by TLC), the reaction mixture was worked-up according to the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with 3% ethyl acetate/petroleum ether gave the compound **7** (8 mg, Yield 47%) as a crystalline solid; m.p. 128-30°C (Lit m.p. 125-26°C)[19]; IR (KBr): 2933, 2858, 2394, 1445, 1360, 1183, 751cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.2- 7.62 (m, 36H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 126.2, 128.8, 131.2, 131.6, 138.6, 140.6, 145.9, 146.7; HRMS: m/z Calcd. for $C_{49}H_{36}$: 624.2816 (M+). Found: 624.2819.

Tetrakis[4-(2-furyl)phenyl]methane 8. To a solution of **4** (25 mg, 0.03 mmole) in THF/toluene (1:1) mixture (4 mL), furanboronic acid (27 mg, 0.24 mmole), aqueous Na_2CO_3 (26 mg in 1.5 mL water) and $Pd(PPh_3)_4$ (4 mg, 11.5 mole %) were added and the resultant reaction mixture was refluxed for 12 h. At the conclusion of the reaction (monitored by TLC), the reaction mixture was worked-up according to the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the compound **8** (12 mg, Yield 77% based on 3 mg of starting material recovered) as a sticky solid; IR (KBr): 3026, 2394, 1663, 1229, 1045, 768 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.44 (s, 4H, H_b), 6.58 (s, 4H, H_a), 7.24-7.26 (m, 8H), 7.43 (s, 4H, H_c), 7.53-7.56 (m, 8H); MS: (m/z) 584 (M$^+$).

Tetrakis(4´-acetylbiphenyl-4-yl)methane 9. To a solution of **4** (25 mg, 0.03 mmole) in THF/toluene (1:1) mixture (4 mL), 4-acetylphenylboronic acid (40 mg, 0.24 mmole), aqueous Na_2CO_3 (26 mg in 1.5 mL water) and $Pd(PPh_3)_4$ (5 mg, 14.4 mole %) were added and the resultant reaction mixture was refluxed for 12 h. At the conclusion of the reaction (monitored by TLC), the reaction mixture was worked-up according to the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with 15% ethyl acetate/petroleum ether gave the compound **9** (7 mg, Yield 33% based on 3 mg of starting material recovered) as a crystalline solid; m.p. 190-92 °C; IR (KBr): 2927, 2389, 2854, 1742, 1676, 1465, 1107, 874, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.65 (s, 12H), 7.23-7.38 (m, 14H), 7.54-7.6 (m, 2H), 7.68-

7.74 (m, 8H), 8.0-8.07 (m, 8H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 29.7, 126.4, 127.0, 127.5, 127.8, 129.1, 131.1, 131.7, 136.6.

General procedure for the Suzuki-Miyaura cross-coupling reaction of monoiodo compound 5.

A mixture of monoiodo compound **5** (1 equiv.), arylboronic acid (2 equiv.), $Pd(PPh_3)_4$ (3 to 8 mole %), Na_2CO_3 (2 equiv.) in water and solvent (THF and toluene 1:1) was heated at 80°C. Typically completion of the coupling reaction requires 12 h. At the conclusion of the reaction (monitored by TLC), the reaction mixture was diluted with water and extracted with chloroform. The combined organic layer was washed with water, brine and dried over $MgSO_4$. The solvent was evaporated and the crude product left was charged on a silica gel column. Elution of the column with ethyl acetate-petroleum ether mixture gave the self-coupling product **14** first and further elution of the column gave the desired cross-coupling product.

Triphenyl[4-(4′-methylphenyl)phenyl]methane 10. To a solution of **5** (50 mg, 0.11 mmole) in THF/toluene (1:1) mixture (4 mL), 4-methylphenylboronic acid (30 mg, 0.22 mmole), aqueous Na_2CO_3 (23 mg in 1.5 mL water) and $Pd(PPh_3)_4$ (5 mg, 3.8 mole %) were added and the resultant reaction mixture was refluxed for 12 h. At the conclusion of the reaction (monitored by TLC), the reaction mixture was worked-up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with petroleum ether gave the compound **14** (32 mg, Yield 45%). Further elution of the column with petroleum ether gave the compound **10** (17 mg, Yield 37%) as a crystalline solid; m.p. 214-16°C; IR (KBr): 3026, 2933, 2861, 2381, 1229, 768, 650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H), 7.16-7.32 (m, 19H), 7.43-7.48 (m, 4H); HRMS: m/z Calcd. for $C_{32}H_{26}$ (M+): 410.2034. Found: 410.2040.

