

Part I

Section A

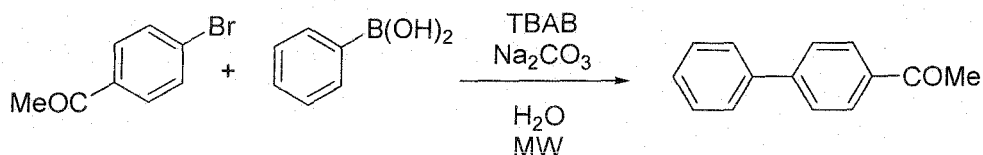
"Poly-ionic Resin Supported Phenylating Agent for Base-free Suzuki-Miyaura Coupling Reaction"

1. A.1. Introduction

Solid phase organic synthesis (SPOS) is now routinely used for the preparation of combinatorial libraries of low molecular weight organic molecules.¹ Recently much of this effort has been focused towards optimisation of biologically active frameworks within the pharmaceutical industry.² Use of solid-supported reagents,³ a novel extension has recently been reported by several groups and its subsequent application towards more efficient solution phase combinatorial chemistry. This technique involves traditional solution phase chemical synthesis in which the reaction mixture is purified by using a solid support (scavenger). These solid supported reagents can be used to remove an excess of reactants and thus give the required product in high yield and in a single operation. This technique offers many of the advantages, such as easy reaction workup, and product purification with the additional advantages associated with traditional solution phase synthesis. Previously this strategy has been referred to as either a solid-supported scavenger (SSS), polymer-supported quench (PSQ), or complementary molecular reactivity and molecular recognition (CMR/R)⁴ and now such reagents will be referred to as polymeric scavenger reagents (PSRs). The development of suitable polymer support to immobilize the reagents/catalysts followed by its applications to various organic transformations constitutes an attractive area of "Green Chemistry". It has become the backbone of modern combinatorial chemistry. The chemical transformation which has received much attention in the modern era is polymer-assisted solution-phase (PASP) Suzuki-Miyaura reaction. The Suzuki-Miyaura reaction has proven to be an extremely versatile and useful in the formation of carbon-carbon bonds, especially the formation of aryl-aryl or vinyl aryl bonds. The Suzuki-Miyaura reaction has gained popularity due to the mild reaction conditions, commercial availability of diverse boronic acids, and the tolerance of a wide range of functional groups that are environmentally safer than the other organometallic reagents⁵. Due to the low toxicity,⁶ air and moisture stability of organoboranes makes this method more attractive alternative over other methods. This coupling reaction generally employ organic solvents such as DMF, THF, CH₃CN etc, in the presence of base, ligand and Pd-catalysts which are soluble in these solvents, the catalysts may also be used on the solid surface in different ways.⁷ Aryl halides and triflates substituted with electron-withdrawing groups (EWGs) are suitable substrates for the cross-coupling reaction. The relative reactivity of leaving groups is normally in the order $I^- > OTf^- > Br^- \gg Cl^-$. The most commonly used base in the SM cross-coupling reaction is K₂CO₃ but this is often ineffective with sterically demanding substrates. In such instances, Ba(OH)₂ or K₃PO₄ has been used to generate good yields of the cross-coupled products. Other bases utilised in the SM coupling reaction include Cs₂CO₃, K₂CO₃, TIOH, KF and NaOH.⁸ It is well known that the base is involved in the coordination

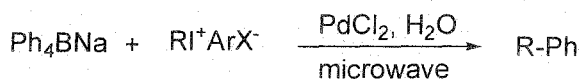
sphere of the palladium and the formation of the $\text{Ar-PdL}_2\text{-OR}$ from $\text{Ar-PdL}_2\text{-X}$ is known to accelerate the transmetallation step. The biaryl motif is found in a range of pharmaceuticals, herbicides, and natural products, liquid crystalline materials, nanotechnology & in conducting polymers. So the development and improvement of the conditions for Suzuki-Miyaura reaction has received much attention. In the past few years, great advances have been made in developing the active and efficient catalyst by modifying the traditional ligands and discovering new ones. Among the variations of the catalyst and the base, Leadbeater *et al.*⁹ reported SM coupling reactions using very low levels of Pd (50 ppb). (Scheme 1)

Scheme 1



Yan and coworkers have recently reported base-free SM reaction using hypervalent iodonium aryl salts instead of aryl halides.¹⁰

Scheme 2



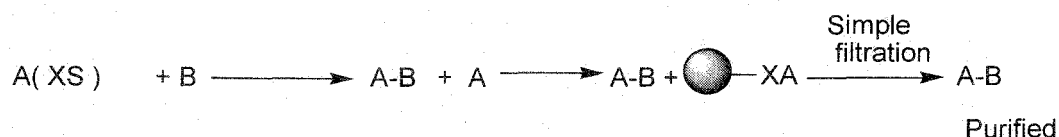
Functionalized solid supports like polymers loaded with homogeneous catalysts and polymer supported reagent are well established in organic synthesis.¹¹ Simple purification of the products and easy recyclability of the catalysts as well as reagent are major advantages of heterogeneous reactions. In general, arylboronic acids are good nucleophilic organoboron reagents in this coupling reaction.¹² However, boronic acids are never ideal because they exhibit several drawbacks, such as the partial formation of dimeric and cyclic trimeric boroxines (which depend on storage water content).¹³ Many functionalized boronic acids are waxy solids that are difficult to purify and electron-deficient heteroaryl-boronic acids, have a short shelf life owing to their tendency to undergo facile proto-deboronation. This instability often requires their storage at low temperatures. Protodeboronate tendency is quite often manifests itself during cross-coupling reactions carried out in polar protic solvents.¹⁴ This structural ambiguity affects the stoichiometry of boronic acids added to the intended reaction and use of excess boronic acids in cross-coupling reactions. In view of the several aspects required for the development of new variants of the organoboron species, the catalyst and the base in the SM coupling reaction and the optimizing process have remained challenging areas of research.

1. A.2. Background and Objective:

In the era of 1990-2000, the concept of a resin-capture-release technique generating the polymer-bound reactive species has been established as a potential method for several organic

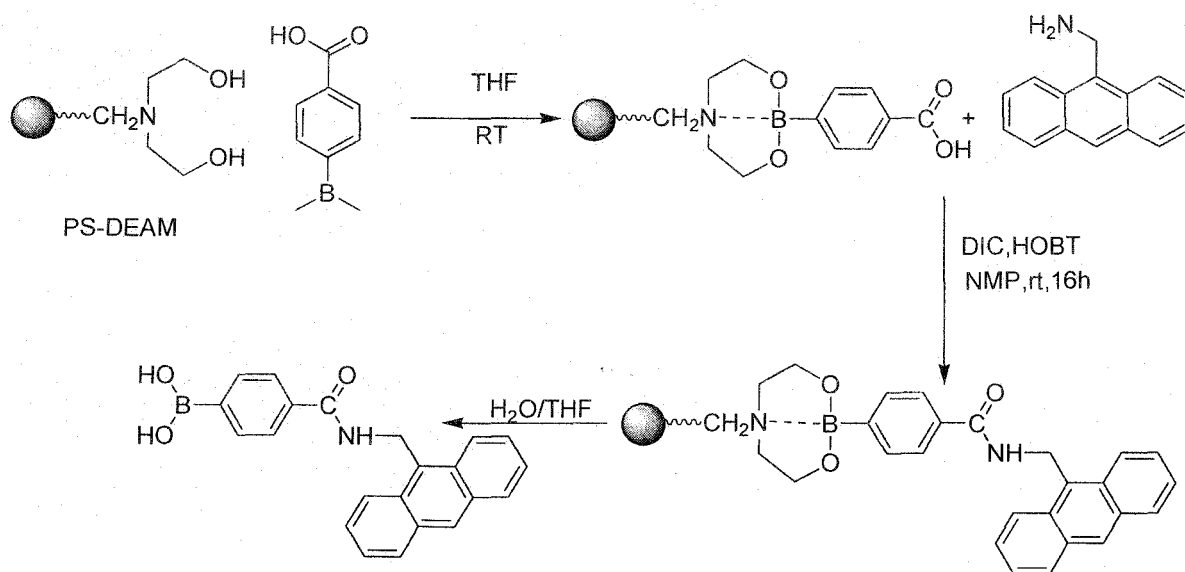
transformations,¹⁵ and the first report of an application of a polymer supported reagent in synthesis was accounted by Keating and Armstrong.¹⁶ Considerable effort has been devoted to the development of new techniques which assist in the rapid purification of solution phase reactions. The solid supported reagents can be used to remove an excess of reactants by simple filtration and thus give the required product in high yield in a single operation step (Scheme 3) without further purification.

