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Authors: Anuj Kumar, A. P. Prakasham, Manoj Kumar Gangwar, Pratap Vishnoi, Raymond J Butcher, and Prasenjit Ghosh

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An Efficient Synthetic Approach to *trans*-(NHC)$_2$Pd(R)Br type Complexes and Their Implications in Suzuki-Miyaura Cross-Coupling Reaction

Anuj Kumar,[†] A. P. Prakasham,[†] Manoj Kumar Gangwar,[†] Pratap Vishnoi,[†] Raymond J. Butcher,[‡] and Prasenjit Ghosh*[,†]

[†]Department of Chemistry

Indian Institute of Technology Bombay

Powai, Mumbai 400 076

[‡] Department of Chemistry

Howard University

Washington DC 20059, USA

Email: pghosh@chem.iitb.ac.in

Fax: +91 22 2572 3480

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Abstract: Mixed organo-halo palladium complexes of the type *trans*-$(NHC)_2Pd(R)Br$ were conveniently obtained from *trans*-$(NHC)_2PdBr_2$ type complexes by the ligand substitution reaction. In particular, the *trans*-[1-(*1S*)-menthyl-4-(R_1)-1,2,4-triazol-5-ylidene]$_2$Pd(R_2)Br [R_1 = Et, R_2 = CH_2Ph (**3a$_1$**); R_1 = Et, R_2 = *o*-$OMeC_6H_4$ (**3a$_2$**); R_1 = R_2 = CH_2Ph (**3b$_1$**); R_1 = CH_2Ph, R_2 = *o*-$OMeC_6H_4$ (**3b$_2$**)] complexes were obtained from the corresponding palladium(II) precursor complexes, **2**(**a**–**b**), by the reaction with the respective Grignard reagents in good to excellent yields (74–93 %). Three of the four mixed organo-halo palladium complexes **3**(**a$_1$**–**a$_2$**) and **3b$_1$**, have been structurally characterized by the single crystal X-ray diffraction technique that revealed the *trans*-disposition of the NHC ligands around the palladium center. The implication of this mixed organo-halo palladium complexes in the Suzuki-Miyaura cross-coupling reaction was established for all of the complexes, **3**(**a$_1$**–**a$_2$**) and **3**(**b$_1$**–**b$_2$**), that yielded the desired cross-coupled products upon treatment with various $ArB(OH)_2$ [Ar = 1-naphthyl, 4-(1,1'-biphenyl), 9-phenanthrenyl, 4-FC_6H_4, and 2,6-$Me_2C_6H_3$] in the presence of NaOH as a base, in CH_3CN in 3 hours under reflux conditions.

Keywords: palladium • N–heterocyclic carbene • Suzuki-Miyaura cross-coupling • organo-halo palladium derivatives • DFT studies

Introduction

As catalytic intermediates provide valuable insights about the reaction mechanism, their isolation and structural characterization are thus of significant interest. From this perspective, despite the fact that a large body of literature dwell on the utility of the C–C cross-coupling reactions including that of the Suzuki-Miyaura cross-coupling reaction,[1] only a handful ones have been reported pertaining to the isolation and characterization of the key intermediates of its catalytic cycles.[2-6] Because of the aforementioned reason, we become interested in isolating and structurally characterizing the mixed organo-halo palladium(II) complexes for their relevance in the C–C cross-coupling reactions and are formed during the oxidative addition of an aryl halide substrate on to a palladium(0) species. With our interest being in exploring the catalytic and biomedical applications of transition metal N–heterocyclic carbene ligands,[7] we chose to isolate the mixed organo-halo palladium complexes stabilized over N–heterocyclic carbene ligands by exploring an alternate pathway involving a ligand substitution reaction on a palladium(II) complex by treatment with Grignard reagent though it is commonly prepared by the oxidative addition route from a palladium(0) precursor complex.[2-5] To our knowledge, in case of the palladium N–heterocyclic carbene complexes, this ligand substitution reaction approach has not been reported for the preparation of the mixed organo-halo $(NHC)_2Pd(R)(halide)$ type complexes, as these have thus far been solely synthesized by the conventional oxidative addition method from a $(NHC)_2Pd$ type palladium(0) precursor complex by the reaction with an aryl halide.[2-5] However, there exists precedence for the Grignard based approach in case of non N–heterocyclic carbene based ligand systems.[8]

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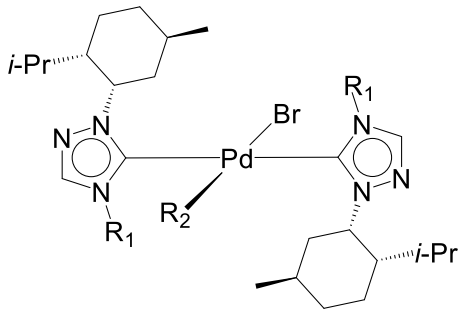
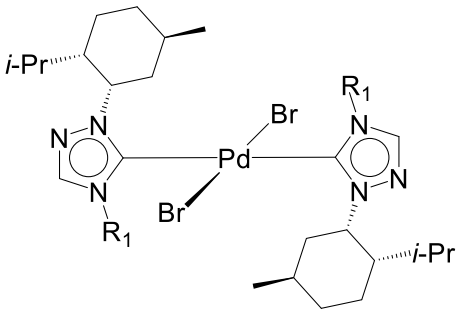
Here in this communication, we report a convenient synthetic approach towards the successful isolation and structural characterization of mixed organo-halo palladium complexes of the type *trans*-$(NHC)_2Pd(R)Br$ in the form of the **3(a$_1$–a$_2$)** and **3(b$_1$–b$_2$)** complexes supported over N–heterocyclic carbene ligands by a ligand substitution reaction on the palladium(II) precursor complexes, **2**(**a**–**b**), using Grignard reagents (Figure 1). The implication of these **3(a$_1$–a$_2$)** and **3(b$_1$–b$_2$)** complexes as intermediates in the Suzuki-Miyaura cross-coupling reaction was established through their reaction with several aryl boronic acids under appropriate Suzuki-Miyaura catalysis conditions yielding the desired cross-coupled products under stoichiometric conditions.



R_1 = Et, R_2 = CH_2Ph (**3a$_1$**)
R_1 = Et, R_2 = *o*-$OMeC_6H_4$ (**3a$_2$**)
R_1 = R_2 = CH_2Ph (**3b$_1$**)
R_1 = CH_2Ph, R_2 = *o*-$OMeC_6H_4$ (**3b$_2$**)



R_1 = Et (**2a**), CH_2Ph (**2b**)

Figure 1. The organo-halo Pd–NHC complexes, **3(a$_1$–a$_2$)** and **3(b$_1$–b$_2$)**, and the dibromo Pd–NHC complexes, **2**(**a**–**b**).

Results and Discussion

The mixed organo-halo $(NHC)_2Pd(R)Br$ type complexes, **3(a$_1$–a$_2$)** and **3(b$_1$–b$_2$)**, of a 1,2,4-triazole derived N–heterocyclic carbene ligand namely, 1-(*1S*)-menthyl-4-(R_1)-1,2,4-triazol-5-ylidene, [R_1 = Et, CH_2Ph], were obtained through a sequence of reactions (Scheme 1). In particular, the 1,2,4-triazole derived N–heterocyclic carbene ligand precursors, **1**(**a**–**b**), were prepared by the alkylation of 1-((*1S,2S,5R*)-2-*i*-propyl-5-methylcyclohexyl)-1H-1,2,4-triazole (**A**) with ethyl and benzyl bromide substrates in *ca*. 40–84 % yields. Subsequent reaction of **1**(**a**–**b**) with $PdBr_2$ in the presence of Et_3N yielded the *trans*-$(NHC)_2PdBr_2$ type complexes **2**(**a**–**b**) in *ca*. 71–94 % yields. Finally, the ligand metathesis reaction on these **2**(**a**–**b**) complexes with Grignard reagents gave the desired *trans*-[1-(*1S*)-menthyl-4-(R_1)-1,2,4-triazol-5-ylidene]$_2$Pd(R_2)Br [R_1 = Et, R_2 = CH_2Ph (**3a$_1$**); R_1 = Et, R_2 = *o*-$OMeC_6H_4$ (**3a$_2$**); R_1 = R_2 = CH_2Ph (**3b$_1$**); R_1 = CH_2Ph, R_2 = *o*-$OMeC_6H_4$ (**3b$_2$**)] complexes in *ca*. 74–93 % yields (Scheme 1). The Pd–CH_2Ph and Pd–(*o*-$OMeC_6H_4$) moieties in the **3(a$_1$–b$_1$)** and **3(a$_2$–b$_2$)** complexes were characterized by ^1H NMR and $^{13}C\{^1H\}$ NMR spectroscopies in accordance with the reported values of the related mixed organo-halo palladium(II) analogs known in the literature.[2, 5]

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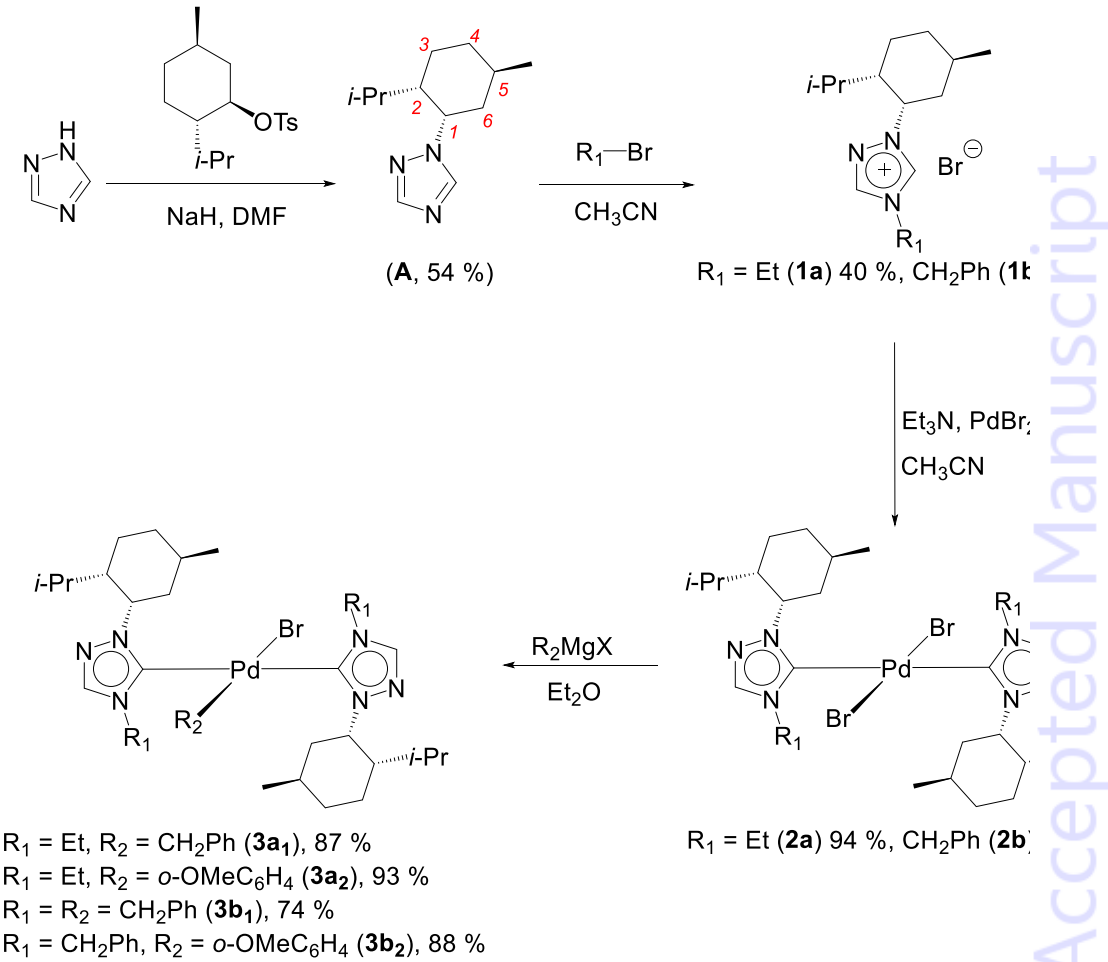

Scheme 1. Synthetic protocol for the organo-halo Pd–NHC complexes, **3(a$_1$–a$_2$)** and **3(b$_1$–b$_2$)**.

Of particular mention is the room temperature ^{1}H NMR of the dibromo derivatives **2**(**a**–**b**) and the mixed organo-halo derivatives **3**(**a**$_1$–**b**$_1$), that indicated the presence of *trans-syn* and *trans-anti* conformers in varying ratios in these complexes, **2a** (*ca*. 1.7:1), **2b** (*ca*.1.7:1), **3a**$_1$ (*ca*. 1:1), and **3b**$_1$ (*ca*. 1:1) (Scheme 2). A variable temperature ^{1}H NMR experiment performed on a representative complex **2a** showed a faster exchange at elevated temperatures leading to coalescence of the resonances at 110 °C (Supporting Information Figure S1). In this context, a Density Functional Theory (DFT) study undertaken at the B3LYP/SDD 6-31G* level of theory for examining the *trans-syn*↔*trans-anti* exchange for the two representative dibromo derivatives, **2**(**a**–**b**), estimated the activation barrier for such exchange to be *ca*. 16.6−17.6 kcal/mol (Supporting Information Figures S22−S23). It is interesting to note that the mixed organo-halo derivatives **3**(**a**$_2$–**b**$_2$), containing the bulky *o*-OMeC$_6$H$_4$ substituent, did not show such conformational exchange as was evident from the presence of only one conformer. Here too, further support came from the Density Functional Theory (DFT) study that estimated the energy difference between the *trans-syn* and *trans-anti* conformers to be the maximum (*ca*. 7.0−7.2 kcal/mol) for the **3**(**a**$_2$–**b**$_2$) complexes, with the *trans-anti* conformer being the stable one in case of both of the complexes (Figure 2).