4,4′-Bis-trityl-biphenyl 14. m.p. 214-16°C; IR (KBr): 2923, 2856, 1588, 1483, 1184, 1013, 818, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12-7.30 (m, 38H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 64.6, 126.1, 127.6, 131.1, 131.8, 132.5, 145.5, 146.4. HRMS m/z: Calcd. for $C_{50}H_{38}$: 639.3051 (M+1). Found: 639.3050.

Triphenyl(4-biphenylyl)methane 11. To a solution of **5** (50 mg, 0.11 mmole) in THF/toluene (1:1) mixture (4 mL), phenylboronic acid (27 mg, 0.22 mmole), aqueous Na_2CO_3 (23 mg in 1.5 mL water) and $Pd(PPh_3)_4$ (6 mg, 4.6 mole %) were added and the resultant reaction mixture was refluxed for 12 h. At the conclusion of the reaction (monitored by TLC), the reaction mixture was worked-up according to the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the compound **14** (20 mg, Yield 28%). Further elution of the column with petroleum ether gave the compound **11** (15 mg, Yield 34%) as a crystalline solid; m.p. 228-30 °C; IR (KBr): 3025, 2918, 2847, 1595, 1484, 1184, 1031, 835, 631 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19-7.66 (m, 24H); HRMS: m/z Calcd. for $C_{31}H_{24}$: 396.1877 (M+). Found: 396.1880.

Triphenyl[4-(4-furyl)phenyl]methane 12. To a solution of **5** (50 mg, 0.11 mmole) in THF/toluene (1:1) mixture (4 mL), 2-furanboronic acid (25 mg, 0.22 mmole), aqueous Na_2CO_3 (24 mg in 1.5 mL water) and $Pd(PPh_3)_4$ (10 mg, 7.7 mole %) were added and the resultant reaction mixture was refluxed for 12 h. At the conclusion of the reaction (monitored by TLC), the reaction mixture was worked-up according to the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the compound **14** (30 mg, Yield 42%). Further elution of the column with petroleum ether gave the compound **12** (15 mg, Yield 35%) as a crystalline solid; m.p. 198-200°C; IR (KBr): 2927, 2400, 1663, 1472, 1110, 1038, 821, 709 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.44 (s, 1H, H_b), 6.59-6.6 (m, 2H), 6.61 (s, 1H, H_a), 7.15-7.28 (m, 17H), 7.44 (s, 1H, H_c); HRMS: m/z Calcd. for $C_{29}H_{22}O$: 386.1670 (M+). Found: 386.1672.

Triphenyl[4-(4′-cyanophenyl)phenyl]methane 13. To a solution of **5** (50 mg, 0.11 mmole) in THF/toluene (1:1) mixture (4 mL), 4-cyanophenylboronic acid (40 mg, 0.27 mmole), aqueous Na_2CO_3 (24 mg in 1.5 mL water) and $Pd(PPh_3)_4$ (7 mg, 5.4 mole %) were added and the resultant reaction mixture was refluxed for 12 h. At the conclusion of the reaction (monitored by TLC), the reaction mixture was worked-up according to the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the compound **14** (20 mg, Yield 28%). Further elution of the column with 15% ethyl acetate/petroleum ether gave the compound **13** (14 mg, Yield 30%) as a crystalline solid; m.p. 240-42 °C; IR (KBr): 3014, 2947, 2394, 2223, 1492, 1222, 1031, 763 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18-7.35 (m, 17H), 7.47-7.66 (m, 2H), 7.69-7.72(m, 4H); HRMS: m/z Calcd. for $C_{32}H_{23}N$: 422.1908 (M+1). Found: 422.1912.

Acknowledgements

The authors thank the DST (NST), New Delhi for the financial support. One of authors (M. B.) thank the CSIR, New Delhi for the award of research fellowship. The authors also thank Dr. J. Singh and Dr. G. Williams, Optima Chemical Group LLC, Douglas, USA for providing gift sample of boronic acid.

References

1 (a) Tour J M, *Chem Rev*, 96, **1996**, 537; (b) Diederich F & Rubin Y, *Angew Chem Int Ed Engl*, 31, **1992**, 1101.