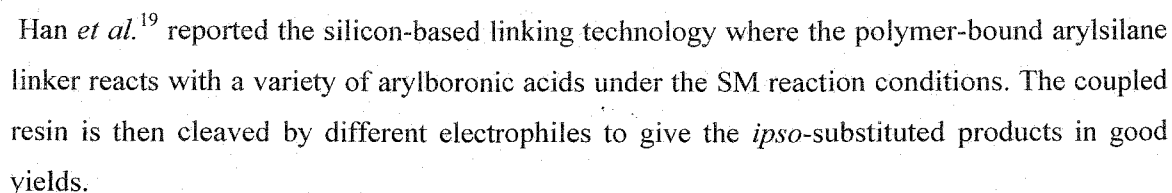
Scheme 3



Polymer-bound boronic acids were first reported in 1976¹⁷ & in 1994, that supported boronic acid was used in SM coupling reaction with the aid of combinatorial chemistry. A variety of techniques to immobilize different components of SM reactions on macroporous solids clearly revealed the lack of application of polyionic resins soaked with organoboron species. Parlow and co-worker¹⁸ synthesized anthracene-tagged boronic acid using polymer supported *N,N*-diethanolaminomethyl polystyrene and applied it for Suzuki-Miyaura reaction to afford > 90% yield of the coupled product, as shown in Scheme 4.

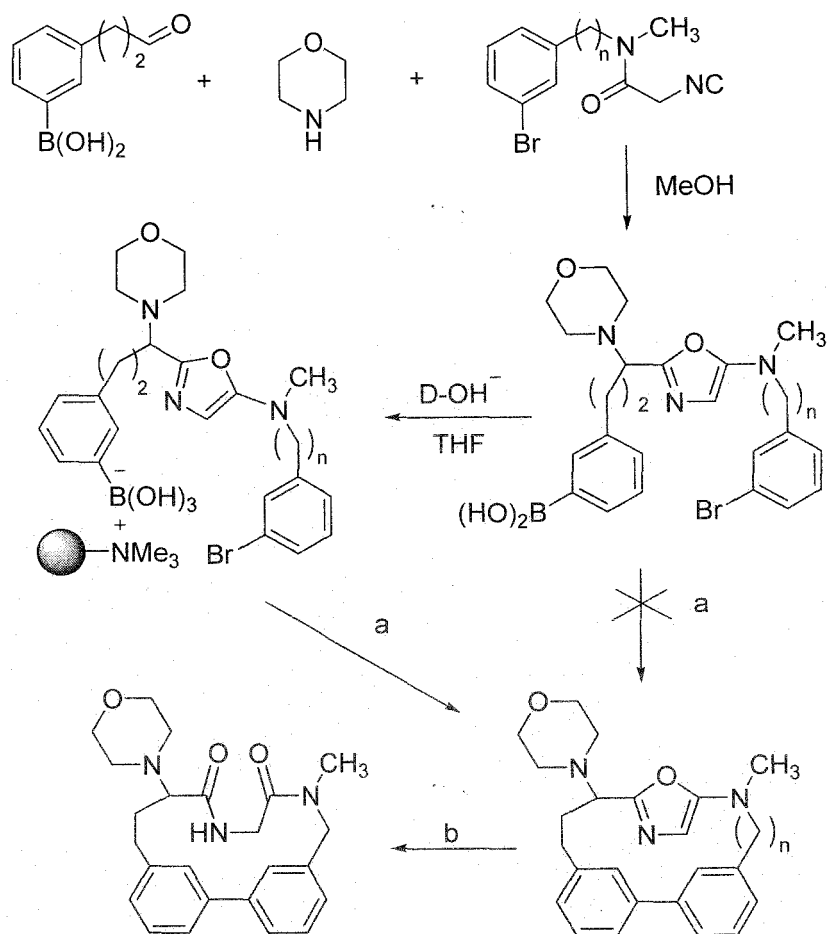
Scheme 4





Scheme 6

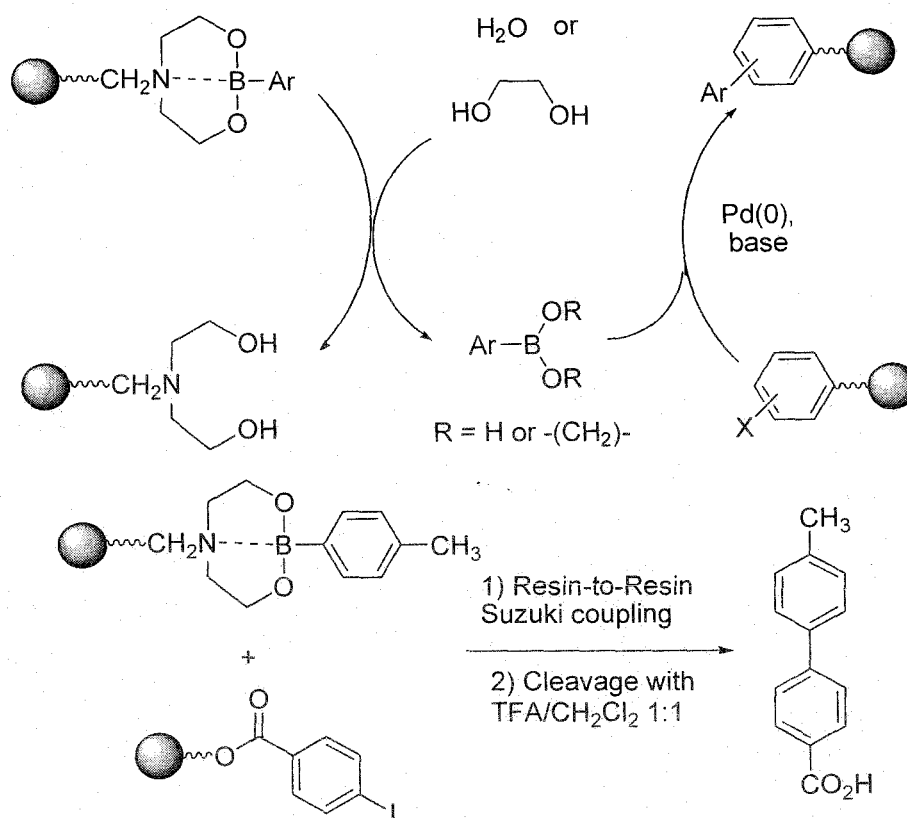




(a) D-Br (1 eq), cat. Pd(OAc)₂ (5 mol%), TPPDS (20 mol%), THF-H₂O (4:1), 40 °C, 40 h; (b) TFA (120 eq), H₂O (30 eq), rt, 2 h

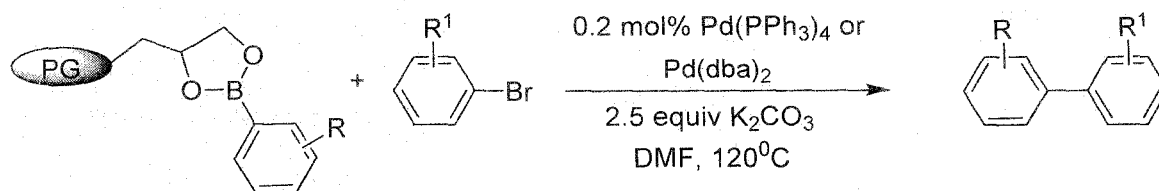
The first resin-to-resin transfer reaction [RRTR] for the formation of carbon-carbon bonds described by Hall *et al.*²¹ is the Suzuki-Miyaura RRTR system which allows the convergent solid-phase synthesis of un-symmetrically functionalized biphenyl compound that would have been difficult to access using a linear solid-phase strategy. They used DEAM-PS resin to generate libraries of several new arylboronic acids as coupling partners.