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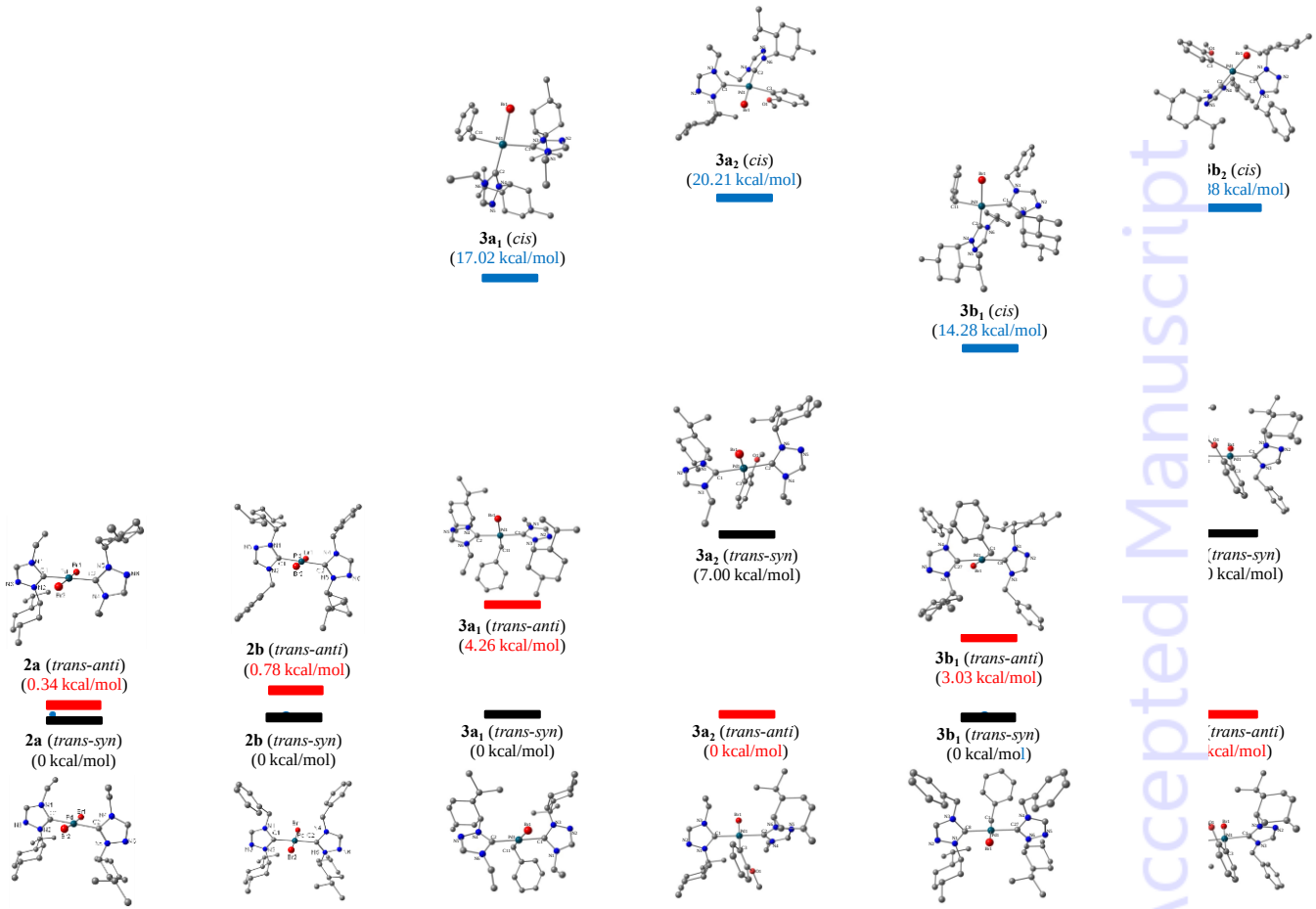

Figure 2. An overlay of the computed total energies (ΔE) for various geometrical isomers of **2(a–b)**, **3(a_1–b_1)** and **3(a_2–b_2)** at B3LYP/SDD 6-31G* level of theory relative to the most stable structure normalized to 0 kcal/mol.

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Furthermore, the total energy of the *trans–syn* and *trans–anti* conformers vary significantly within the organo-halo derivatives, **3(a$_1$–a$_2$)** and **3(b$_1$–b$_2$)**, with the *trans–syn* conformer being stable for the **3a$_1$** and **3b$_1$** complexes and the *trans–anti* conformer being stable for the **3a$_2$** and **3b$_2$** complexes. In this context it is to be noted that the single crystal X-ray diffraction study yielded a *trans–syn* structure for the **3a$_1$** complex (Figure 3) and a *trans–anti* structure for the **3a$_2$** complex (Figure 4) along the expected lines, except for the **3b$_1$** complex, for which the higher energy *trans-anti* conformer was observed (Figure 5). It may be stated here that the DFT studies undertaken at B3LYP/SDD 6-31G* level of theory indicated the energy difference between *trans-syn* and *trans-anti* conformers for the **3(a$_1$–a$_2$)** and **3(b$_1$–b$_2$)** complexes to be the least in case of the **3b$_1$** complex (3.03 kcal/mol), and for which the higher energy *trans-anti* structure is seen.

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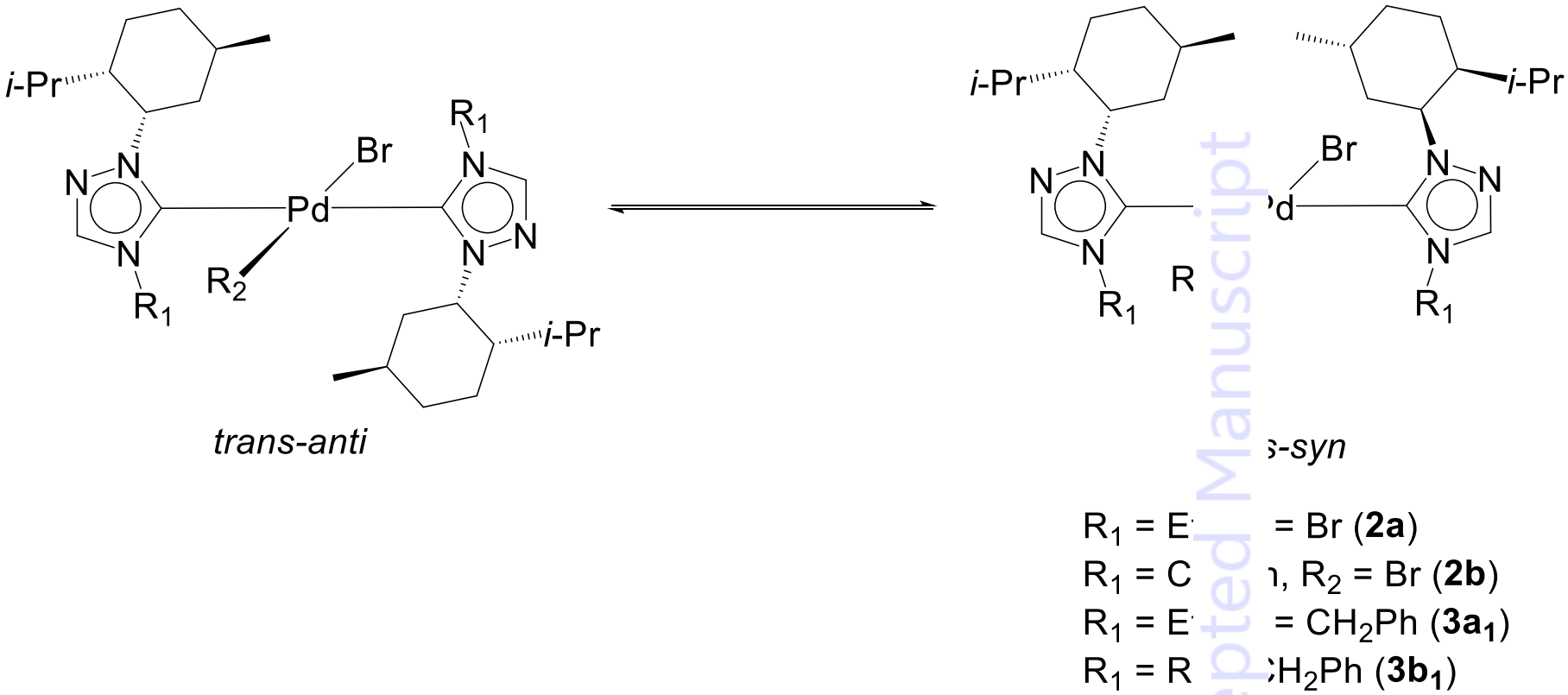

Scheme 2. Conformational exchange in **2**(**a**–**b**) and **3**(**a**$_1$–**b**$_1$) complexes.

The molecular structures of all but one of the complexes **2**(**a**−**b**), **3**(**a**$_1$−**a**$_2$) and **3b**$_1$, as determined by the single crystal X-ray diffraction method, revealed that the palladium center was in a square-planar geometry with the two NHC ligands being bound *trans* to each other (Figures 3−5 and Table S1). Quite interestingly, the Pd−$C_{carbene}$ bond distances in the *trans*-$(NHC)_2PdBr_2$ type complexes, **2**(**a**−**b**) [2.003(8)−2.028(8) Å] were shorter than that in the *trans*-$(NHC)_2Pd(R)Br$ type complexes **3**(**a**$_1$−**a**$_2$) and **3b**$_1$ [2.008(8)−2.040(9) Å], and which has been attributed to a more electron rich palladium center in the latter as opposed to that in the former. The same rationalization can further be extended to explain the observation of a shorter Pd−Br bond distances in the dibromo derivatives, **2**(**a**−**b**) [2.4275(10)−2.4452(9) Å] as compared to that of the mixed organo-halo derivatives **3**(**a**$_1$−**a**$_2$) and **3b**$_1$ [2.5114(7)−2.5525(9) Å]. Lastly, a comparison of the Pd−C(alkyl/aryl) bond distances among the mixed organo-halo complexes **3**(**a**$_1$−**a**$_2$) and **3b**$_1$ revealed a longer Pd−C(CH_2Ph) bond distances in **3a**$_1$ [2.087(8) Å] and **3b**$_1$ [2.094(4) Å] as compared to the corresponding Pd−C(*o*-$OMeC_6H_4$) bond distance in **3a**$_2$ [2.016(3) Å], and this is explained by the presence of a longer radius of a C_{sp^3} center (0.76 Å) in the Pd−C($\underline{C}H_2Ph$) moiety in **3a**$_1$ and **3b**$_1$ as opposed to that of a C_{sp^2} center (0.73 Å) in the Pd−C(*o*-$OMe\underline{C}_6H_4$) moiety in **3a**$_2$.[9]

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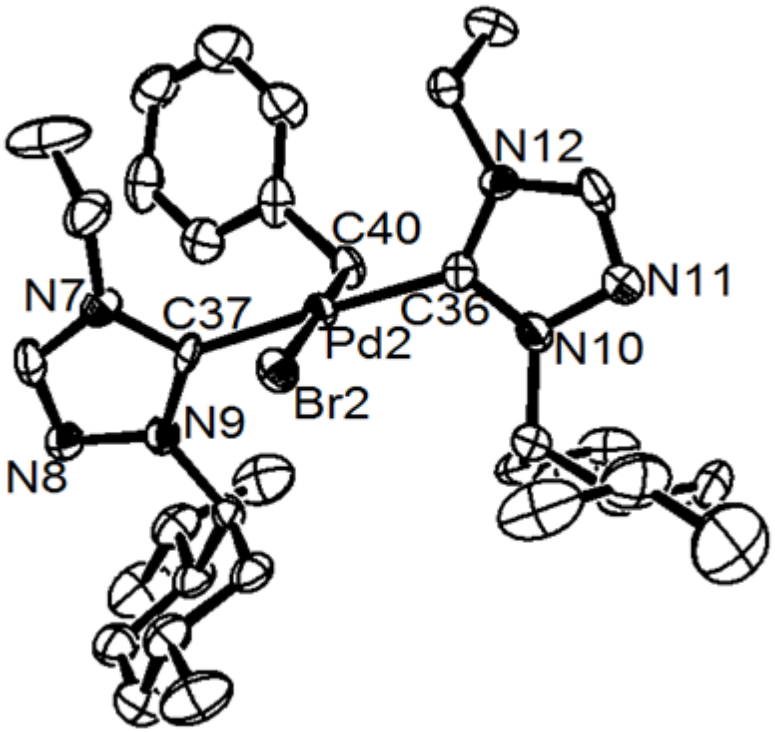

Figure 3. ORTEP of **3a$_1$** with thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Pd(2)−C(37) 2.008(8), Pd(2)−C(36) 2.040(9), Pd(2)−Br(2) 2.5525(9), Pd(2)−C(40) 2.087(8), C(37)−Pd(2)−C(36) 177.4(3), Br(2)−Pd(2)−C(40) 178.0(2), C(37)−Pd(2)−C(40) 88.8(3), C(36)−Pd(2)−Br(2) 92.3(2).