2 Gaylord B S, Heeger A J & Bazan G C, *J Am Chem Soc*, 125, **2003**, 896.

3 Constable E C, Eich O, Housecroft C E & Johnston L A, *Chem Commun*, **1998**, 2661.

4 Guay J, Diaz A, Wu R & Tour J M, *J Am Chem Soc*, 115, **1993**, 1869.

5 (a) Guo W, Galoppini E, Rydja G & Pardi G, *Tetrahedron Lett,* 41, **2000**, 7419; (b) Gong C & Gibson H W, *Macromolecules,* 29**,** **1996**, 7029; (c) Hoskins B F & Robson R, *J Am Chem Soc,* 112, **1990**, 1546; (d) Thompson A M W C, Hock, J, McCleverty J A & Ward M D, *Inorg Chim* (e) *Acta,* 256, **1997**, 331;

6 Rathore R, Burns C L & Guzei I A, *J Org Chem,* 69, **2004**, 1524; (a) Langhals H, Wagner C & Ismael R, *New J Chem*, 25, **2001** 1047; (b) Langhals H, Ismael R & Yürük O, *Tetrahedron*, 56, **2000**, 5435; (c) Shi M, Okamoto Y & Takamuku S, *Bull Chem Soc Jpn*, 63, **1990,** 2731.

7 Tomalia D A, Naylor A M & Goddard W A, *Angew Chem Int Ed Engl,* 29, **1990**, 138.

8 Fischer M & Vogtle F, *Angew Chem Int Ed,* 38, **1999**, 885.

9 Thaimattam R, Xue F, Sarma J A R P, Mak T C W & Desiraju G R, *J Am Chem Soc*, 123, **2001**, 4432.

10 Robinson M R, Wang S, Bazan G C & Cao Y, *Adv Mater*, 12, **2000**, 1701.

11 (a) Sengupta S & Sadhukhan S K, *Tetrahedron Lett,* 40, **1999**, 9157; (b) Sengupta S & Sadhukhan S K, *Tetrahedron Lett*, 42, **2001**, 3659; (c) Sengupta S & Purkayastha P, *Org Biomol Chem*, 1, **2003**, 436.

12 Eldin S, Liebman J F, Reynolds L D & Dowd P, *Tetrahedron Lett*, 33, **1992**, 4525.

13 (a) Simard M, Su D & Wuest J D, *J Am Chem Soc,* 113, **1991**, 4696; (b) Mongin O & Gossauer A, *Tetrahedron*, 53, **1997**, 6835.

14 Zimmermann T J & Müller T J J, *Synthesis*, **2002**, 1157.

15 (a) Sagl D J & Martin J C, *J Am Chem Soc*, 110, **1988**, 5827; (b) Tellenbröker J & Kuck D, *Eur J Org Chem*, **2001**, 1483; (c) Rodríguez-Franco M I, Dorronsoro I, Hernández-Higueras A I & Antequera G, *Tetrahedron Lett*, 42, **2001**, 863; (d) Sugiyama T, *Bull Chem Soc Jpn,* 54, **1981**, 2847; (e)Wassmundt F W & Kiesman W F, *J Org Chem*, 60, **1995**, 1713; (f)Wan W B & Haley M M, *J Org Chem*, 66, **2001**, 3893.

16 Sengupta S, Sadhukhan S K & Singh R S, *Indian J Chem*, 41B, **2002**, 642.

17 Alcock N W & Waddington T C, *J Chem Soc*, **1963**, 4107.

18 Mattern D L, *J Org Chem*, 48, **1983**, 4772.

19 Merkushev E B, Simakhina N D & Koveshnikova G M, *Synthesis*, **1980**, 486.

20 (a) Su D & Menger F M, *Tetrahedron Lett*, 38, **1997**, 1485; (b) Grimm M, Kirste B & Kurreck H, *Angew Chem Int Ed Engl*, 25, **1986**, 1097.

21 (a) Miyaura N & Suzuki A, *Chem Rev*, 95, **1995**, 2457; (b) Kotha S, Lahiri K & Kashinath D, *Tetrahedron*, 58, **2002**, 9633; (c) Lakshman M K, *J Organomet Chem,* 653, **2002**, 234.

22 Grimsdale A C, Bauer R, Weil T, Tchebotareva N, Wu J, Watson M & Müllen K, *Synthesis*, **2002**, 1229.

23 Miyaura N, in *Advances in Metal-Organic Chemistry*, edited by L S Libeskind, Vol. 6, (Jai Press, London) **1998**, p.187.