Scheme 7



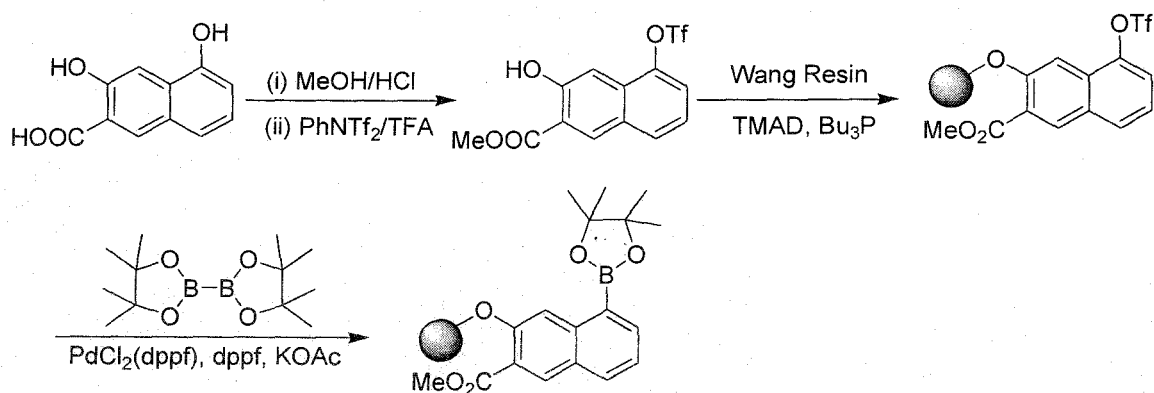
Haag *et al.*²² first synthesized the soluble high-loading polyglycerol support for functionalized boronic acids or ester and subsequently employed in homogeneous Suzuki-Miyaura cross-coupling reactions & isolated high yields (84-91%) of functional biaryls with minimal amounts of the Pd catalyst.

Scheme 8



Kim *et al.* has prepared polymer bound naphthyl boronate²³ in different way which is used for Suzuki-Miyaura cross coupling reaction.

Scheme 9

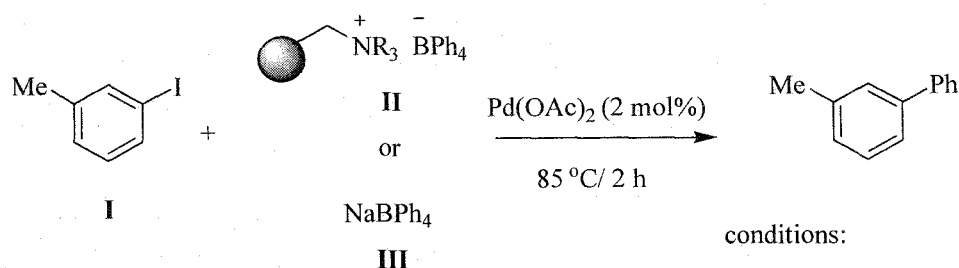


1. A.3. Results and discussion:

In connection with our interest in the development of ionic resin-bound reagents and/or catalysts,²⁴ we have an idea to develop an ion-exchange resin-supported borate species as a heterogeneous phenylating agent. Our initial studies began with Amberlite[®] IRA-900 (chloride form) ion-exchange resins, which were exchanged with tetraphenylborate anion (Ph₄B⁻) by continuous rinsing with an aqueous solution of NaBPh₄ until the washings gave negative response to chloride anion (monitored with AgNO₃ solution followed by addition of aqueous ammonia). The exchange resin beads were then washed successively with water (to make it free from sodium ions), acetone and finally dried under vacuum for several hours to afford the Amberlite resin (Ph₄B⁻ form). Loading of the borate anion was determined by differential weighing between the quantities of dried resin (chloride form) initially taken and recovered after several washings with aqueous solution of NaBPh₄, water, acetone and drying.

The Amberlite (Ph₄B⁻) resin thus prepared was used directly for the SM coupling with 3-iodotoluene in the presence of Pd(OAc)₂ (2 mol%) and Na₂CO₃ (1 equiv) and the corresponding unsymmetrical biphenyl was isolated in 90% yield (Scheme 10, conditions a). Similar coupling of 3-iodotoluene and NaBPh₄ in the presence of Na₂CO₃ afforded only 43% yield of the coupled product (Scheme 10, conditions b). However, on increasing the quantity of NaBPh₄ in 3-iodotoluene–NaBPh₄ (1:2.5), the resulting coupled product could be isolated in 88% yield (Scheme 10, conditions c). A further interesting observation was that the yield of the coupled product was not influenced by the absence of base (Scheme 10, conditions d and e). Such base-free conditions for SM reactions offer significant practical advantages and have not previously been reported with the organoborate ion immobilized onto polymers.

Scheme10



conditions:

- (a) $\text{I/II/Na}_2\text{CO}_3 = 1:1 \text{ g/mmol:1}$; 90%
- (b) $\text{I/III/Na}_2\text{CO}_3 = 1:1:1$; 43%
- (c) $\text{I/III/Na}_2\text{CO}_3 = 1:2.5:1$; 88%
- (d) $\text{I/III} = 1:2.5$; 88%
- (e) $\text{I/II} = 1:1 \text{ g/mmol}$; 96%

The common mechanism of SM coupling reactions (i.e., sequential oxidative addition, transmetalation, and reductive elimination) includes a base,²⁵ which is believed to be involved in several steps of the catalytic cycle, most notably the transmetalation process.²⁶

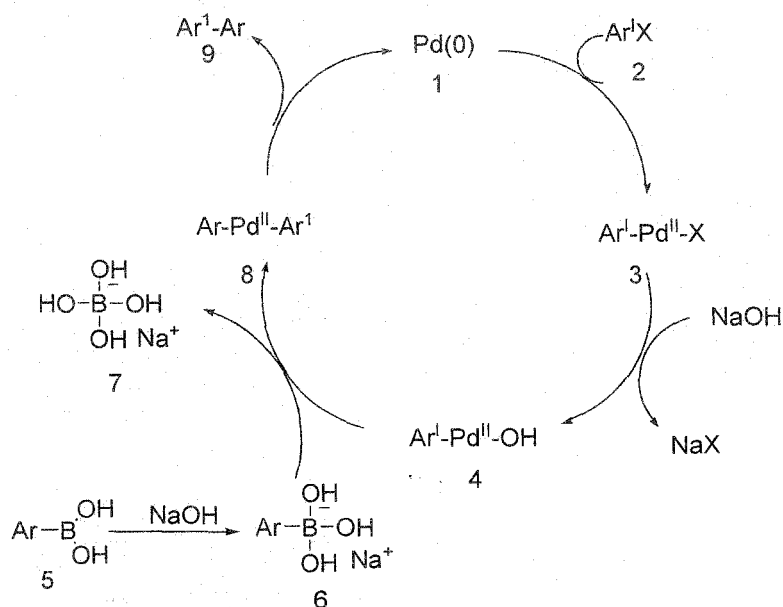
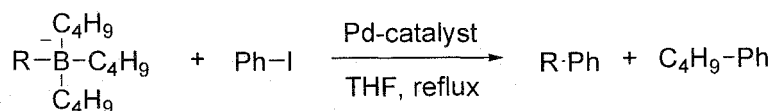


Fig. 1 A general catalytic cycle for Suzuki-Miyaura coupling reaction

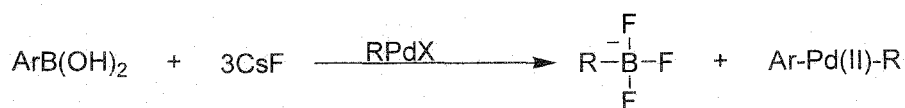
The efficiency of palladium originates from its ability, when it is zerovalent, to activate C-X bonds ($X=\text{I}, \text{Br}, \text{Cl}$) by an oxidative addition which provides an organopalladium (II) complex prone to react with nucleophiles.²⁷ This is followed by the transmetalation step between the organopalladium (II) complex and the organoboron compound in the presence of a base. The transmetalation between organopalladium (II) halides and organoboron compounds does not occur readily due to the low nucleophilicity of organic group on boron atom.²⁸ However, the nucleophilicity of organic group on boron atom can be enhanced by quarternization of the

boron with negatively charged bases giving the corresponding “ate” complexes.²⁹ It is reported that such “ate” complexes undergo a clean coupling reaction with organic halide³⁰ (Scheme 11). Scheme 11