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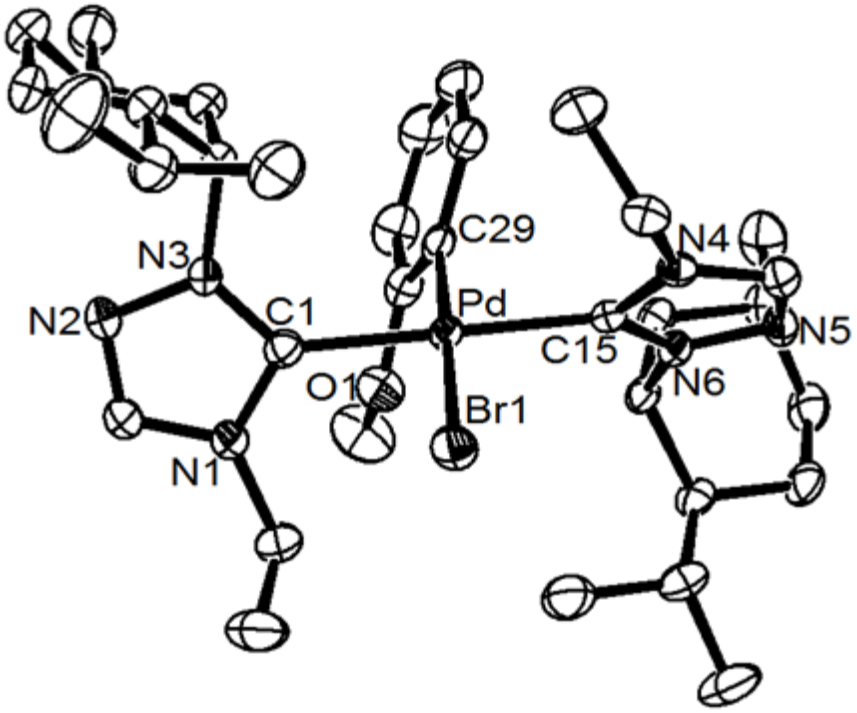

Figure 4. ORTEP of **3a$_2$** with thermal ellipsoids are shown at the 50 % probability level. Co-crystalized CH_3CN solvent molecule is omitted for clarity. Selected bond lengths (Å) and angles (°): Pd−C(1) 2.036(3), Pd−C(15) 2.039(3), Pd−Br(1) 2.5403(3), Pd−C(29) 2.016(3), C(1)−Pd−C(15) 176.21(12), Br(1)−Pd−C(29) 178.21(8), C(15)−Pd−C(29) 88.03(11), C(1)−Pd−Br(1) 90.69(8).

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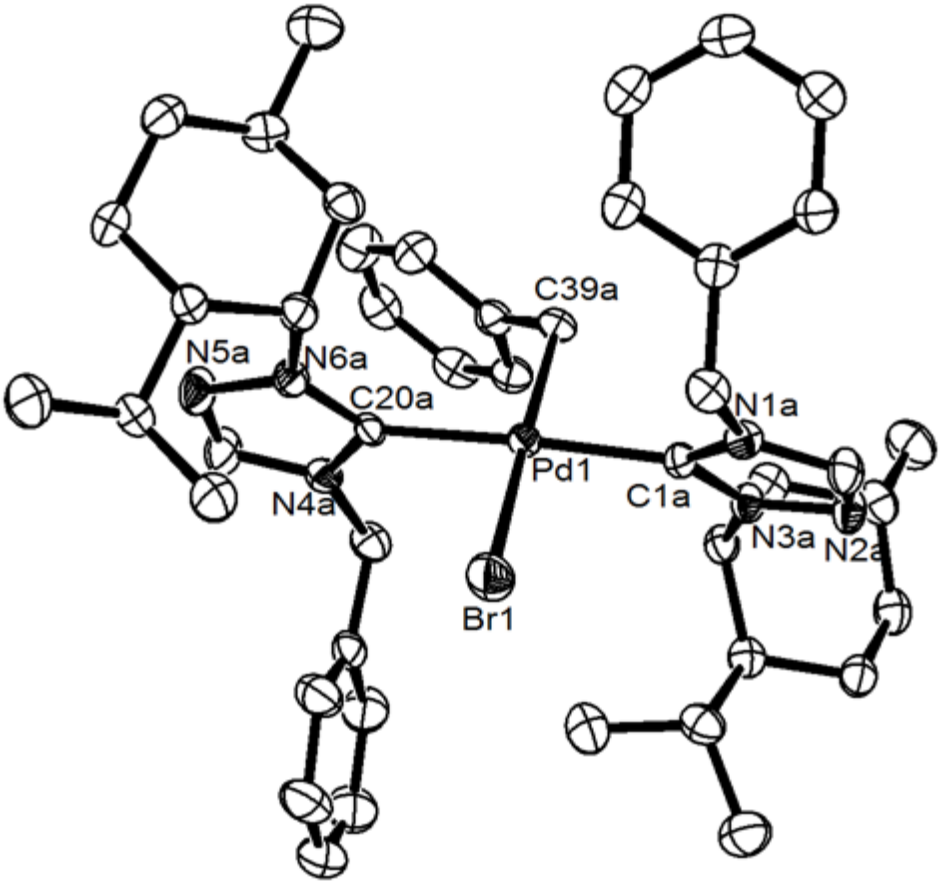

Figure 5. ORTEP of **3b$_1$** with thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Pd(1)−C(1a) 2.030(5), Pd(1)−C(20a) 2.038(4), Pd(1)−Br(1) 2.5114(7), Pd(1)−C(39a) 2.094(4), C(1a)−Pd(1)−C(20a) 176.43(18), Br(1)−Pd(1)−C(39a) 174.16(14), C(1a)−Pd(1)−C(39a) 88.88(19), C(20a)−Pd(1)−Br(1) 90.69(13).

With regard to the consistent observation of a *trans*-geometry in all of the structurally characterized mixed organo-halo complexes, **3(a$_1$−a$_2$)** and **3b$_1$**, the DFT investigation at B3LYP/SDD 6-31G* level of theory, revealed the *trans*-isomer to be more stable than the *cis*-isomer for all of the **3(a$_1$−a$_2$)** and **3(b$_1$−b$_2$)** complexes by *ca*. 14.3−20.2 kcal/mol (Figure 2). Worth noting that a computational study, investigating the mechanism of aryl amination reaction also reported similar stabilization of the *trans*-isomer of a mixed organo-halo intermediate complex of the type *trans*-(NHC)$_2$Pd(Ph)Cl, (NHC = 1,3-di-*t*-butyl-imidazol-2-ylidene) over its *cis*-isomer by 17.0 kcal/mol.[10] Further justification of the *trans*-isomer as the C–C cross-coupling intermediates came from the observation that the oxidative addition of aryl halide on the palladium(0) N−heterocyclic carbene complexes too yielded analogous *trans*-(NHC)$_2$Pd(R)X type complexes [NHC = 1,3,4,5-tetramethyl-imidazol-2-ylidene, R = C_6H_5, X = I; R = *p*-$NO_2C_6H_4$, X = I;[3] NHC = 1,3-di-*t*-butyl-imidazol-2-ylidene, R = *p*-$CH_3C_6H_4$, X = Cl;[5] R = *p*-$CO_2MeC_6H_4$, X = Cl; R = *p*-$OMeC_6H_4$, X = Cl;[4] NHC = 1,3-*bis*(2,6-di-*i*-propylphenyl)imidazolidin-2-ylidene, R = CH_2Cl, X = Cl.[2]

All of the **3(a$_1$−a$_2$)** and **3(b$_1$−b$_2$)** complexes, under Suzuki-Miyaura coupling conditions, effectively yielded the desired coupling products upon the treatment with stoichiometric amounts of aryl boronic acids in the presence of a base in low to good isolated yields (*ca*. 7–80 %) (Equation 1 and Table 1). Interestingly, the ethyl derivatives, **3(a$_1$−a$_2$)**, were significantly more effective, displaying a higher yield of *ca*. 33−80 % (Entries 1-7 Table 1) except entry 8 where the steric crowding of (2,6-dimethylphenyl)boronic acid and *o*-methoxy phenyl in **3a$_2$** may be considered for low yield (8 %). The benzyl derivatives, **3(b$_1$−b$_2$)** gave yields in the range 7−32 % (Entries 9-12 Table 1).

Also noteworthy is the fact that in addition to the more common C_{sp^2}–C_{sp^2} cross-coupling (Entries 6-8 and 12 Table 1), the not-so-common C_{sp^3}–C_{sp^2} cross-couplings could also be observed in form of the representative Suzuki-Miyaura coupling products (**5**–**9**) (Entries 1-5 and 9-11 Table 1). As expected of a Suzuki-Miyaura coupling reaction, the formations of the catalytically active $(NHC)_2Pd$ type palladium(0) species (**4a**) and (**4b**) were observed by mass spectrometry for the two representative couplings between the mixed organo-halo complex $\mathbf{3a_1}$ and the *p*-fluorophenyl boronic acid (Entry 4 Table 1 and Supporting Information Figure S81) and the mixed organo-halo complex $\mathbf{3b_1}$ and the naphthyl boronic acid (Entry 9 Table 1 and Supporting Information Figure S82).

The moderate to good yields of the desired Suzuki-Miyaura cross-coupled products indicated the existence of possible decomposition pathways operational under these conditions. Indeed, substantial formation of the homo-coupled products of the aryl boronic acid reagents was observed under the catalysis conditions in a competitive manner resulting in the lowering of the overall yields of the desired cross-coupling products. For a representative Suzuki-Miyaura cross-coupling run as given by entry 12 of Table 1, a homo-coupled binaphthyl product, **10a** was observed in 52 % yield with respect to the starting naphthyl boronic acid reagent (See Supporting Information S103–S105).

Further mass spectrometric investigation of the catalysis reaction mixture revealed the presence of the free N–heterocyclic carbene species (free-NHC), observed as a $[(NHC)H]^+$ under mass spectrometric conditions, and formed from its dissociation

from the $(NHC)_2Pd(R)Br$ type palladium N–heterocyclic carbene complexes in line with what had been observed earlier.[4] For example, the mass spectrometric analysis of the catalysis mixture revealed a cationic triazolium species peak at 236.2118 *m/z*, representing **1a**, for the Suzuki-Miyaura coupling reaction between the mixed organo-halo complex $\mathbf{3a_2}$ and naphthyl boronic acid substrate (Entry 6 Table 1 and Supporting Information Figure S114) and an another cationic triazolium species peak at 298.2280 *m/z*, representing **1b**, for the coupling reaction between $\mathbf{3b_2}$ and naphthyl boronic acid substrate (Entry 12 Table 1 and Supporting Information Figure S115). In this regard it is worth noting that the NHC dissociation is suggestive of the generation of a *cis*-$(NHC)_2Pd(organo)(aryl)$ intermediates that are formed prior to the required reductive elimination step.[4] Lastly, as had been noted earlier,[3, 11] the decomposed (NHC)-organyl species namely, $\mathbf{3c_1}$ (at 326.2587 *m/z*) (Entry 1, Table 1 and Supporting Information Figure S116), $\mathbf{3c_2}$ (at 342.2536 *m/z*) (Entry 6, Table 1 and Supporting Information Figure S117), $\mathbf{3d_1}$ (at 388.2748 *m/z*) (Entry 9, Table 1 and Supporting Information Figure S118) and $\mathbf{3d_2}$ (at 404.1176 *m/z*) (Entry 12, Table 1 and Supporting Information Figure S119) were observed by mass spectrometry, thus pointing to the decomposition of the palladium-organo-halide complexes, $\mathbf{3(a_1–a_2)}$ and $\mathbf{3(b_1–b_2)}$ under the Suzuki-Miyaura catalysis conditions.

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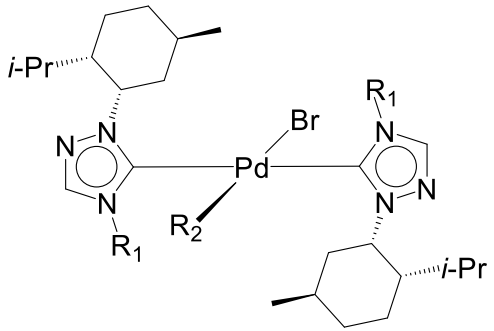
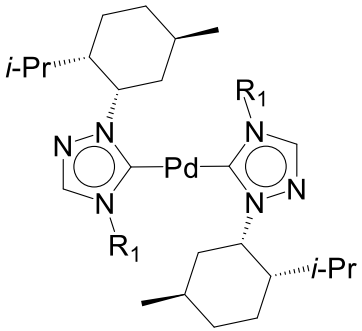