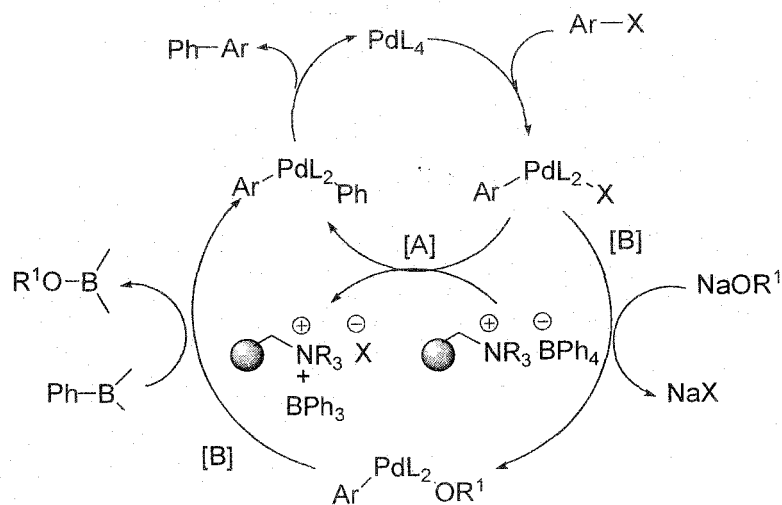


The final step is reductive elimination which takes place giving the product and regenerating the Pd(0) species. Recently, fluoride salts have been found to affect to the cross-coupling reactions of 1-alkenyl and arylboronic acids (scheme 12)³¹. The species that undergoes transmetalation is assumed to be organo(trifluoro) borate ion.

Scheme 12



The reaction protocol reported herein precludes the use of any base. Hence we propose a plausible base-free mechanism vis-à-vis the catalytic cycle using a base as shown below.



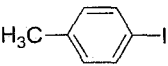
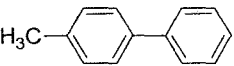
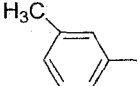
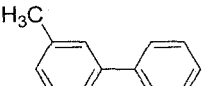
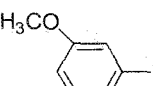

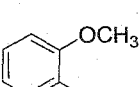
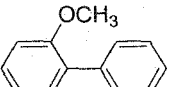
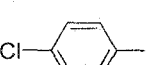
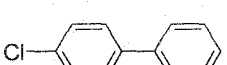
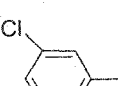
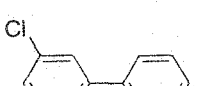

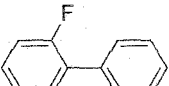
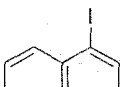
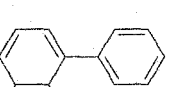
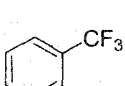
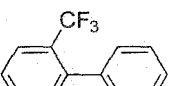
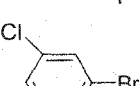

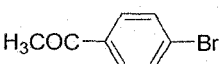
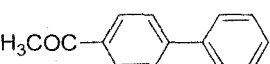
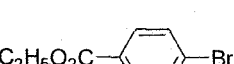
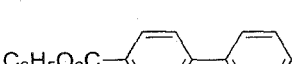
[A] Proposed catalytic cycle for cross-coupling of aryl halide with organoborane species without any base.
[B] Catalytic cycle for cross-coupling of aryl halides with organoborane species using base.

Fig. 2 - Plausible mechanism for the Suzuki-Miyaura coupling reaction using the borate resin

The transmetalation process releases triphenylborane, which being water-sensitive may be hydrolyzed during work-up producing phenylboronic acid. Indeed new isolated and characterised phenylboronic from the reaction mixture. Therefore it may be proposed that the


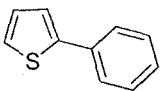
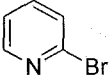
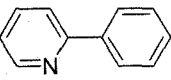
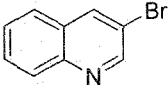
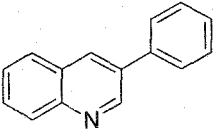
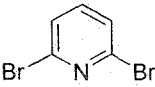
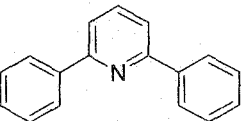
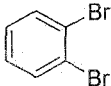
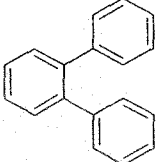
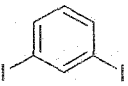
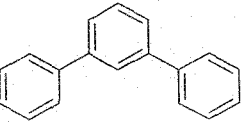


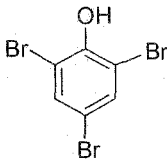
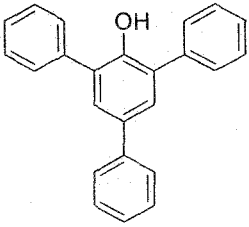
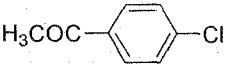

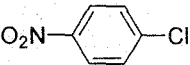
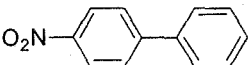
resin-supported tetraphenyl borate not only serves as an efficient phenylating agent but also acts as a suitable nucleophile requisite in the transmetalation process. A variety of aryl bromides and iodides bearing electron donating or withdrawing groups as well as heteroaryl halides underwent SM coupling in either DMF or water at 80-90 °C. Many examples have been illustrated in Table 1. Typical problems encountered during SM coupling reactions using the base, such as saponification of esters or aldol-type condensations of carbonyl compounds were successfully overcome using our reaction protocol (Table 1, entries 11, 12). Bis- and tris-aryl halides underwent SM cross-coupling with ease giving the desired adducts in good yields (Table 1, entries 19, 20). Activated aryl chlorides are known to undergo SM coupling reactions.³² Using the immobilized borate we performed base-free couplings with activated aryl chlorides successfully (Table 1, entries 21 and 22) in presence of one equivalent of tetrabutylammonium salts (TBAB).³³

Table 1: Suzuki-Miyaura Couplings Using Amberlite Resin (Tetraphenylborate Form)

Entry No.	Aromatic Halide ^[a]	Temp./ Time	Product ^[b]	% of Yield ^[c]
1		80 °C / 2 h		91 (91)
2		85 °C / 2 h		96 (95)
3		85 °C / 3 h		89
4		90 °C / 4 h		76
5		80 °C / 2.5 h		95 (92)
6		80 °C / 2 h		95
7		90 °C / 3 h		88
8		85 °C / 4 h		91
9		80 °C / 6 h		71
10		80 °C / 2 h		86 (88)
11		80 °C / 3 h		92
12		80 °C / 3 h		83

Continued.....

Table 1: Suzuki-Miyaura Couplings Using Amberlite Resin (Tetraphenylborate Form)

Entry No.	Aromatic Halides ^[a]	Temp/ Time	Products ^[b]	% of yield ^[c]
13		80 °C / 3 h		90
14 ^[d]		85 °C / 6 h		80 (75)
15 ^[d]		80 °C / 4 h		97
16 ^[d]		90 °C / 3 h		84
17		90 °C / 4 h		77
18		80 °C / 3 h		78 (85)
19		85 °C / 3 h		87
20		90 °C / 8 h		58
21 ^[e]		90 °C / 5 h		(88)
22 ^[e]		85 °C / 5 h		(95)

[a] 1 mmol aryl halide : 1 g resinTPB : 2 mol% Pd(OAc)₂ in DMF or water.

[b] All compounds were characterized by known mp; IR, ¹H- and ¹³C-spectral data.

[c] Yields in the parentheses represent reactions carried out in water.

[d] 1.5 mol% of Pd₂(dba)₃ was used instead of Pd(OAc)₂.

[e] TBAB (1 Equiv.) and Na₂CO₃ (1 Equiv.) were required.

1. A.4. Conclusion

Many of the methods employed for C-C bond formation involve the direct coupling of highly reactive organometallic reagents with aryl halides in the presence of various catalysts. Suzuki-Miyaura coupling reaction is one of the example where C-C bond formation occur under ordinary condition. Here tetraphenylborate ions are immobilized on polyionic resin surface and the resulting species can be used as phenylating reagents in SM coupling reactions as well as it also fulfills the function of base. Attaching of tetraphenylborate to a solid phase has many advantages compared to running the reaction in solution, not only in terms of simplified purification but also in minimizing contamination of the final product. Easy isolation of the desired coupled product in high yields along with base- and ligand-free conditions offer distinct advantages over the direct use of the corresponding metal salt and phenyl boronic acid. Aryl chlorides are also arylated under this reaction conditions.