R_3—B(OH)$_2$

NaOH



+ R_2—R_3

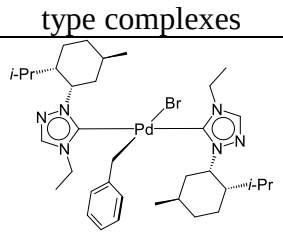
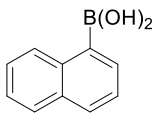
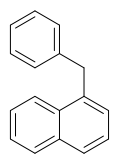
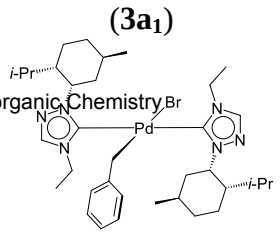
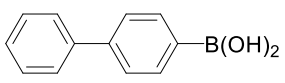
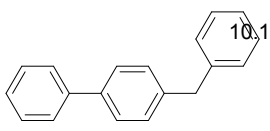
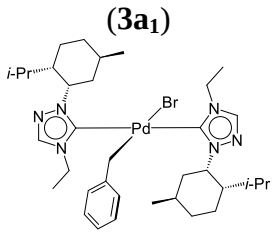
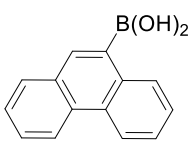
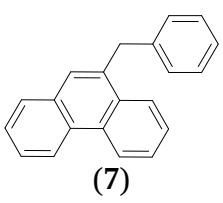
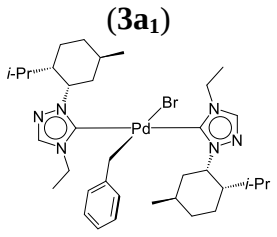
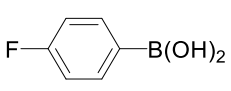
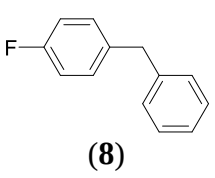
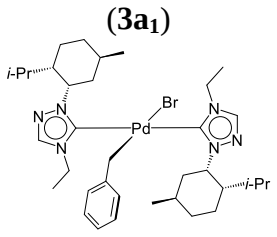
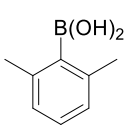
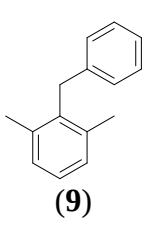
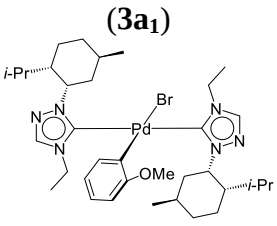
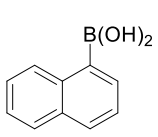
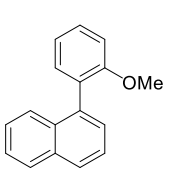
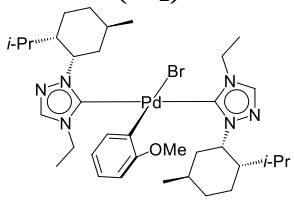
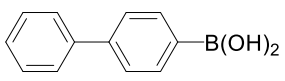
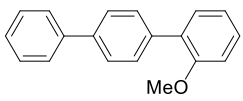
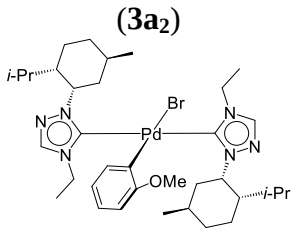
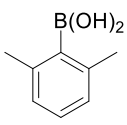
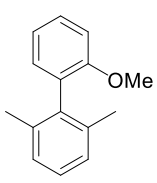
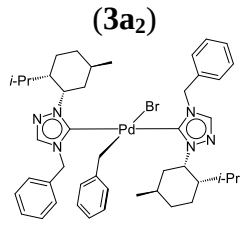
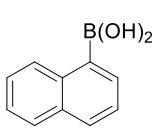
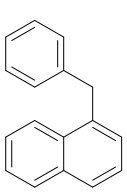
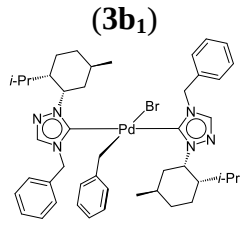
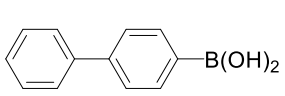
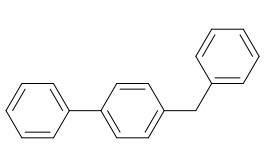
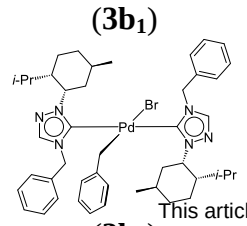
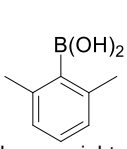
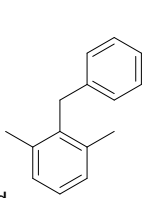
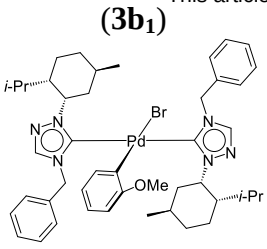
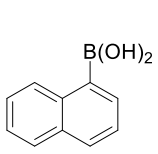
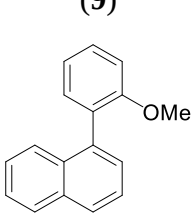
R_1 = Et, R_2 = CH_2Ph (**3a$_1$**)
R_1 = Et, R_2 = *o*-$OMeC_6H_4$ (**3a$_2$**)
R_1 = R_2 = CH_2Ph (**3b$_1$**)
R_1 = CH_2Ph, R_2 = *o*-$OMeC_6H_4$ (**3b$_2$**)

R_1 = Et (**4a**), CH_2Ph (**4b**)

R_2 = Cl R_3 = 1-naphthyl (**5**)
R_2 = Cl R_3 = 4-biphenyl (**6**)
R_2 = Cl R_3 = 9-phenanthrenyl (**7**)
R_2 = Cl R_3 = 4-FC_6H_4 (**8**)
R_2 = Cl R_3 = 2,6-$Me_2C_6H_3$ (**9**)
R_2 = *o*- $_6H_4$, R_3 = 1-naphthyl (**10**)
R_2 = *o*- $_6H_4$, R_3 = 4-biphenyl (**11**)
R_2 = *o*- $_6H_4$, R_3 = 2,6-$Me_2C_6H_3$ (**12**)

Equation 1. Suzuki-Miyaura cross-coupling reaction of the mixed organo-halo derivatives **3(a$_1$–a$_2$)** ar –**b$_2$**) with R_3–B(OH)$_2$.

Table 1. Suzuki-Miyaura cross-coupling reaction of the mixed organo-halo derivatives **3(a$_1$−a$_2$)** and **3(b$_1$−b$_2$)** with Ar−B(OH)$_2$.

S.No	*trans*-(NHC)$_2$Pd(R)Br type complexes	Ar−B(OH)$_2$	Suzuki-Miyaura product	yield[a] (%)
1.	 **(3a$_1$)**		 **(5)**	50
2.	 **(3a$_1$)**		 **(6)**	41
3.	 **(3a$_1$)**		 **(7)**	33
4.	 **(3a$_1$)**		 **(8)**	59
5.	 **(3a$_1$)**		 **(9)**	80
6.	 **(3a$_2$)**		 **(10)**	33
7.	 **(3a$_2$)**		 **(11)**	42
8.	 **(3a$_2$)**		 **(12)**	8
9.	 **(3b$_1$)**		 **(5)**	7
10.	 **(3b$_1$)**		 **(6)**	32
11.	 **(3b$_1$)**		 **(9)**	27
12.	 **(3b$_2$)**		 **(10)**	17

Reaction condition: *trans*-(NHC)$_2$Pd(R)Br type complexes (**3a$_1$**/**3a$_2$**/**3b$_1$**/**3b$_2$**) (1 equiv.), boronic acid (1.2 equiv.), NaOH (5 equiv.) in 3 mL of CH_3CN. Reaction time 3 hours, temperature 80 °C, (a) isolated yields.

In summary, the structurally characterized examples of the N–heterocyclic carbene bearing palladium organo-halo complexes of the type, $(NHC)_2Pd(R)Br$ namely, *trans*-[1-(*1S*)-menthyl-4-(R_1)-1,2,4-triazol-5-ylidene]$_2$Pd(R_2)Br [R_1 = Et, R_2 = CH_2Ph (**3a$_1$**); R_1 = Et, R_2 = *o*-$OMeC_6H_4$ (**3a$_2$**); R_1 = R_2 = CH_2Ph (**3b$_1$**); R_1 = CH_2Ph, R_2 = *o*-$OMeC_6H_4$ (**3b$_2$**)], have been isolated from the palladium(II) dihalo precursor complexes by a convenient synthetic route involving a ligand metathesis reaction. This approach provides an easy access to the important $(NHC)_2Pd(R)Br$ type of complexes that are a common C–C cross-coupling catalytic intermediate in various palladium mediated cross-coupling reactions and has been successfully demonstrated through the much popular Suzuki-Miyaura coupling in the current study. The mass spectrometric detection and characterization of the species present in the catalysis reaction mixture provided additional insight on the various competing decomposition pathways operational under catalysis conditions. These primarily were, the formation of the homo-coupling products from the aryl boronic acid reagents, the dissociation of free-NHC ligands from the $(NHC)_2Pd(R)Br$ type palladium N–heterocyclic carbene complexes and the formation of the (NHC)–organyl species from the decomposition of the $(NHC)_2Pd(R)Br$ type organo-halo palladium N–heterocyclic carbene complexes **3(a$_1$−a$_2$)** and **3(b$_1$−b$_2$)**. In overall, through the isolation and the structural characterization of the mixed organo-halo palladium complexes, **3(a$_1$−a$_2$)** and **3(b$_1$−b$_2$)**, a realistic insight on the Suzuki-Miyaura coupling, with respect to the decomposed products, has thus been obtained in the current study.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk techniques. Palladium bromide, (1*R*)-(−)-menthol, benzyl magnesium chloride, and (2-methoxyphenyl)magnesium bromide were purchased from Sigma Aldrich. (1*R*,2*S*,5*R*)-2-*i*-propyl-5-methylcyclohexyl *p*-toluenesulphonate was synthesized according to modified literature procedures.[12] ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{19}F{^{1}H} NMR spectrum were recorded on Bruker 400 MHz and Bruker 500 MHz NMR spectrometer. ^{1}H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), broad (br), triplet of triplet (tt), doublet of doublet (dd), multiplet (m) and septet (sept). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer and Bruker maxis impact spectrometer. Elemental Analysis was carried out on Thermo Finnigan FLASH EA 1112 SERIES (CHNS) Elemental Analyzer. Specific optical rotations were measured with JASCO P-2000 polarimeter and Autopol IV, Serial #82083 polarimeter. X-ray diffraction data for compounds **2a**, **2b**, **3a$_1$**, **3a$_2$** and **3b$_1$** were collected on Oxford Diffraction XCALIBUR-S diffractometer and Rigaku Hg 724+ diffractometer. Crystal data collection and refinement parameters are summarized in Table S1. The structures were solved using direct method and standard difference map techniques, and refined by full-matrix least-squares procedures on F^2.[13],[14] CCDC-**1003752** (for **2a**), CCDC-**919871** (for **2b**), CCDC-**1061784** (for **3a$_1$**), CCDC-**1447720** (for **3a$_2$**) and CCDC-**1037151** (for **3b$_1$**) contain the supplementary crystallographic data related to this article. These data can be obtained free of charge from the Cambridge Crystallographic Data center via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 1-(1*S*)-menthyl-1H-1,2,4-triazole (A)

A mixture of 1,2,4-triazole (3.52 g, 51.01 mmol), (1R,2S,5R)-2-*i*-propyl-5-methylcyclohexyl-4-methylbenzenesulfonate (7.00 g, 22.5 mmol) was stirred in DMF (*ca*. 70 mL) at 0 °C and NaH was added portion wise (2.00 g, 83.3 mmol) over 20 minutes. After which the reaction mixture was allowed to stir at room temperature for 30 minutes and then refluxed for 24 hours. The reaction mixture was cooled to room temperature and EtOAc (*ca*. 400 mL) was added. The reaction mixture was washed with water (*ca*. 12 × 50 mL). The organic layer was collected and vacuum dried to give crude product as a colorless liquid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (90 : 10 *v/v*) to give the product **A** as a colorless solid (2.52 g, 54 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.06 (s, 1H, N-C(5)*H*-N), 7.84 (s, 1H, N-C(3)*H*-N), 4.75 (br, 1H, $CH_3C_6H_9CH(CH_3)_2$), 2.05-1.00 (m, 9H, $CH_3C_6H_9CH(CH_3)_2$ & $CH_3C_6H_9CH(CH_3)_2$), 0.87 (d, 3H, $^{3}J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.84 (d, 3H, $^{3}J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.78 (d, 3H, $^{3}J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 151.0 (N-*C*(5)H-N), 143.6 (N-*C*(3)H-N), 58.2 ($CH_3C_6H_9CH(CH_3)_2$), 46.8 ($CH_3C_6H_9CH(CH_3)_2$), 41.2 ($CH_3C_6H_9CH(CH_3)_2$), 34.9 ($CH_3C_6H_9CH(CH_3)_2$), 29.3 ($CH_3C_6H_9CH(CH_3)_2$), 26.5 ($CH_3C_6H_9CH(CH_3)_2$), 25.1 ($CH_3C_6H_9CH(CH_3)_2$), 22.4 ($CH_3C_6H_9CH(CH_3)_2$), 21.2 ($CH_3C_6H_9CH(CH_3)_2$), 20.6 ($CH_3C_6H_9CH(CH_3)_2$). IR data (KBr pellet) cm^{-1}: 3436 (m), 3108 (w), 2953 (s), 2926 (s), 2869 (s), 2844 (m), 2351 (w), 1639 (w), 1518 (w), 1504 (m), 1475 (m), 1455 (m), 1444 (m), 1370 (w), 1288 (w), 1270 (m), 1195 (w), 1175 (m), 1136 (m), 1129 (m), 1069 (w), 1024 (m), 1014 (m), 999 (m), 868 (m), 726 (w), 676 (m), 599 (w). HRMS (ES): *m/z* 208.1810

$[M+H]^+$, calcd. 208.1814. Anal. Calcd. for $C_{12}H_{21}N_3$: C, 69.52; H, 10.21; N, 20.27. Found: C, 68.97; H, 9.71; N, 19.69 %. $[\alpha]_D^{25}$ + 43.8 (*c* 1.00 in $CHCl_3$).

Synthesis of 1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazolium bromide (1a)

A mixture of 1-(1*S*)-menthyl-1H-1,2,4-triazole (1.52 g, 7.33 mmol) (**A**) and ethyl bromide (3.18 g, 29.2 mmol) was refluxed overnight in CH_3CN (*ca*. 40 mL), after which the solvent was removed under vacuum. The residue was washed with hot Et_2O (*ca.* 3 × 10 mL) and vacuum dried to give the product **1a** as a white solid (0.924 g, 40 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 11.9 (s, 1H, N-C(5)*H*-N), 8.92 (s, 1H, N-C(3)*H*-N), 5.30 (br, 1H, $CH_3C_6H_9CH(CH_3)_2$), 4.69 (q, 2H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 2.11-1.00 (m, 9H, $CH_3C_6H_9CH(CH_3)_2$ & $CH_3C_6H_9CH(CH_3)_2$), 1.69 (t, 3H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 0.93 (d, 3H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.88 (d, 3H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.80 (d, 3H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 143.8 (N-*C*(5)H-N), 142.1 (N-*C*(3)H-N), 62.4 ($CH_3C_6H_9CH(CH_3)_2$), 46.3 ($CH_3C_6H_9CH(CH_3)_2$), 44.4 (CH_2), 40.2 ($CH_3C_6H_9CH(CH_3)_2$), 34.5 ($CH_3C_6H_9CH(CH_3)_2$), 29.3 ($CH_3C_6H_9CH(CH_3)_2$), 26.0 ($CH_3C_6H_9CH(CH_3)_2$), 24.3 ($CH_3C_6H_9CH(CH_3)_2$), 22.2 ($CH_3C_6H_9CH(CH_3)_2$), 21.5 ($CH_3C_6H_9CH(CH_3)_2$), 20.6 ($CH_3C_6H_9CH(CH_3)_2$), 15.8 (CH_2CH_3). IR data (KBr pellet) cm^{-1}: 3091 (m), 3028 (m), 2947 (s), 2866 (m), 2810 (m), 1820 (m), 1583 (m), 1510 (m), 1456 (m), 1417 (w), 1369 (w), 1352 (w), 1320 (w), 1291 (w), 1216 (m), 1202 (w), 1173 (m), 1141 (w), 1095 (w), 1070 (w), 1009 (w), 991 (w), 941 (w), 913 (w), 870 (w), 802 (w), 774 (w), 724 (w), 683 (w), 631 (s). HRMS (ES): *m/z* 236.2129 $[M–Br]^+$, calcd. 236.2127. Anal. Calcd. for $C_{14}H_{26}BrN_3$: C, 53.17; H, 8.29; N, 13.29. Found: C, 53.44; H, 8.07; N, 13.13 %. $[\alpha]_D^{25}$ + 23.3 (*c* 1.00 in $CHCl_3$).

Synthesis of *trans*-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$PdBr$_2$ (2a)

A mixture of 1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazolium bromide (0.474 g, 1.50 mmol) (**1a**), $PdBr_2$ (0.200 g, 0.751 mmol) and Et_3N (0.606 g, 5.99 mmol) in CH_3CN (*ca*. 50 mL) was refluxed for 12 hours. The reaction mixture was filtered and solvent was removed under vacuum to obtain the product as a yellow color solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (85 : 15 *v/v*) to give the product **2a** as a light yellow solid (0.519 g, 94 %). Both the ^{1}H NMR and ^{13}C{^{1}H} NMR spectrum showed the presence of two isomers, *trans-syn* and *trans-anti*. The major to minor isomer ratio was 1.7:1. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): (Major) δ 7.87 (s, 2H, N-C(3)*H*-N), 5.70 (br, 2H, $CH_3C_6H_9CH(CH_3)_2$), 4.78 (qd, 2H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 4.46 (qd, 2H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 2.59-1.00 (m, 18H, $CH_3C_6H_9CH(CH_3)_2$ & $CH_3C_6H_9CH(CH_3)_2$), 1.73 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 1.12 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.85 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.74 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$). (Minor) δ 7.87 (s, 2H, N-C(3)*H*-N), 5.61 (br, 2H, $CH_3C_6H_9CH(CH_3)_2$), 4.74 (qd, 2H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 4.42 (qd, 2H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 2.59-1.00 (m, 18H, $CH_3C_6H_9CH(CH_3)_2$ & $CH_3C_6H_9CH(CH_3)_2$), 1.71 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 1.09 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.84 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.72 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 ^{o}C): (Major) δ 172.2 (Pd-N*C*N), 140.7 (N-*C*(3)H-N), 60.7 ($CH_3C_6H_9CH(CH_3)_2$), 47.6 ($CH_3C_6H_9CH(CH_3)_2$), 44.1 (CH_2CH_3), 41.6 ($CH_3C_6H_9CH(CH_3)_2$), 35.5 ($CH_3C_6H_9CH(CH_3)_2$), 29.1 ($CH_3C_6H_9CH(CH_3)_2$), 26.2 ($CH_3C_6H_9CH(CH_3)_2$), 24.3 ($CH_3C_6H_9CH(CH_3)_2$), 23.3 ($CH_3C_6H_9CH(CH_3)_2$), 22.6 ($CH_3C_6H_9CH(CH_3)_2$), 20.3 ($CH_3C_6H_9CH(CH_3)_2$), 16.1 (CH_2CH_3). (Minor) δ 172.1

(Pd-N<u>C</u>N), 140.5 (N-<u>C</u>(3)H-N), 60.7 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 47.5 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 44.1 ($\underline{C}H_2CH_3$), 41.3 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 35.5 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), (29.0) ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 26.2 ($CH_3C_6H_9\underline{C}H(CH_3)_2$), 24.2 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 23.3 ($\underline{C}H_3C_6H_9CH(CH_3)_2$), 22.6 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 20.3 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 16.0 ($CH_2\underline{C}H_3$). IR data (KBr pellet) cm^{-1}: 3434 (w), 3126 (m), 3055 (w), 2950 (s), 2870 (s), 1699 (w), 1540 (m), 1443 (s), 1387 (m), 1352 (w), 1283 (w), 1262 (w), 1212 (m), 1189 (w), 1140 (w), 1096 (w), 1008 (w), 981 (w), 940 (w), 872 (w), 846 (w), 801 (w), 777 (w), 659 (m). HRMS (ES): *m/z* 657.2304 $[M–Br]^+$, calcd. 657.2308. Anal. Calcd. for $C_{28}H_{50}PdBr_2N_6$: C, 45.63; H, 6.84; N, 11.40. Found: C, 45.90; H, 6.67; N, 11.39 %. $[\alpha]_D^{25}$ – 29.4 (*c* 1.00 in $CHCl_3$).

Synthesis of *trans*-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)($CH_2C_6H_5$) ($\mathbf{3a_1}$)

To a suspension of *trans*-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$$PdBr_2$ (**2a**) (0.200 g, 0.271 mmol) in Et_2O (*ca.* 10 mL), benzyl magnesium chloride (*ca.* 1 mL, 1.00 M in Et_2O) was added through syringe at –78 °C temperature under nitrogen atmosphere. The reaction mixture was stirred at –78 °C for 30 minutes, followed by at room temperature for 16 hours. The solvent was removed under vacuum and CH_2Cl_2 (*ca.* 50 mL) was added. The reaction mixture was filtered through celite and filtrate was vacuum dried to give the crude product as light brown solid. The crude product was finally purified by column chromatography using neutral Al_2O_3 as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (90 : 10 *v/v*) to give the product $\mathbf{3a_1}$ as a colorless solid (0.177 g, 87 %). Both the ^1H NMR and $^{13}C\{^1H\}$ NMR spectrum showed the presence of two isomers, *trans-syn* and *trans-anti* with the ratio 1:1. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): (One isomer) δ 7.88 (s,

2H, N-C(3)*H*-N), 6.93 (t, 2H, $^3J_{HH}$ = 7 Hz, C_6H_5), 6.84 (t, 1H, $^3J_{HH}$ = 7 Hz, C_6H_5), 6.47-6.44 (m, 2H, C_6H_5), 5.72 (br, 2H, $CH_3C_6H_9CH(CH_3)_2$), 4.37 (qd, 2H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 4.15 (qd, 2H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 2.78-0.80 (m, 20H, $CH_2C_6H_5$, $CH_3C_6H_9CH(CH_3)_2$ & $CH_3C_6H_9CH(CH_3)_2$), 1.43 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 1.15 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.91 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.80 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$). (Second isomer) δ 7.84 (s, 2H, N-C(3)*H*-N), 6.93 (t, 2H, $^3J_{HH}$ = 7 Hz, C_6H_5), 6.84 (t, 1H, $^3J_{HH}$ = 7 Hz, C_6H_5), 6.47-6.44 (m, 2H, C_6H_5), 5.61 (br, 2H, $CH_3C_6H_9CH(CH_3)_2$), 4.27 (qd, 2H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 3.80 (qd, 2H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 2.78-0.80 (m, 20H, $CH_2C_6H_5$, $CH_3C_6H_9CH(CH_3)_2$ & $CH_3C_6H_9CH(CH_3)_2$), 1.41 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 1.08 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.88 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.65 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): (One isomer) δ 185.8 (Pd-N*C*N), 150.4 (*C*$_6H_5$), 140.2 (N-*C*(3)H-N), 128.2 (*C*$_6H_5$), 127.2 (*C*$_6H_5$), 122.2 (*C*$_6H_5$), 60.7 (CH_3*C*$_6H_9CH(CH_3)_2$), 47.9 (CH_3*C*$_6H_9CH(CH_3)_2$), 43.8 (*C*H_2CH_3), 42.0 (CH_3*C*$_6H_9CH(CH_3)_2$), 35.6 (CH_3*C*$_6H_9CH(CH_3)_2$), 29.2 (CH_3*C*$_6H_9CH(CH_3)_2$), 26.5 ($CH_3C_6H_9$*C*$H(CH_3)_2$), 24.5 (CH_3*C*$_6H_9CH(CH_3)_2$), 23.9 (*C*$H_3C_6H_9CH(CH_3)_2$) 22.8 ($CH_3C_6H_9CH($*C*$H_3)_2$), 22.5 ($CH_3C_6H_9CH($*C*$H_3)_2$), 15.5 (CH_2*C*$_6H_5$), 15.1 (CH_2*C*H_3). (Second isomer) δ 185.3 (Pd-N*C*N), 150.4 (*C*$_6H_5$), 139.6 (N-*C*(3)H-N), 128.2 (*C*$_6H_5$), 127.2 (*C*$_6H_5$), 122.2 (*C*$_6H_5$), 60.3 (CH_3*C*$_6H_9CH(CH_3)_2$), 47.5 (CH_3*C*$_6H_9CH(CH_3)_2$), 43.3 (*C*H_2CH_3), 41.8 (CH_3*C*$_6H_9CH(CH_3)_2$), 35.5 (CH_3*C*$_6H_9CH(CH_3)_2$), 28.8 (CH_3*C*$_6H_9CH(CH_3)_2$), 26.0 ($CH_3C_6H_9$*C*$H(CH_3)_2$), 23.8 (CH_3*C*$_6H_9CH(CH_3)_2$), 22.8 (*C*$H_3C_6H_9CH(CH_3)_2$), 22.5 ($CH_3C_6H_9CH($*C*$H_3)_2$), 20.0 ($CH_3C_6H_9CH($*C*$H_3)_2$), 15.5 (CH_2*C*$_6H_5$), 15.0 (CH_2*C*H_3). IR data (KBr pellet) cm^{-1}: 3105 (w), 3044 (w), 2951 (s), 2922 (s), 2868 (m), 1632 (w), 1595 (w), 1540 (w), 1455 (m), 1368 (w), 1305 (w), 1261 (m), 1212 (w), 1186 (w),

1096 (w), 1026 (w), 980 (w), 941 (w), 872 (w), 800 (m), 754 (w), 717 (w), 697 (w). HRMS (ES): *m/z* 667.3683 $[M–Br]^+$, calcd. 667.3687. Anal. Calcd. for $C_{35}H_{57}N_6BrPd$: C, 56.19; H, 7.68; N, 11.23. Found: C, 56.58; H, 7.81; N, 10.49 %. $[\alpha]_D^{25}$ + 3.4 (*c* 1.00 in $CHCl_3$).

Synthesis of *trans*-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)(*o*-OMeC$_6$H$_4$) (3a$_2$)

To a suspension of *trans*-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$PdBr$_2$ (**2a**) (0.400 g, 0.543 mmol) in Et_2O (*ca.* 15 mL), (2-methoxyphenyl)magnesium bromide (*ca.* 3 mL, 1.00 M in Et_2O) was added through syringe at –78 °C temperature under nitrogen atmosphere. The reaction mixture was stirred at –78 °C for 30 minutes, followed by at room temperature for 16 hours. The solvent was removed under vacuum and CH_2Cl_2 (*ca.* 100 mL) was added. The reaction mixture was filtered through celite and filtrate was vacuum dried to give the crude product as white solid. The crude product was finally purified by column chromatography using neutral Al_2O_3 as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (90 : 15 *v/v*) to give the product **3a$_2$** as a white solid (0.387 g, 93 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.84 (s, 2H, N-C(3)*H*-N), 6.93 (dd, 1H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, C_7H_7O), 6.77 (dt, 1H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, C_7H_7O), 6.52-6.48 (m, 2H, C_7H_7O), 5.38 (br, 2H, $CH_3C_6H_9CH(CH_3)_2$), 4.98-4.94 (m, 2H, CH_2CH_3), 4.80-4.73 (m, 2H, CH_2CH_3), 3.61 (s, 3H, CH_3 of C_7H_7O), 1.98-0.08 (m, 18H, $CH_3C_6H_9CH(CH_3)_2$ & $CH_3C_6H_9CH(CH_3)_2$), 1.67 (t, 6H, $^3J_{HH}$ = 7 Hz, CH_2CH_3), 1.34 (br, 6H, $CH_3C_6H_9CH(CH_3)_2$), 0.78 (d, 6H, $^3J_{HH}$ = 6 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.50 (d, 6H, $^3J_{HH}$ = 6 Hz, $CH_3C_6H_9CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): δ 181.1 (Pd-N*C*N), 161.3 (C_7H_7O), 140.0 (N-*C*(3)H-N), 138.0 (C_7H_7O), 135.5 (C_7H_7O),

123.6 ($\underline{C}_7H_7O$), 120.7 ($\underline{C}_7H_7O$), 109.0 ($\underline{C}_7H_7O$), 58.9 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 55.0 ($\underline{C}H_3$ of C_7H_7O) 47.6 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 44.3 ($\underline{C}H_2CH_3$), 39.9 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 35.4 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 28.9 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 27.1 ($CH_3C_6H_9\underline{C}H(CH_3)_2$), 25.7 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 23.3 ($\underline{C}H_3C_6H_9CH(CH_3)_2$) 22.5 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 20.7 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 15.7 ($CH_2\underline{C}H_3$) IR data (KBr pellet) cm^{-1}: 3111 (w), 3051 (w), 2948 (s), 2868 (m), 1662 (w), 1564 (w), 1540 (w), 1456 (m), 1427 (m), 1386 (w), 1368 (w), 1285 (w), 1258 (w), 1219 (m), 1188 (w), 1172 (w), 1055 (w), 1024 (w), 1008 (w), 981 (w), 872 (w), 837 (w), 782 (w), 747 (w), 718 (w), 676 (w), 571 (w). HRMS (ES): *m/z* 683.3628 $[M–Br]^+$, calcd. 683.3636. Anal. Calcd. for $C_{35}H_{57}N_6OBrPd$: C, 55.01; H, 7.52; N, 11.00. Found: C, 55.64; H, 7.89; N, 11.00 %. $[\alpha]_D^{25}$ + 28.5 (*c* 1.00 in $CHCl_3$).