A limitation of the process is that although there are four Ph-groups on the immobilized tetraphenylborate, it was possible to utilize only one in the arylation whereas the other three get converted to phenylboronic acid during the work-up. Another drawback is that the resin functions only as a phenylating agent. In order to introduce other aryl groups the protocol needs some improvement. This can be done by immobilizing substituted phenyl borates onto the resin which would indeed broaden the scope of our methodology. Further exploration regarding this work is underway in our laboratory.

1. A.5. Experimental Section:

All reactions were performed in round bottom flask in air and refluxing condition. The minimal reaction times were determined by monitoring TLC of the reaction mixture. Silica gel (60–120 mesh) was used for chromatographic purifications. DMF was dried by distillation over P_2O_5 . 1H NMR and ^{13}C NMR were recorded at 300 MHz and 75 MHz respectively using Bruker AV-300 spectrometer. TMS was used as an internal standard and NMR spectral values are reported in ppm unit. Amberlite® IRA-420 Cl^- standard grade (14–52 mesh) and palladium acetate were purchased from commercial suppliers and were used directly.

1. A.6. Preparation of Polymer Supported Borate (PS-Borate)

Amberlite® IRA-900 resin (chloride form; 2.50 g) was stirred with aq. $NaBPh_4$ (1.73 g) until complete exchange as judged by Cl^- loss (tested with $AgNO_3$). The exchanged resin was washed with H_2O , acetone and dried to give the tetraphenylborate $^-$ form resin (3.92 g). The mass difference between product and starting materials (ca. 310 mg) was comparable with the calculated difference (296 mg). The resulting borate-bound resin thus contained a 1.14 mmol g^{-1} loading of the borate ions and was used directly in the SM coupling reactions.

1. A.7. General Reaction Procedure

A mixture of aryl halide (1 mmol), Amberlite resin (Ph_4B^- form) (1 g, 1.14 mmol) and $\text{Pd}(\text{OAc})_2$ (4.5 mg, 2 mol%) was taken in DMF (2 mL) and heated in an oil bath at 85 °C for 2 h. After cooling, the reaction mixture was diluted with H_2O (5 mL) and the resin was filtered off. The filtrate was extracted with Et_2O (3×15 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 . Removal of the solvent left an oily residue, which was passed through a short column of silica gel (60–120 mesh) and eluting with light petroleum to afford 3-phenyltoluene as a colourless liquid.

1. A.8. Physical Properties and Spectral Data of Compounds:

Entry 1: 4-Methyl biphenyl

Reaction temp: 80 °C; Time: 2h; Yield: 91%, mp. 46-48 °C

IR (nujol): ν_{max} 2924, 2858, 2360, 2337, 1458, 1377 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ = 7.52-7.10 (m, 9H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 141.1, 138.3, 136.9, 129.5, 128.7, 128.6, 127.0, 126.9, 21.1.

Entry 2: 3-Methyl biphenyl

Reaction temp: 85 °C; Time: 2h; Yield: 96%, (obtained as liquid).

IR (nujol): ν_{max} 3031, 2900, 1604 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ = 7.87-7.43 (m, 9H), 2.67 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 141.3, 141.2, 138.2, 128.6, 127.9, 127.8, 127.2, 127.1, 126.7, 124.2, 21.4.

Entry-3: 3-Methoxy biphenyl

Reaction temp: 85 °C; Time: 3h; Yield: 89%, (obtained as liquid).

IR (neat): ν_{max} 1574, 1610 cm^{-1} . ^1H NMR (CDCl_3): δ = 3.75 (s, 3H); 6.77–6.81 (m, 1H), 7.03–7.10 (m, 2H), 7.21–7.36 (m, 4H), 7.47–7.51 (m, 2H); ^{13}C NMR (CDCl_3), δ = 55.2, 112.6, 112.8, 119.6, 127.1, 127.4, 128.7, 129.7, 141.0, 142.7, 159.9.

Entry 5: 4-Chloro biphenyl

Reaction temp: 80 °C; Time: 2h; Yield: 91%, mp. 77-78 °C.

IR (nujol): ν_{max} 2924, 2854, 2357, 2337, 1454, 1377 cm^{-1} ; ^1H NMR (CDCl_3): δ = 7.60-7.31 (m, 9H). ^{13}C NMR (CDCl_3): δ = 140.0, 139.7, 133.4, 128.96, 128.94, 128.4, 127.7, 127.0.

Entry 6: 3-Chlorobiphenyl.

Reaction temp: 80 °C, Time: 2 h, Yield: 95% (obtained as liquid).

IR (neat): ν_{max} 3062, 3032, 2360, 2341, 1593, 1566 cm^{-1} ; ^1H NMR (CDCl_3): δ = 7.60-7.30 (m, 8H); ^{13}C NMR (CDCl_3): δ = 140.0, 139.7, 133.4, 129.0, 128.9, 128.4, 127.6, 127.0.

Entry 7: 2-Fluorobiphenyl.

Reaction temp: 90 °C, Time: 3 h, Yield: 88%; mp 70-72 °C.

IR (nujol): ν_{\max} 2924, 1716 cm^{-1} ; ^1H NMR (CDCl_3): δ = 7.15 – 7.57(m, 9H); ^{13}C NMR (CDCl_3): δ = 159.76, 135.82, 130.8, 130.7, 129.2, 129.0, 128.9, 128.7, 128.4, 127.6, 124.3, 116.2.

Entry 8: 1-Phenyl naphthalene

Reaction temp: 85 °C; Time: 4h, Yield: 91% (obtained as liquid).

IR (neat): ν_{\max} 3059, 1493, 1396 cm^{-1} ; ^1H NMR (CDCl_3): δ = 8.00-7.98 (m, 1H), 7.94-7.87 (m, 2H), 7.65-7.34(m, 9H). ^{13}C NMR (CDCl_3): δ = 141.0, 140.5, 134.1, 131.9, 130.3, 129.1, 128.5, 127.9, 127.5, 127.4, 127.2, 126.3, 126.0, 125.6.

Entry 9: 2-Trifluoromethyl biphenyl

Reaction temp: 80 °C, Time: 6 h, Yield: 71% (obtained as liquid).

IR (neat): ν_{\max} 3067, 2360, 1481, 1450, 1315, 1126, 767 cm^{-1} ; ^1H NMR (CDCl_3): δ = (dd, 2H, j = 7.8 & 0.9 Hz); 7.58-7.26 (m, 8H); ^{13}C NMR (CDCl_3): δ = 141.4, 141.2, 139.9, 132.0, 131.2, 129.0, 128.8, 128.7, 127.8, 127.6, 127.3, 127.2, 126.2, 126.1, 126.0, 125.9, 122.4, 118.8, 30.3, 29.8.

Entry 12: 4-Phenylethyl benzoate

Reaction temp: 80 °C; Time: 8 h; Yield: 83%; mp 38 °C.

IR (nujol): ν_{\max} 2930, 2346, 1780, 1681, cm^{-1} ; ^1H NMR (CDCl_3): δ = 8.11 (d, 2H, J = 8.4 Hz), 7.67-7.61 (m, 4H), 7.49-7.38 (m, 3H), 4.40 (q, 2H, J = 7.2 Hz), 1.41 (t, 3H, J = 7.2 Hz); ^{13}C NMR (CDCl_3): δ = 166.5, 145.5, 140.1, 130.1, 129.2, 128.9, 128.1, 127.0, 60.9, 14.4.

Entry 14: 2- Phenylpyridine

Reaction temp: 85 °C; Time: 6h; Yield: 80% (obtained as liquid)

IR (nujol): ν_{\max} 3060, 1585 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ = 7.23-7.27 (m, 1H), 7.42-7.46 (m, 3H); 7.49-7.51 (m, 2H); 7.75-7.78 (m, 2H); 7.98-8.01 (m, 1H);. ^{13}C NMR (75 MHz, CDCl_3): δ = 157.4, 149.5, 139.2, 137.0, 129.1, 128.8, 127.0, 122.2, 120.7.