Synthesis of 1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazolium bromide (1b)

A mixture of 1-(1*S*)-menthyl-1H-1,2,4-triazole (**A**) (0.928 g, 4.48 mmol) and benzyl bromide (0.766 g, 4.48 mmol) was refluxed in CH_3CN (*ca*. 40 mL) for overnight, after which the solvent was removed under vacuum. The residue was washed with hot Et_2O (*ca*. 3 × 10 mL) and vacuum dried to give the product **1b** as a white solid (1.42 g, 84 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 11.9 (s, 1H, N-C(5)$\underline{H}$-N), 9.15 (s, 1H, N-C(3)$\underline{H}$-N), 7.68 (dd, 2H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, $C_6\underline{H}_5$), 7.39 (br, 3H, $C_6\underline{H}_5$), 5.92 (s, 2H, $C\underline{H}_2$), 5.12 (br, 1H, NC$\underline{H}$), 1.99-1.00 (m, 9H, $CH_3C_6\underline{H}_9CH(CH_3)_2$ & $CH_3C_6H_9C\underline{H}(CH_3)_2$), 0.89 (d, 3H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(C\underline{H}_3)_2$), 0.85 (d, 3H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(C\underline{H}_3)_2$), 0.76 (d, 3H, $^3J_{HH}$ = 7 Hz, $C\underline{H}_3C_6H_9CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 143.4 (N-$\underline{C}$(5)H-N), 142.9 (N-$\underline{C}$(3)H-N), 132.9 (*ipso*-$\underline{C}_6H_5$), 129.8 ($\underline{C}_6H_5$), 129.6 ($\underline{C}_6H_5$), 129.5 ($\underline{C}_6H_5$), 62.2 ($\underline{C}H_2$), 51.6 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 46.3 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 40.0 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 34.3

($CH_3\underline{C}_6H_9CH(CH_3)_2$), 29.1 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 25.8 ($CH_3C_6H_9\underline{C}H(CH_3)_2$), 24.2 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 22.1 ($\underline{C}H_3C_6H_9CH(CH_3)_2$), 21.3 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 20.5 ($CH_3C_6H_9CH(\underline{C}H_3)_2$). IR data (KBr pellet) cm^{-1}: 3069 (m), 3003 (s), 2950 (s), 2850 (s), 1563 (m), 1509 (w), 1454 (m), 1402 (w), 1203 (w), 1159 (m), 1122 (w), 1008 (w), 982 (w), 912 (w), 874 (w), 820 (w), 706 (m), 650 (m). HRMS (ES): *m/z* 298.2287, $[M–Br]^+$, calcd. 298.2283. Anal. Calcd. for $C_{19}H_{28}BrN_3$: C, 60.32; H, 7.46; N, 11.11. Found: C, 60.11; H, 7.86; N, 10.16 %. $[\alpha]_D^{25}$ + 16.7 (*c* 1.00 in $CHCl_3$).

Synthesis of *trans*-[1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazol-5-ylidene]$_2$PdBr$_2$ (2b)

A mixture of 1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazolium bromide (**1b**) (0.568 g, 1.50 mmol), $PdBr_2$ (0.200 g, 0.751 mmol) and Et_3N (0.606 g, 5.99 mmol) in CH_3CN (*ca*. 50 mL) was refluxed for 12 hours. The reaction mixture was filtered and solvent was removed under vacuum to obtain the product as a yellow color solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (88 : 12 *v/v*) to give the product **2b** as a light yellow solid (0.458 g, 71 %). Both the ^1H NMR and $^{13}C\{^1H\}$ NMR spectrum showed the presence of two isomers, *trans-syn* and *trans-anti*. The major to minor isomer ratio was 1.7:1. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): (Major) δ 7.65 (s, 2H, N-C(3)$\underline{H}$-N), 7.53 (br, 2H, ($C_6\underline{H}_5$), 7.45 (br, 4H, $C_6\underline{H}_5$), 7.35 (br, 4H, $C_6\underline{H}_5$), 5.73 (d, 2H, $^2J_{HH}$ = 15 Hz, $C\underline{H}_2$), 5.67 (br, 2H, $CH_3C_6\underline{H}_9CH(CH_3)_2$), 5.53 (d, 2H, $^2J_{HH}$ = 15 Hz, $C\underline{H}_2$), 2.55-0.88 (m, 18H, $CH_3C_6\underline{H}_9CH(CH_3)_2$ & $CH_3C_6H_9C\underline{H}(CH_3)_2$), 1.17 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(C\underline{H}_3)_2$), 0.84 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(C\underline{H}_3)_2$), 0.74 (d, 6H, $^3J_{HH}$ = 7 Hz, $C\underline{H}_3C_6H_9CH(CH_3)_2$). (Minor) δ 7.60 (s, 2H, N-C(3)$\underline{H}$-N), 7.52 (br, 2H, ($C_6\underline{H}_5$), 7.43 (br, 4H, $C_6\underline{H}_5$), 7.33 (br, 4H, $C_6\underline{H}_5$), 5.95 (d, 2H, $^2J_{HH}$ = 15 Hz, $C\underline{H}_2$),

5.69 (d, 2H, $^{2}J_{HH}$ = 15 Hz, C$\underline{H}_2$), 5.65 (br, 2H, $CH_3C_6\underline{H}_9CH(CH_3)_2$), 2.55-0.88 (m, 18H, $CH_3C_6\underline{H}_9CH(CH_3)_2$ & $CH_3C_6H_9C\underline{H}(CH_3)_2$), 1.02 (d, 6H, $^{3}J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(C\underline{H}_3)_2$), 0.81 (d, 6H, $^{3}J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(C\underline{H}_3)_2$), 0.64 (d, 6H, $^{3}J_{HH}$ = 7 Hz, $C\underline{H}_3C_6H_9CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ^{o}C): (Major) δ 172.5 (Pd-N$\underline{C}$N), 141.0 (N-$\underline{C}$(3)H-N), 134.8 (*ipso*-$\underline{C}_6H_5$), 129.3 ($\underline{C}_6H_5$), 129.2 ($\underline{C}_6H_5$), 129.0 ($\underline{C}_6H_5$), 60.8 ($\underline{C}H_2$), 52.8 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 47.6 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 41.5 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 35.5 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 29.2 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 26.2 ($CH_3C_6H_9\underline{C}H(CH_3)_2$), 24.2 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 23.9 ($\underline{C}H_3C_6H_9CH(CH_3)_2$), 22.6 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 20.3 ($CH_3C_6H_9CH(\underline{C}H_3)_2$). (Minor) δ 172.5 (Pd-N$\underline{C}$N), 140.9 (N-$\underline{C}$(3)H-N), 134.6 (*ipso*-$\underline{C}_6H_5$), 129.0 ($\underline{C}_6H_5$), 128.9 ($\underline{C}_6H_5$), 128.8 ($\underline{C}_6H_5$), 60.6 ($\underline{C}H_2$), 52.8 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 47.4 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 41.4 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 35.4 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 29.1 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 26.2 ($CH_3C_6H_9\underline{C}H(CH_3)_2$), 24.2 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 23.3 ($\underline{C}H_3C_6H_9CH(CH_3)_2$), 22.6 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 20.1 ($CH_3C_6H_9CH(\underline{C}H_3)_2$). IR data (KBr pellet) cm^{-1}: 3436 (m), 3150 (w), 3054 (w), 2950 (s), 2867 (s), 2844 (m), 1666 (w), 1538 (m), 1498 (w), 1453 (m), 1386 (w), 1367 (m), 1242 (w), 1216 (w), 1201 (w), 980 (w), 938 (w), 775 (w), 718 (m), 660 (w), 474 (w). HRMS (ES): *m/z* 781.2610 $[M–Br]^{+}$, calcd. 781.2623. Anal. Calcd. for $C_{38}H_{54}PdBr_2N_6$: C, 53.00; H, 6.32; N, 9.76. Found: C, 53.14; H, 6.87; N, 8.92 %. $[\alpha]_D^{25}$ – 45.2 (*c* 1.00 in $CHCl_3$).

Synthesis of *trans*-[1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)($CH_2C_6H_5$) ($3b_1$)

To a suspension of *trans*-[1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazol-5-ylidene]$_2PdBr_2$ (**2b**) (0.200 g, 0.232 mmol) in Et_2O (*ca.* 10 mL), benzyl magnesium chloride (*ca.* 1 mL, 1.00 M in Et_2O) was added through syringe at –78 °C temperature under nitrogen

atmosphere. The reaction mixture was stirred at –78 °C for 30 minutes, followed by at room temperature for 16 hours. The solvent was removed under vacuum and CH_2Cl_2 (*ca.* 50 mL) was added. The reaction mixture was filtered through celite and filtrate was vacuum dried to give the crude product as light brown solid. The crude product was finally purified by column chromatography using neutral Al_2O_3 as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (94 : 6 *v/v*) to give the product **3b$_1$** as a colorless solid (0.151 g, 74 %). Both the ^{1}H NMR and ^{13}C{^{1}H} NMR spectrum showed the presence of two isomers, *trans-syn* and *trans-anti* with the ratio 1:1. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): (One isomer) δ 7.50 (s, 2H, N-C(3)*H*-N), 7.38-7.34 (m, 10H, C_6H_5), 6.93-6.91 (m, 3H, C_6H_5), 6.43-6.41 (m, 2H, C_6H_5),), 5.51 (d, 2H, $^2J_{HH}$ = 15 Hz, $CH_2C_6H_5$), 5.78 (br, 2H, $CH_3C_6H_9CH(CH_3)_2$), 4.81 (d, 2H, $^2J_{HH}$ = 15 Hz, $CH_2C_6H_5$), 2.81-0.79 (m, 18H, $CH_3C_6H_9CH(CH_3)_2$ & $CH_3C_6H_9CH(CH_3)_2$), 2.80 (d, 1H, $^2J_{HH}$ = 8 Hz, $CH_2C_6H_5$), 2.72 (d, 1H, $^2J_{HH}$ = 8 Hz, $CH_2C_6H_5$), 1.18 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.90 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.83 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$). (Second isomer) δ 7.42 (s, 2H, N-C(3)*H*-N), 7.38-7.34 (m, 10H, C_6H_5), 6.93-6.91 (m, 3H, C_6H_5), 6.43-6.41 (m, 2H, C_6H_5), 5.65 (d, 2H, $^2J_{HH}$ = 15 Hz, $CH_2C_6H_5$), 5.64 (br, 2H, $CH_3C_6H_9CH(CH_3)_2$), 4.60 (d, 2H, $^2J_{HH}$ = 15 Hz, $CH_2C_6H_5$), 2.81-0.79 (m, 18H, $CH_3C_6H_9CH(CH_3)_2$ & $CH_3C_6H_9CH(CH_3)_2$), 2.80 (d, 1H, $^2J_{HH}$ = 8 Hz, $CH_2C_6H_5$), 2.72 (d, 1H, $^2J_{HH}$ = 8 Hz, $CH_2C_6H_5$), 1.12 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.89 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$), 0.65 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH_3C_6H_9CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 ^{o}C): (One isomer) δ 186.2 (Pd-N*C*N), 150.8 (C_6H_5), 140.9 (N-*C*(3)H-N), 134.8 (C_6H_5), 129.7 (C_6H_5), 129.3 (C_6H_5), 128.8 (C_6H_5), 128.4 (C_6H_5), 127.4 (C_6H_5), 122.2 (C_6H_5), 60.7 ($CH_3C_6H_9CH(CH_3)_2$), 52.6 ($CH_2C_6H_5$), 47.9 ($CH_3C_6H_9CH(CH_3)_2$), 42.2

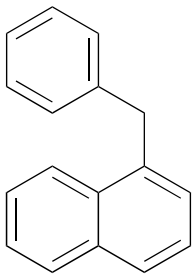
($CH_3\underline{C}_6H_9CH(CH_3)_2$), 35.6 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 29.3 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 26.5 ($CH_3C_6H_9\underline{C}H(CH_3)_2$), 24.6 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 23.7 ($\underline{C}H_3C_6H_9CH(CH_3)_2$) 22.8 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 20.6 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 15.6 ($C\underline{H}_2C_6H_5$). (Second isomer) δ 185.6 (Pd-N$\underline{C}$N), 150.8 ($\underline{C}_6H_5$), 140.1 (N-$\underline{C}$(3)H-N), 134.6 ($\underline{C}_6H_5$), 129.6 ($\underline{C}_6H_5$), 129.2 ($\underline{C}_6H_5$), 128.4 ($\underline{C}_6H_5$), 127.4 ($\underline{C}_6H_5$), 127.2 ($\underline{C}_6H_5$), 122.2 ($\underline{C}_6H_5$), 60.6 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 52.3 ($C\underline{H}_2C_6H_5$), 47.6 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 41.8 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 35.5 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 28.9 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 26.0 ($CH_3C_6H_9\underline{C}H(CH_3)_2$), 24.0 ($CH_3\underline{C}_6H_9CH(CH_3)_2$), 22.8 ($\underline{C}H_3C_6H_9CH(CH_3)_2$), 22.5 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 19.9 ($CH_3C_6H_9CH(\underline{C}H_3)_2$), 15.6 ($C\underline{H}_2C_6H_5$). IR data (KBr pellet) cm^{-1}: 3122 (w), 3050 (w), 2947 (s), 2922 (s), 2867 (m), 1645 (w), 1593 (w), 1540 (w), 1455 (w), 1355 (w), 1305 (w), 1261 (m), 1212 (w), 1094 (s), 1026 (s), 871 (w), 801 (s), 759 (w), 717 (w), 696 (w), 670 (w). HRMS (ES): *m/z* 791.3994 $[M–Br]^+$, calcd. 791.4003. Anal. Calcd. for $C_{45}H_{61}N_6BrPd$: C, 61.96; H, 7.05; N, 9.63. Found: C, 61.92; H, 6.40; N, 9.56 %. $[\alpha]_D^{25}$ + 19.2 (*c* 1.00 in $CHCl_3$).