Entry 15: 3-Phenyl quinoline

Reaction temp: 80 °C; Time: 4 h; Yield: 97% (obtained as liquid)

IR (nujol): ν_{\max} 3074, 2935, 2341, 1500 cm^{-1} ; ^1H NMR (CDCl_3): δ = 8.01-7.98 (m, 1H), 7.94-7.87 (m, 2H), 7.65-7.37 (m, 9H); ^{13}C NMR (CDCl_3): δ = 141.0, 140.5, 134.1, 131.9, 130.3, 129.0, 128.5, 127.5, 127.4, 127.2, 126.3, 126.0, 125.6.

Entry 17: 1, 2- Diphenylbenzene

Reaction temp: 90 °C, Time: 4 h; Yield: 77%, (solid) mp 54–56 °C (lit.³⁴ 58 °C);

IR (Nujol): ν_{\max} 1600, 1578, 1480 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 7.46–7.33 (m, 4H), 7.22–7.01 (m, 10H); ^{13}C NMR (CDCl_3 , 75 MHz): δ = 141.5, 140.5, 130.6, 129.9, 127.8, 127.4, 126.4.

Entry 18: 1, 3-Diphenylbenzene

Reaction temp: 80 °C; Time: 3 h; Yield: 78%, (solid) mp 87–88 °C (lit³⁵ mp 89 °C)

IR (Nujol): ν_{\max} 1454, 1377 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 300K): δ = 7.78 (s, 1H), 7.62–7.28 (m, 13H); ^{13}C NMR (75 MHz, CDCl_3 , 300K): δ = 141.7, 141.1, 129.1, 128.7, 127.3, 127.20, 126.1.

Entry 19: 1, 4-Diphenyl benzene

Reaction temp: 85 °C; Time: 3 h; Yield: 87%; mp 212–214 °C. (lit³⁴)

IR (nujol): ν_{\max} 1454, 1377 cm^{-1} ; ^1H NMR (CDCl_3): δ = 7.60–7.54 (m, 8H), 7.41–7.36 (m, 4H), 7.31–7.26 (m, 2H); ^{13}C NMR (CDCl_3): δ = 140.7, 140.1, 128.8, 127.5, 127.4, 127.0.

Entry 20: 2, 4, 6-Triphenyl phenol

Reaction temp: 90 °C; Time: 8 h; Yield: 58%; mp. 144–145 °C.

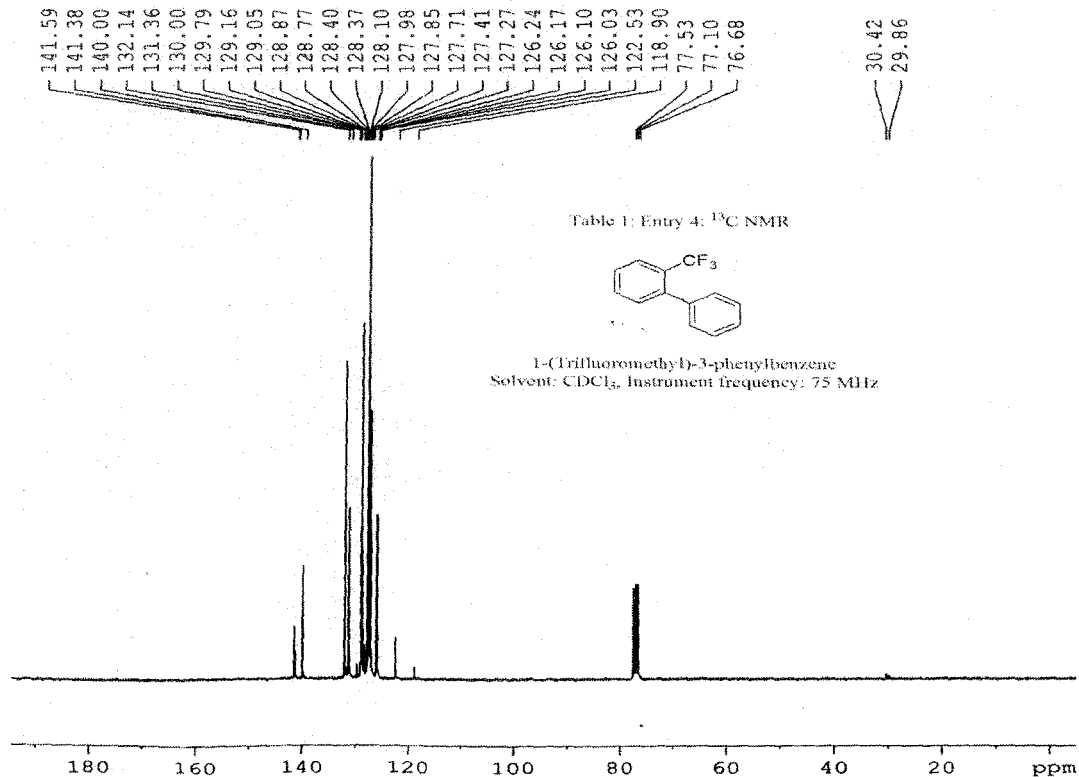
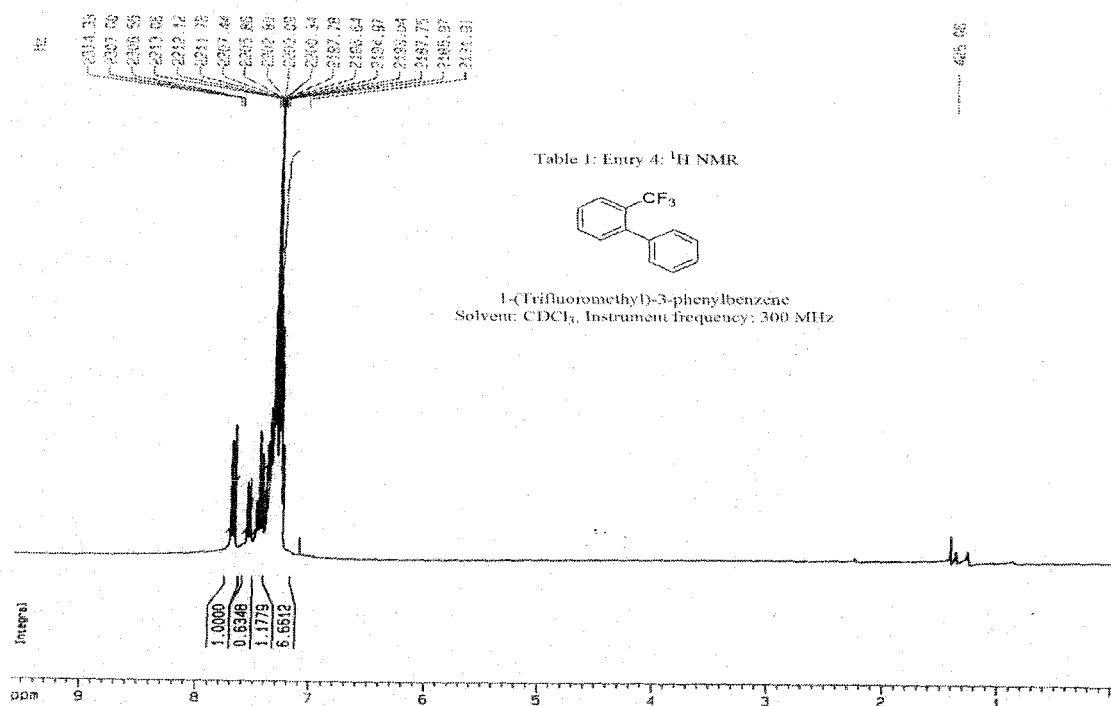
IR (nujol): ν_{\max} 3512, 1595, 1227 cm^{-1} ; ^1H NMR (CDCl_3): δ = 7.61–7.26 (m, 17H), 5.43 (s, 1H); ^{13}C NMR (CDCl_3): δ = 148.9, 140.5, 137.5, 133.8, 129.4, 129.1, 128.9, 128.8, 128.6, 127.8, 126.9, 126.7.

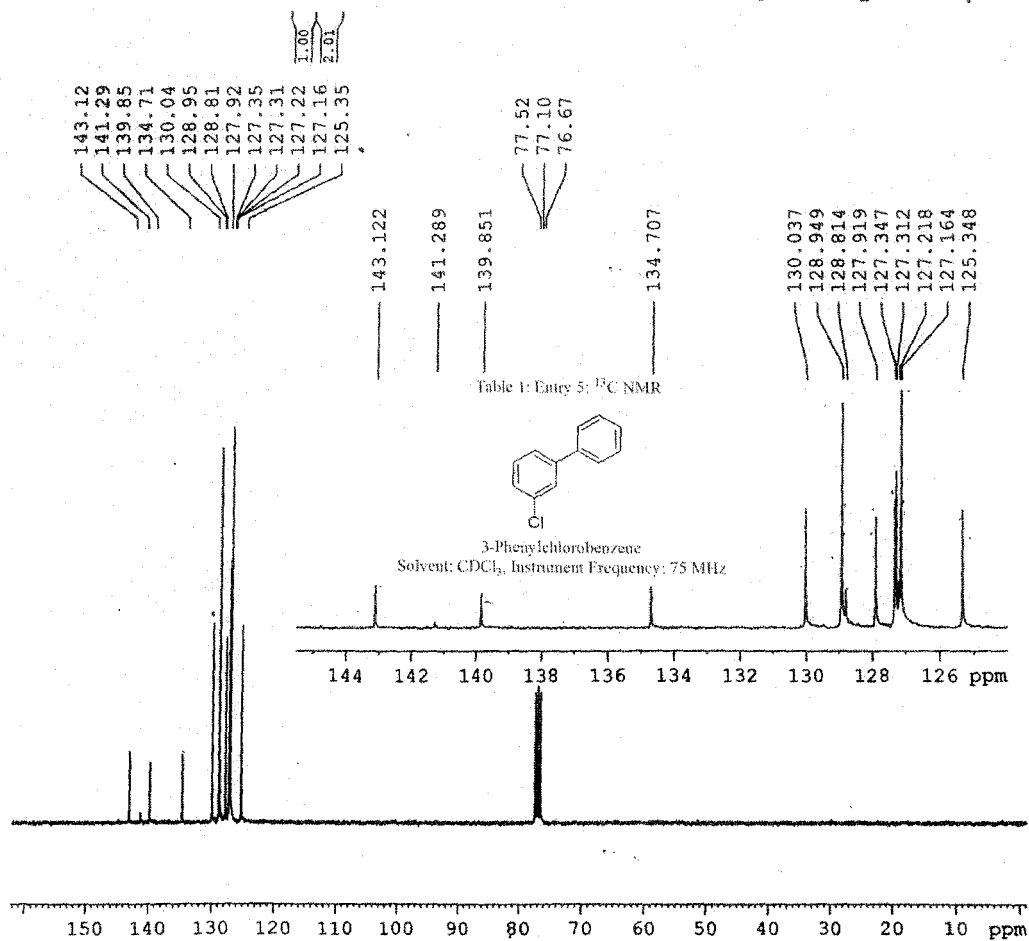
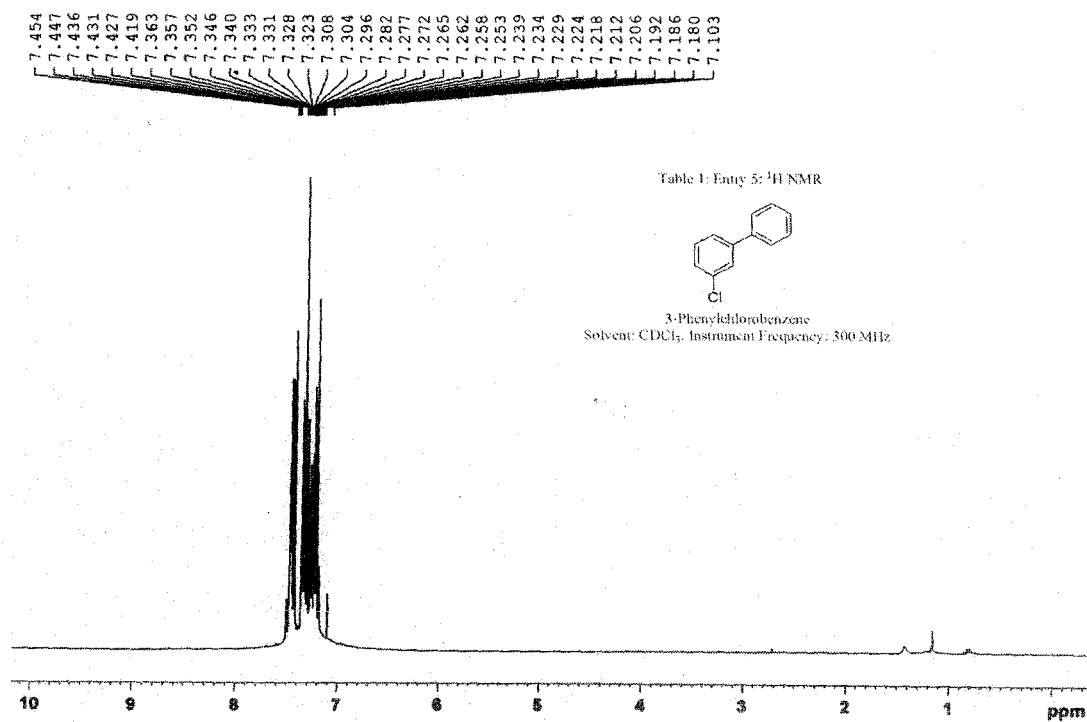
Entry 22: 4-Nitro biphenyl

Reaction temp: 85 °C; Time: 5h; Yield: 95%; (solid) mp. 112–113 °C. (lit³⁶)

IR(nujol): ν_{\max} 2924, 2855, 2360, 2337, 1512, 1458, 1346 cm^{-1} ; ^1H NMR (CDCl_3): δ = 8.29 (td, 2H, J = 9 & 2.1 Hz), 7.73 (td, 2H, J = 8.7 & 1.8 Hz), 7.64–7.61 (m, 2H), 7.53–7.44 (m, 3H); ^{13}C NMR (CDCl_3): δ = 147.6, 147.1, 138.8, 129.2, 128.9, 127.8, 127.4, 124.1.