Synthesis of *trans*-[1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)(*o*-OMeC$_6$H$_4$) (3b$_2$)

To a suspension of *trans*-[1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazol-5-ylidene]$_2$PdBr$_2$ (**2b**) (0.400 g, 0.465 mmol) in Et_2O (*ca.* 15 mL), (2-methoxyphenyl)magnesium bromide (*ca.* 3 mL, 1.00 M in Et_2O) was added through syringe at –78 °C temperature under the nitrogen atmosphere. The reaction mixture was stirred at –78 °C for 30 minutes, followed by at room temperature for 16 hours. The solvent was removed under vacuum and CH_2Cl_2 (*ca.* 100 mL) was added. The reaction mixture was filtered through celite and filtrate was vacuum dried to give the crude product as white solid. The crude product was finally purified by column chromatography using

neutral Al_2O_3 as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (90 : 10 *v/v*) to give the product **3b$_2$** as a white solid (0.362 g, 88 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.74-7.53 (m, 12H, N-C(3)*H*-N & C_6H_5), 6.97-6.90 (m, 2H, C_7H_7O), 6.66-6.60 (m, 2H, C_7H_7O), 6.29-6.17 (m, 4H, $CH_2C_6H_5$), 5.62 (br, 2H, $CH_3C_6H_9CH(CH_3)_2$), 3.88 (s, 3H, CH_3 of C_7H_7O), 2.14-0.35 (m, 18H, $CH_3C_6H_9CH(CH_3)_2$ & $CH_3C_6H_9CH(CH_3)_2$), 1.53 (br, 6H, $CH_3C_6H_9CH(CH_3)_2$), 0.93 (br, 6H, $CH_3C_6H_9CH(CH_3)_2$), 0.71 (br, 6H, $CH_3C_6H_9CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 ^{o}C): δ 181.4 (Pd-N*C*N), 161.3 (C_7H_7O), 140.6 (N-*C*(3)H-N), 138.2 (C_7H_7O), 135.4 (C_7H_7O), 135.3 (C_6H_5), 129.6 (C_6H_5), 129.3 (C_6H_5), 128.7 (C_6H_5), 123.6 (C_7H_7O), 120.7 (C_7H_7O), 109.0 (C_7H_7O), 59.1 ($CH_3C_6H_9CH(CH_3)_2$), 55.3 (CH_3 of C_7H_7O), 53.3 ($CH_2C_6H_5$), 47.6 ($CH_3C_6H_9CH(CH_3)_2$), 40.2 ($CH_3C_6H_9CH(CH_3)_2$), 35.4 ($CH_3C_6H_9CH(CH_3)_2$), 29.0 ($CH_3C_6H_9CH(CH_3)_2$), 25.8 ($CH_3C_6H_9CH(CH_3)_2$), 24.3 ($CH_3C_6H_9CH(CH_3)_2$), 23.5 ($CH_3C_6H_9CH(CH_3)_2$) 22.6 ($CH_3C_6H_9CH(CH_3)_2$), 20.5 ($CH_3C_6H_9CH(CH_3)_2$). IR data (KBr pellet) cm^{-1}: 3045 (w), 2949 (s), 2925 (s), 2867 (m), 2841 (m), 1563 (w), 1537 (w), 1497 (w), 1455 (s), 1424 (m), 1386 (w), 1355 (w), 1287 (w), 1242 (w), 1220 (s), 1172 (w), 1115 (w), 1055 (w), 1024 (w), 1008 (w), 979 (w), 871 (w), 841 (w), 783 (w), 749 (w), 718 (s), 696 (w), 665 (w). HRMS (ES): *m/z* 807.3946 [M–Br]$^+$, calcd. 807.3952. Anal. Calcd. for $C_{45}H_{61}N_6OBrPd$: C, 60.84; H, 6.92; N, 9.46. Found: C, 61.22; H, 7.27; N, 8.35 %. $[\alpha]_D^{25}$ + 59.0 (*c* 1.00 in $CHCl_3$).

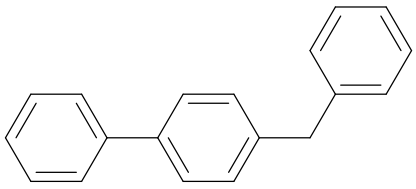
1-benzylnaphthalene (5), Entry 1, Table 1



(**5**)

A mixture of trans-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)($CH_2C_6H_5$) (**3a$_1$**) (0.108 g, 0.144 mmol), 1-naphthaleneboronic acid (0.030 g, 0.173 mmol), and NaOH (0.029 g, 0.722 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as brown solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with petroleum ether to give the product **5** as a white solid (0.016 g, 50 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 8.07-8.06 (m, 1H, $C_{10}\underline{H}_7$), 7.94-7.82 (m, 1H, $C_{10}\underline{H}_7$), 7.84-7.82 (m, 1H, $C_{10}\underline{H}_7$), 7.53-7.48 (m, 4H, $C_{10}\underline{H}_7$ & $C_6\underline{H}_5$), 7.37-7.27 (m, 3H, $C_{10}\underline{H}_7$), 7.28-7.26 (m, 2H, $C_6\underline{H}_5$), 4.52 (s, 2H, $C\underline{H}_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25 ^{o}C): δ 140.8 ($\underline{C}_{10}H_7$), 136.8 ($\underline{C}_{10}H_7$), 134.1 ($\underline{C}_6H_5$), 132.3 ($\underline{C}_{10}H_7$), 128.9 ($\underline{C}_6H_5$), 128.8 ($\underline{C}_{10}H_7$), 128.6 ($\underline{C}_6H_5$), 127.5 ($\underline{C}_{10}H_7$), 127.3 ($\underline{C}_{10}H_7$), 126.2 ($\underline{C}_{10}H_7$), 126.1 ($\underline{C}_{10}H_7$), 125.7 ($\underline{C}_{10}H_7$), 125.7 ($\underline{C}_{10}H_7$), 124.5 ($\underline{C}_6H_5$), 39.2 ($\underline{C}H_2$).

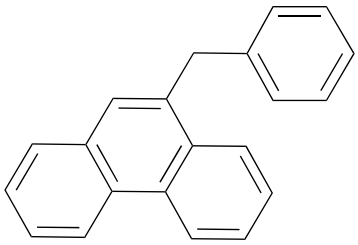
4-benzyl-1,1'-biphenyl (6), Entry 2, Table 1



(**6**)

A mixture of trans-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)($CH_2C_6H_5$) (**3a$_1$**) (0.125 g, 0.167 mmol), [1,1'-biphenyl]-4-ylboronic acid (0.040 g, 0.200 mmol), and NaOH (0.033 g, 0.835 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as brown solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with petroleum ether to give the product **6** as a white solid (0.017 g, 41 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.57 (d, 2H, $^3J_{HH}$ = 8 Hz, $C_{12}\underline{H}_9$), 7.52 (d, 2H, $^3J_{HH}$ = 8 Hz, $C_{12}\underline{H}_9$), 7.43 (t, 2H, $^3J_{HH}$ = 8 Hz, $C_{12}\underline{H}_9$), 7.33-7.28 (m, 2H, $C_{12}\underline{H}_9$ & $C_6\underline{H}_5$), 7.26-7.22 (m, 6H, $C_{12}\underline{H}_9$ & $C_6\underline{H}_5$), 4.03 (s, 2H, $C\underline{H}_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 ^oC): δ 141.19 ($\underline{C}_{12}H_9$), 141.18 ($\underline{C}_{12}H_9$), 140.3 ($\underline{C}_{12}H_9$), 140.3 ($\underline{C}_6H_5$), 129.5 ($\underline{C}_{12}H_9$), 129.2 ($\underline{C}_6H_5$), 128.9 ($\underline{C}_{12}H_9$), 128.7 ($\underline{C}_6H_5$), 127.4 ($\underline{C}_{12}H_9$), 127.3 ($\underline{C}_{12}H_9$), 127.2 ($\underline{C}_{12}H_9$), 126.3 ($\underline{C}_6H_5$), 41.8 ($\underline{C}H_2$).

9-benzylphenanthrene (7), Entry 3, Table 1

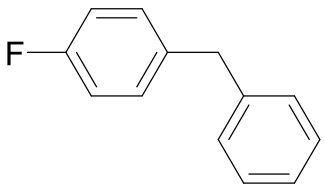


(**7**)

A mixture of *trans*-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)($CH_2C_6H_5$) (**3a$_1$**) (0.160 g, 0.214 mmol), phenanthren-9-ylboronic acid (0.057 g, 0.257 mmol), and NaOH (0.043 g, 1.07 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as brown solid. The crude product was finally purified by column chromatography

using silica gel as a stationary phase and eluting with petroleum ether to give the product **7** as a white solid (0.019 g, 33 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 8.74 (d, 1H, $^{3}J_{HH}$ = 8 Hz, $C_{14}\underline{H}_9$), 8.68 (d, 1H, $^{3}J_{HH}$ = 8 Hz, $C_{14}\underline{H}_9$), 8.36 (d, 1H, $^{3}J_{HH}$ = 8 Hz, $C_{14}\underline{H}_9$), 7.82 (d, 1H, $^{3}J_{HH}$ = 8 Hz, $C_{14}\underline{H}_9$), 7.65-7.54 (m, 5H, $C_{14}\underline{H}_9$ & $C_6\underline{H}_5$), 7.30-7.21 (m, 5H, $C_{14}\underline{H}_9$ & $C_6\underline{H}_5$), 4.50 (s, 2H, $C\underline{H}_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 25 ^{o}C): δ 140.5 ($\underline{C}_{14}H_9$), 134.9 ($\underline{C}_6H_5$), 132.0 ($\underline{C}_{14}H_9$), 131.6 ($\underline{C}_{14}H_9$), 131.0 ($\underline{C}_{14}H_9$), 130.1 ($\underline{C}_{14}H_9$), 129.0 ($\underline{C}_6H_5$), 128.7 ($\underline{C}_6H_5$), 128.4 ($\underline{C}_{14}H_9$), 128.1 ($\underline{C}_{14}H_9$), 126.8 ($\underline{C}_{14}H_9$), 126.4 ($\underline{C}_{14}H_9$), 126.3 ($\underline{C}_{14}H_9$), 125.2 ($\underline{C}_6H_5$), 123.3 ($\underline{C}_{14}H_9$), 122.7 ($\underline{C}_{14}H_9$) 39.8 ($\underline{C}H_2$).

1-benzyl-4-fluorobenzene (8), Entry 4, Table 1

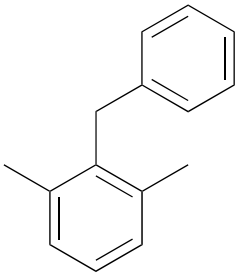


(**8**)

A mixture of *trans*-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)($CH_2C_6H_5$) (**3a$_1$**) (0.280 g, 0.374 mmol), (4-fluorophenyl)boronic acid (0.063 g, 0.449 mmol), and NaOH (0.075 g, 1.87 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as brown solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with petroleum ether to give the product **8** as a white solid (0.041 g, 59 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.30-7.27 (m, 2H, $C_6\underline{H}_4F$), 7.23-7.20 (m, 1H, $C_6\underline{H}_5$), 7.18-7.11 (m, 4H, $C_6\underline{H}_4F$ & $C_6\underline{H}_5$), 6.98-6.94 (m, 2H, $C_6\underline{H}_5$), 3.94 (s, 2H, $C\underline{H}_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 25 ^{o}C): δ 161.4 (d, $^{1}J_{CF}$ = 242 Hz, $\underline{C}_6H_4F$), 141.0 ($\underline{C}_6H_5$), 136.8 (d, $^{4}J_{CF}$ = 4 Hz, $\underline{C}_6H_4F$), 130.3 (d, $^{3}J_{CF}$ = 8

Hz, $\underline{C}_6H_4F$), 128.9 ($\underline{C}_6H_5$), 128.6 ($\underline{C}_6H_5$), 126.2 ($\underline{C}_6H_5$), 115.2 (d, $^2J_{CF}$ = 16 Hz, $\underline{C}_6H_4F$), 41.1 ($\underline{C}H_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 470 MHz, 25 ^oC): δ -117.4 ($C_6H_4\underline{F}$).

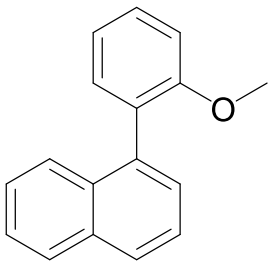
2-benzyl-1,3-dimethylbenzene (9), Entry 5, Table 1



(**9**)

A mixture of *trans*-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)($CH_2C_6H_5$) (**3a$_1$**) (0.200 g, 0.267 mmol), (2,6-dimethylphenyl)boronic acid (0.048 g, 0.321 mmol), and NaOH (0.053 g, 1.34 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as brown solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with petroleum ether to give the product **9** as a white solid (0.042 g, 80 %). ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.29 (t, 2H, $^3J_{HH}$ = 7 Hz, $C_6\underline{H}_5$), 7.21 (t, 1H, $^3J_{HH}$ = 7 Hz, $C_8\underline{H}_9$), 7.15-7.11 (m, 3H, $C_6\underline{H}_5$), 7.06 (d, 2H, $^3J_{HH}$ = 7 Hz, $C_8\underline{H}_9$), 4.11 (s, 2H, $C\underline{H}_2$), 2.29 (s, 6H, $C\underline{H}_3$ of C_8H_9). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 ^oC): δ 140.0 ($\underline{C}_8H_9$), 137.4 ($\underline{C}_8H_9$), 137.0 ($\underline{C}_6H_5$), 128.5 ($\underline{C}_6H_5$), 128.3 ($\underline{C}_8H_9$), 128.0 ($\underline{C}_6H_5$), 126.5 ($\underline{C}_8H_9$), 125.9 ($\underline{C}_6H_5$), 35.2 ($\underline{C}H_2$), 20.4 ($\underline{C}H_3$ of C_8H_9).