NMR Spectra of Some Selected Compounds





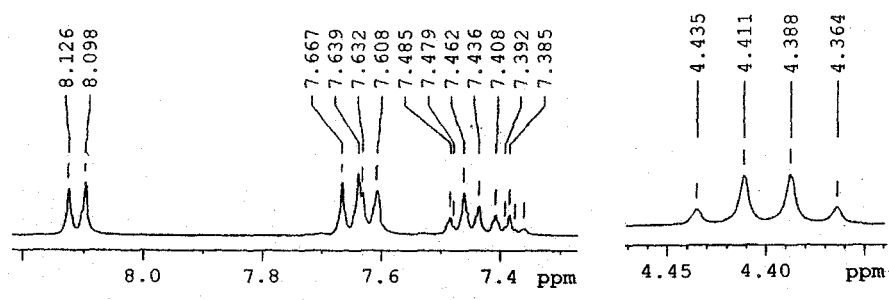


Table 1: Entry 6: ¹H NMR

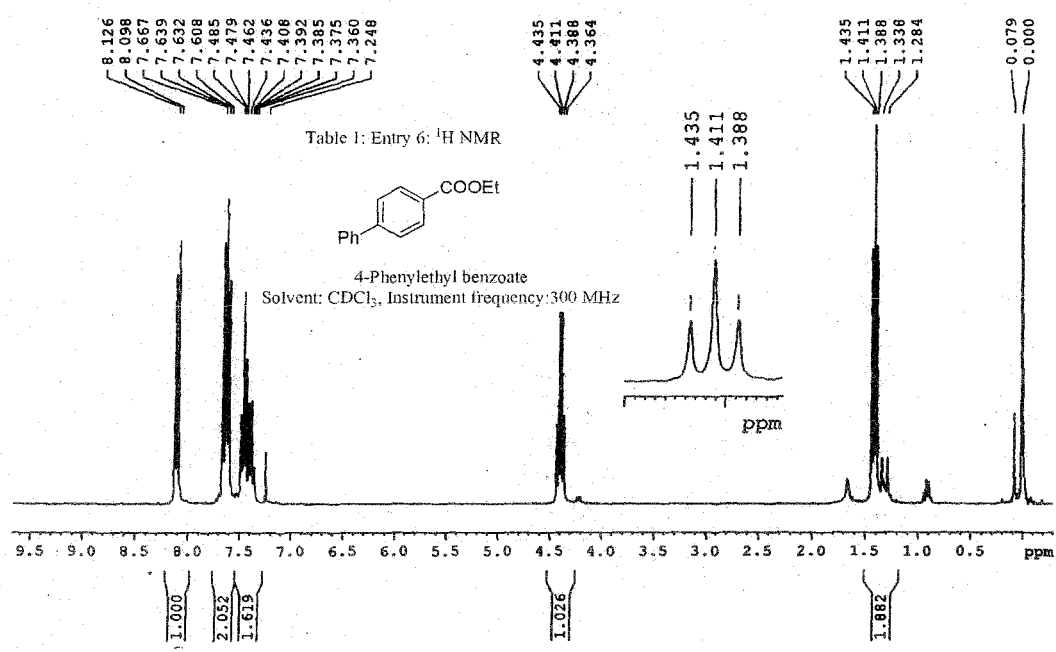
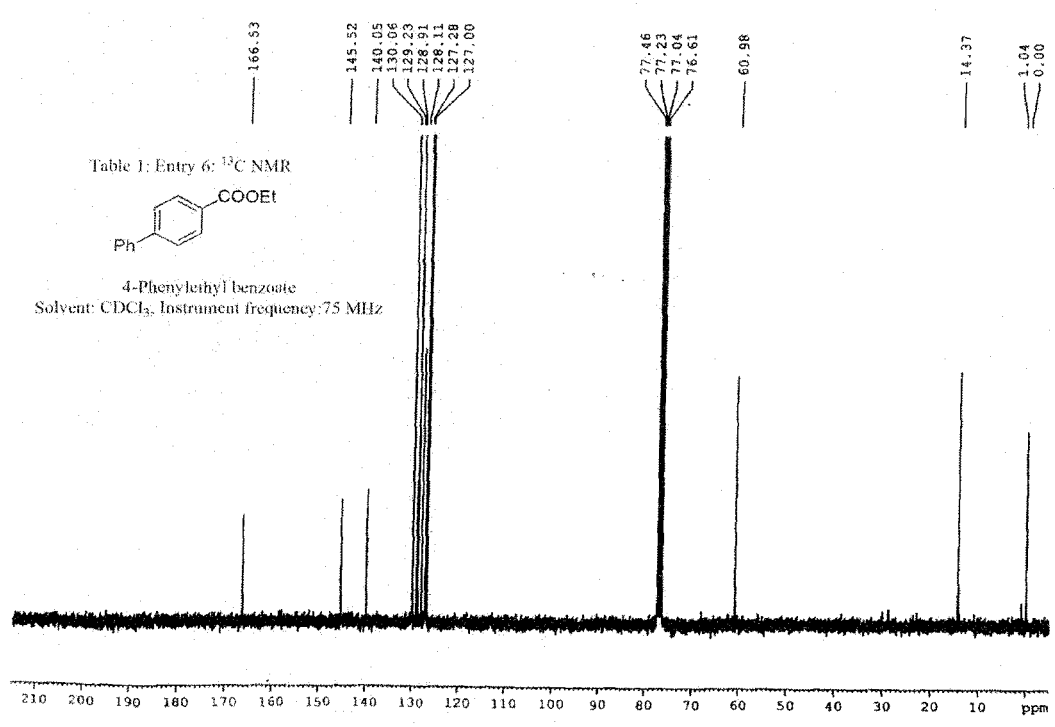


Table 1: Entry 6: ¹³C NMR



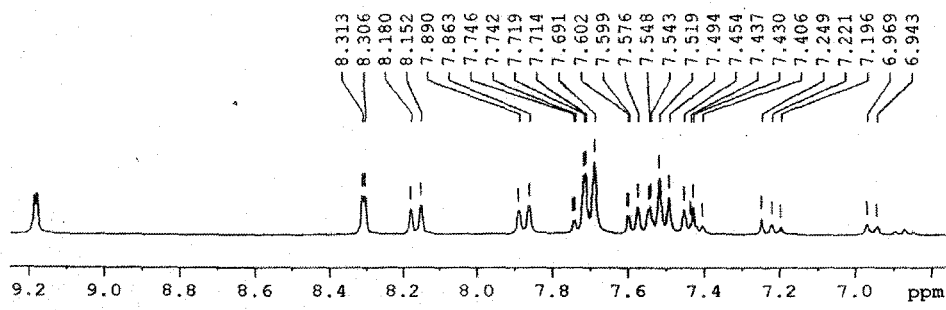
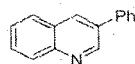


Table 1: Entry 9: ¹H NMR



3-Phenylquinoline
Solvent: CDCl₃, Instrument frequency: 300 MHz

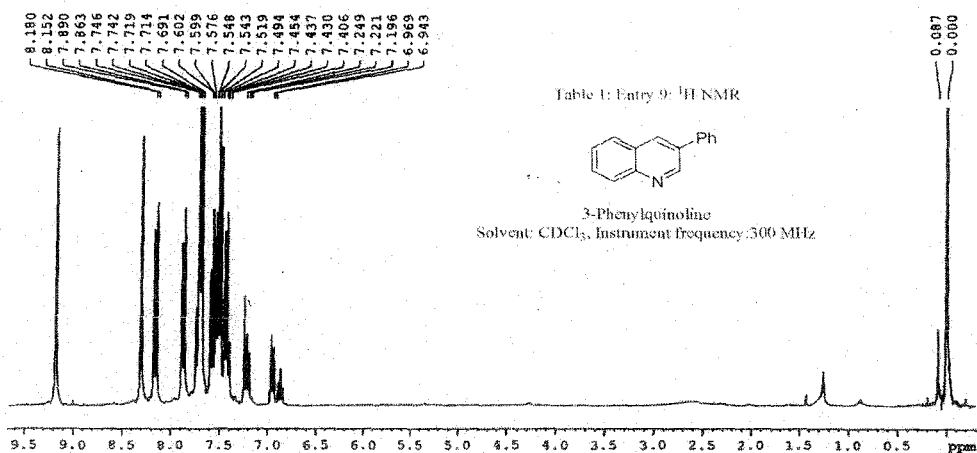
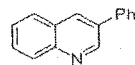
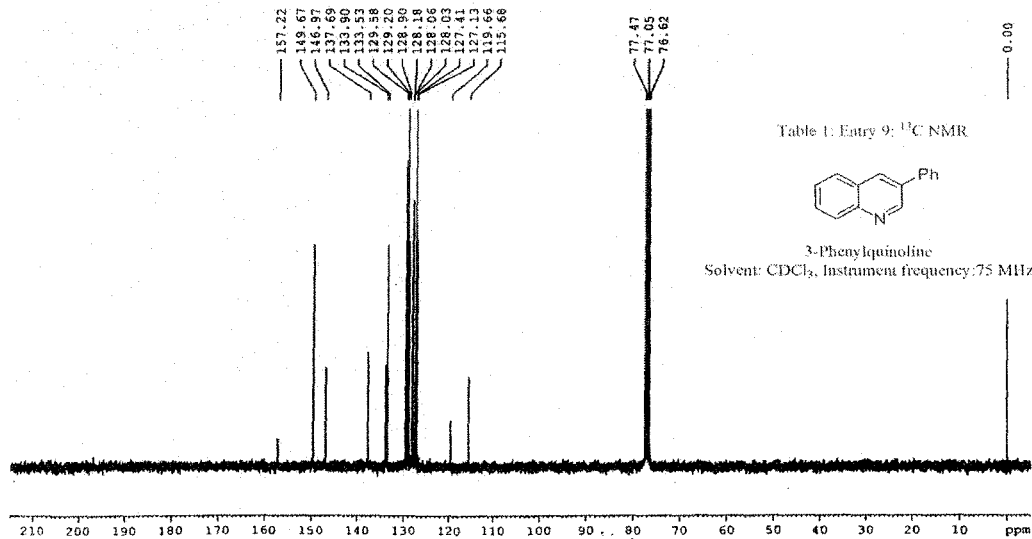


Table 1: Entry 9: ¹³C NMR



3-Phenylquinoline
Solvent: CDCl₃, Instrument frequency: 75 MHz



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