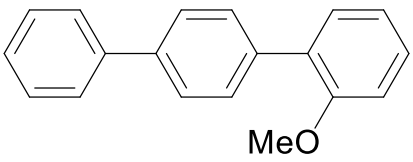
1-(2-methoxyphenyl)naphthalene (10), Entry 6, Table 1



(**10**)

A mixture of *trans*-[1-(1*S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)(*o*-OMeC$_6$H$_4$) (**3a$_2$**) (0.140 g, 0.183 mmol), 1-naphthaleneboronic acid (0.038 g, 0.220 mmol), and NaOH (0.037 g, 0.916 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as off white solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (98 : 2 *v/v*) to give the product **10** as a white solid (0.014 g, 33 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (t, 2H, $^3J_{HH}$ = 9 Hz, C$_{10}$*H*$_7$), 7.64 (d, 1H $^3J_{HH}$ = 8 Hz, C$_{10}$*H*$_7$), 7.55-7.51 (m, 1H, C$_{10}$*H*$_7$), 7.43-7.51 (m, 4H, C$_{10}$*H*$_7$ and C$_7$*H*$_7$O), 7.34 (dd, 1H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, C$_7$*H*$_7$O), 7.10-7.04 (m, 2H, C$_7$*H*$_7$O), 3.69 (s, 3H, C*H*$_3$ of C$_7$H$_7$O). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.4 (*C*$_7$H$_7$O), 137.1 (*C*$_{10}$H$_7$), 133.6 (*C*$_{10}$H$_7$), 132.3 (*C*$_{10}$H$_7$), 132.1 (*C*$_7$H$_7$O), 129.7 (*C*$_{10}$H$_7$), 129.2 (*C*$_{10}$H$_7$), 128.3 (*C*$_{10}$H$_7$), 127.8 (*C*$_{10}$H$_7$), 127.5 (*C*$_{10}$H$_7$), 126.6 (*C*$_7$H$_7$O), 125.8 (*C*$_{10}$H$_7$), 125.7 (*C*$_{10}$H$_7$), 125.5 (*C*$_7$H$_7$O), 120.7 (*C*$_7$H$_7$O), 111.2 (*C*$_7$H$_7$O), 55.7 (*C*H$_3$ of C$_7$H$_7$O).

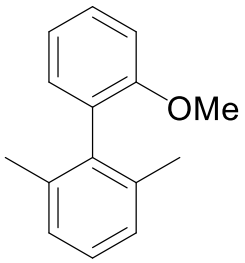
2-methoxy-1,1':4',1''-terphenyl (11), Entry 7, Table 1



(**11**)

A mixture of trans-[1-(*1S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)(*o*-OMeC$_6$H$_4$) (**3a$_2$**) (0.225 g, 0.294 mmol), [1,1'-biphenyl]-4-ylboronic acid (0.070 g, 0.353 mmol), and NaOH (0.059 g, 1.47 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as off white solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (98 : 2 *v/v*) to give the product **11** as a white solid (0.032 g, 42 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.67-7.63 (m, 6H, $C_{18}\underline{H}_{13}OCH_3$), 7.47 (t, 2H, $^3J_{HH}$ = 8 Hz, $C_{18}\underline{H}_{13}OCH_3$), 7.40-7.34 (m, 3H, $C_{18}\underline{H}_{13}OCH_3$), 7.07 (td, 1H, $^4J_{HH}$ = 1 Hz, $^3J_{HH}$ = 7 Hz, $C_{18}\underline{H}_{13}OCH_3$), 7.02 (d, 1H, $^3J_{HH}$ = 8 Hz, $C_{18}\underline{H}_{13}OCH_3$), 3.86 (s, 3H, $C_{18}H_{13}OC\underline{H}_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C): δ 156.7 ($\underline{C}_{18}H_{13}OCH_3$), 141.2 ($\underline{C}_{18}H_{13}OCH_3$), 139.9 ($\underline{C}_{18}H_{13}OCH_3$), 137.7 ($\underline{C}_{18}H_{13}OCH_3$), 131.0 ($\underline{C}_{18}H_{13}OCH_3$), 130.4 ($\underline{C}_{18}H_{13}OCH_3$), 130.1 ($\underline{C}_{18}H_{13}OCH_3$), 128.92 ($\underline{C}_{18}H_{13}OCH_3$), 128.88 ($\underline{C}_{18}H_{13}OCH_3$), 127.4 ($\underline{C}_{18}H_{13}OCH_3$), 127.3 ($\underline{C}_{18}H_{13}OCH_3$), 127.0 ($\underline{C}_{18}H_{13}OCH_3$), 121.1 ($\underline{C}_{18}H_{13}OCH_3$), 111.4 ($\underline{C}_{18}H_{13}OCH_3$), 55.8 ($C_{18}H_{13}O\underline{C}H_3$).

2'-methoxy-2,6-dimethyl-1,1'-biphenyl (12), Entry 8, Table 1

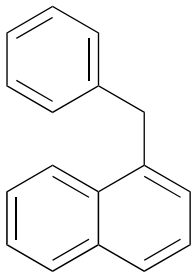


(**12**)

A mixture of trans-[1-(*1S*)-menthyl-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)(*o*-OMeC$_6$H$_4$) (**3a$_2$**) (0.180 g, 0.236 mmol), (2,6-dimethylphenyl)boronic acid (0.042 g, 0.283 mmol), and NaOH (0.047 g, 1.18 mmol) was refluxed in CH_3CN for 3 hours.

After which the reaction mixture was vacuum dried and finally purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (98 : 2 *v/v*) to give the product **12** as a colorless oil (0.004 g, 8 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.36-7.32 (m, 1H, $(CH_3)_2C_{12}\underline{H}_7OCH_3$), 7.18-7.15 (m, 1H, $(CH_3)_2C_{12}\underline{H}_7OCH_3$), 7.10 (d, 2H, $^{3}J_{HH}$ = 7 Hz, $(CH_3)_2C_{12}\underline{H}_7OCH_3$), 7.05-6.97 (m, 3H, $(CH_3)_2C_{12}\underline{H}_7OCH_3$), 3.73 (s, 3H, $(CH_3)_2C_{12}H_7OC\underline{H}_3$), 2.01 (s, 6H, $(C\underline{H}_3)_2C_{12}H_7OCH_3$).

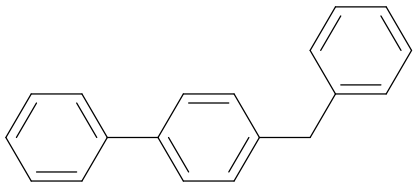
1-benzylnaphthalene (5), Entry 9, Table 1



(**5**)

A mixture of *trans*-[1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)($CH_2C_6H_5$) (**3b$_1$**) (0.241 g, 0.276 mmol), 1-naphthaleneboronic acid (0.057 g, 0.332 mmol), and NaOH (0.055 g, 1.38 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as brown solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with petroleum ether to give the product **5** as a white solid (0.004 g, 7 %).

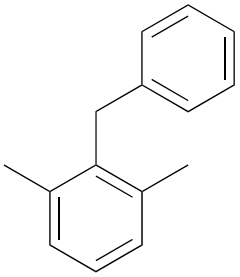
4-benzyl-1,1'-biphenyl (6), Entry 10, Table 1



(**6**)

A mixture of *trans*-[1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)($CH_2C_6H_5$) (**3b$_1$**) (0.325 g, 0.373 mmol), [1,1'-biphenyl]-4-ylboronic acid (0.089 g, 0.447 mmol), and NaOH (0.075 g, 1.86 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as brown solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with petroleum ether to give the product **6** as a white solid (0.029 g, 32 %).

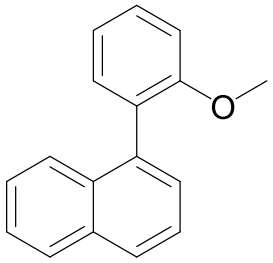
2-benzyl-1,3-dimethylbenzene (9), Entry 11, Table 1



(**9**)

A mixture of *trans*-[1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)($CH_2C_6H_5$) (**3b$_1$**) (0.230 g, 0.264 mmol), (2,6-dimethylphenyl)boronic acid (0.047 g, 0.316 mmol), and NaOH (0.053 g, 1.32 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as brown solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with petroleum ether to give the product **9** as a white solid (0.014 g, 27 %).

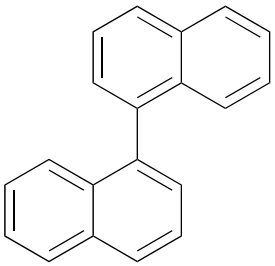
1-(2-methoxyphenyl)naphthalene (10), Entry 12, Table 1



(**10**)

A mixture of *trans*-[1-(1*S*)-menthyl-4-(benzyl)-1,2,4-triazol-5-ylidene]$_2$Pd(Br)(*o*-OMeC$_6$H$_4$) (**3b$_2$**) (0.115 g, 0.129 mmol), 1-naphthaleneboronic acid (0.027 g, 0.155 mmol), and NaOH (0.026 g, 0.647 mmol) was refluxed in CH_3CN for 3 hours. After which the mixture was vacuum dried to give the crude product as off white solid. The crude product was finally purified by column chromatography using silica gel as a stationary phase and eluting with a mixed medium of petroleum ether/EtOAc (98 : 2 *v/v*) to give the product **10** as a white solid (0.05 g, 17 %).

1,1'-binaphthalene (10a), Entry 12, Table 1



(**10a**)

The homo-coupled binaphthyl product (**10a**) was obtained from another fraction of the chromatographic separation procedure as a white solid in 52 % yield with respect to naphthyl boronic acid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.954 (d, 2H, $^3J_{HH}$ = 8 Hz,

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$C_{20}\underline{H}_{14}$), 7.947 (d, 2H $^{3}J_{HH}$ = 8 Hz, $C_{20}\underline{H}_{14}$), 7.595 (t, 2H, $^{3}J_{HH}$ = 8 Hz, $C_{20}\underline{H}_{14}$), 7.50-7.46 (m, 4H, $C_{20}\underline{H}_{14}$), 7.39 (d, 2H, $^{3}J_{HH}$ = 8 Hz, $C_{20}\underline{H}_{14}$), 7.30-7.27 (m, 2H, $C_{20}\underline{H}_{14}$).

Computational Methods

Density functional theory (DFT) calculations were performed on the **2**(**a**–**b**), **3**(**a**$_1$–**a**$_2$) and **3**(**b**$_1$–**b**$_2$) complexes with the GAUSSIAN 09[15] set of programs. In particular, various conformations of the **2**(**a**–**b**), **3**(**a**$_1$–**a**$_2$) and **3**(**b**$_1$–**b**$_2$) complexes namely, that of the *trans-anti*, *trans-syn* and *cis* structures, were computed by taking the X-ray coordinates of the respective structurally characterized complexes and subsequently applying suitable modifications to the structures. The transition state (TS) optimization method based on the Berny algorithm was used for transition state calculations. The Becke three-parameter exchange functional along with the Lee–Yang-Par correlational functions (B3LYP) were used in all of the computations.[16] The Pople split-valence double-zeta polarized basis set 6-31G* was used to describe carbon, hydrogen, oxygen, nitrogen and bromine atoms,[17] whereas the Stuttgart–Dresden effective core potential (ECP) along with valence basis sets (SDD) was used for the palladium.[18] Frequency calculations were performed for all of the optimized structures and the stationary points were characterized as minima while the transition states as maxima. Transition states were characterized by the observation of single imaginary frequency while the stationary points possessed only real frequency.

Acknowledgements

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Computer Center are gratefully acknowledged. AK, APP and MKG thank CSIR, New Delhi for research fellowship.

Supporting Information Available

The ^{1}H NMR, ^{13}C{^{1}H} NMR, IR, HRMS and the CHN data of the 1,2,4-triazolium bromide salts, **1**(**a**–**b**), and the palladium **2**(**a**–**b**), **3**(**a**$_1$–**a**$_2$) and **3**(**b**$_1$–**b**$_2$) complexes; X-ray metrical data comparison table; ORTEPs of **2**(**a**–**b**); CIF files giving X-ray crystallographic data; GCMS and HRMS chromatograms of the catalysis reaction; Density functional theory (DFT) geometry optimized *trans-anti*, *trans-syn* and *cis* structures of **2**(**a**–**b**), **3**(**a**$_1$–**a**$_2$) and **3**(**b**$_1$–**b**$_2$) complexes along with the B3LYP coordinates of the optimized *trans-anti*, *trans-syn* and *cis* geometries for **2**(**a**–**b**), **3**(**a**$_1$–**a**$_2$) and **3**(**b**$_1$–**b**$_2$) associated with this article can be found in the journal webpage. This material is available free of charge *via* the journal webpage.

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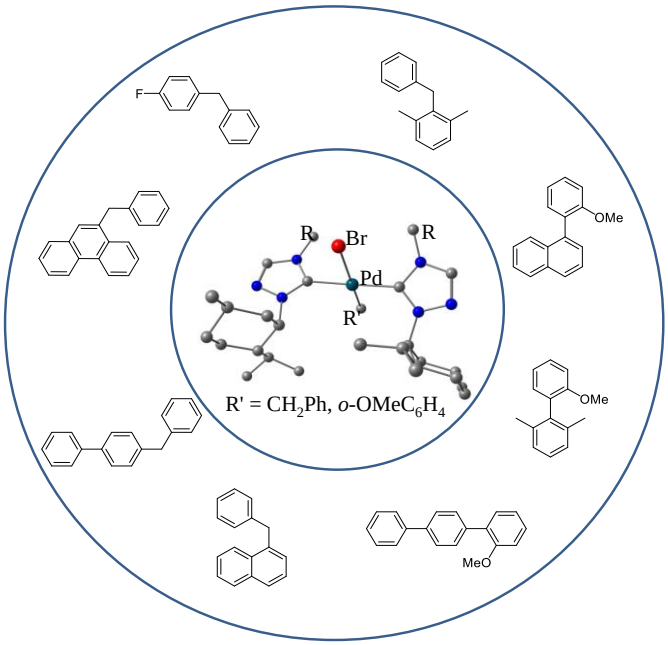
Graphics for Table of Contents

An Efficient Synthetic Approach to trans-(NHC)$_2$Pd(R)Br type Complexes and Their Implications in Suzuki-Miyaura Cross-Coupling Reaction

*Anuj Kumar, A. P. Prakasham, Manoj Kumar Gangwar, Pratap Vishnoi, Raymond J. Butcher, and Prasenjit Ghosh**



A convenient access leading to the isolation and structural characterization of the 1,2,4-triazole based mixed organo-halo *trans*-(NHC)$_2$Pd(R)Br (R = alkyl, aryl) type complexes was achieved along with their implication in the Suzuki-Miyaura cross-coupling reaction was demonstrated by the reactivity study with various aryl boronic acids.

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