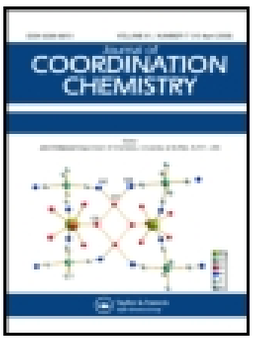

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Convenient and efficient Suzuki–Miyaura and Heck–Mizoroki cross–coupling reactions catalyzed by 1,3,4–trisubstituted–1,2,3–triazolium iodide and palladium salt systems

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ABSTRACT

A series of 1,3,4–trisubstituted–1,2,3–triazolium iodide salts (**4a–c**) were synthesized *via* a three–step reaction sequence. Corresponding anilines (**1a–c**) were converted to azides (**2a–c**) which were then treated with phenylacetylene with "Click" chemistry to access 1,4–disubstituted–1,2,3–triazoles (**3a–c**). Subsequent methylation of 1,4–disubstituted–1,2,3–triazoles (**3a–c**) yielded 1,3,4–trisubstituted–1,2,3–triazoliumiodide salts (**4a–c**) in appreciable yields. All the synthesized compounds were characterized by ^{1}H and ^{13}C NMR, ATR–IR spectroscopic techniques and elemental analyses. Additionally, the structure of 1–(4–chlorophenyl)–4–phenyl–1,2,3–triazole (**3b**) was confirmed by single crystal X–ray diffraction analysis. The catalytic activity of **4a–c** in a catalytic system consisting of 1,3,4–trisubstituted–1,2,3–triazoliumiodide salt/palladium(II) acetate/base were investigated towards Suzuki–Miyaura and Heck–Mizoroki cross–coupling reactions. The Suzuki–Miyaura cross–coupling reactions were carried out under mild reaction conditions with good to excellent yields, whereas Heck–Mizoroki cross–coupling reactions were performed at elevated temperature with moderate yields. Further, *in situ* method skips the synthetic procedure of preparing the palladium(II) complexes and hence is more economical and less tedious.

Keywords: 1,2,3–triazole; 1,2,3–triazolium iodide salt; palladium(II) acetate; crystal structure; Suzuki–Miyaura cross–coupling; Heck–Mizoroki cross–coupling

1. Introduction

Organometallic chemistry involving *N*–heterocyclic carbenes (NHCs) and their metal complexes have been dominated by imidazole and its derivatives including xanthines, oxazoles, thiazoles, 1,2,4–triazoles, pyrimidines and related saturated systems that have been employed in wide ranges of applications such as pharmaceutical, catalysis, luminescence, functional materials, etc.[1–4]. However, the mainstream NHC chemistry diverged towards an interesting contrast type, the abnormal NHCs that were first described by Crabtree *et al.* in 2001 and received enormous attention due to their stronger electron–donating abilities compared to normal NHCs, a result of decreased π–stabilizing and inductive effects due to lower number of adjacent heteroatoms that renders them a competitive class of ligands [5–8]. Although normal NHCs have been explored with various transition metal centres towards broad applications, the abnormal analogues are relatively unexplored. Nevertheless, since the introduction of "Click" chemistry involving CuAAC (Copper–Catalyzed Azide–Alkyne Cycloaddition) to access 1,4–disubstituted 1,2,3–triazoles by Sharpless *et al.* in 2001, the 1,3,4–trisubstituted–1,2,3–triazol–5–ylidene species have been extensively studied, instigated by Albrecht *et al.* in 2008, employing various substitutions which act as excellent ligand species and possess applications such as optics, redox sensing, biomedicine and catalysis upon complexation with a metal centre [9–13]. Further, a library of abnormal NHCs can be derived from imidazolium, thiazolium, oxazolium, pyrazolium, isothiazolium, pyridinium and quinolinium salts among others [14–16]. However, 1,3,4–trisubstituted–1,2,3–triazolium species are of interest owing to new synthetic and catalytic opportunities [17–24]. Among the transition metals for complexation with 1,3,4–trisubstituted–1,2,3–triazole based ligands, palladium(II) is the prime option owing to the success of palladium–based complexes as exceptional catalysts for a variety of reactions such as oxidation, substitution and cross–

coupling reactions [25]. Despite the palladium(II) centre being the active species participating in catalysis, the supporting ligand plays a pivotal role in the efficiency of the catalyst. Evolution of such supporting ligands from phosphine–based compounds that were expensive and air, temperature and moisture sensitive to NHC–based ligands that are relatively easier in storage and handling and also more versatile in substitutions with a possibility of electronic and steric property modifications has occurred [26, 27]. Additionally, the study conducted by Xu *et al.* in 2010 revealed that abnormal NHC–palladium(II) complexes performed better than normal NHC analogues in C–C cross–coupling reactions and another study conducted by Bertrand *et al.* on a free 1,2,3–triazol–5–ylidene established that the donor properties were superior to those of imidazol–2–ylidenes and 1,2,4–triazol–5–ylidenes and inferior to those of imidazol–4–ylidenes rendering abnormal NHCs the more sought after ligand species [28, 29].

Additionally, C–C bond forming reactions such as Suzuki–Miyaura cross coupling and Heck–Mizoroki cross coupling have importance due to employment of biaryls and functionalized olefins in pharmaceuticals, conducting polymers, molecular wires, liquid crystals and in supramolecular chemistry [30, 31]. Recent research involving 1,2,3–triazol–5–ylidene based palladium(II) complexes in Suzuki–Miyaura cross coupling and Heck–Mizoroki cross coupling reactions demonstrate potential and motivate further research to improve catalyst efficiency [32–36]. In this aspect, the present study investigates the base–palladium–abnormal NHC–catalyzed Suzuki–Miyaura and Heck–Mizoroki cross–coupling reactions under mild reaction conditions.

2. Experimental

2.1. *Materials and methods*

All experiments were conducted in normal laboratory conditions without precautionary measures to eliminate air and moisture. 4–Bromoaniline, 4–chloroaniline, 4–toluidine,

sodium azide, sodium nitrite, magnesium sulphate, phenylacetylene, bromotris(triphenylposphine) copper(I), methyl iodide, alkyl halides, phenyl boronic acid, styrene, potassium carbonate, sodium carbonate, cesium carbonate, potassium hydroxide, tripotassium phosphate, sodium tertiary butoxide, palladium(II) acetate, palladium(I) chloride bis–acetonitrile, hexane, toluene, methanol, ethanol and tetrahydrofuran were procured from commercial sources and used without purification or distillation. All reactions were carried out in oven dried glassware and heating was accomplished by a silicone oil bath. Progression of the reactions was monitored by thin–layer chromatography (TLC) performed on 0.25 mm Merck TLC silica gel plates, using UV light as a visualizing agent. Purification of reaction products was executed by column chromatography using silica gel 60 (230–400 mesh). The melting points were determined using a Stuart Scientific (UK) instrument. Further, volatile solvents were removed using a rotary evaporator attached to a dry diaphragm pump (10–15 mm Hg), followed by pumping to a constant weight with an oil pump (< 300 mTorr). ^{1}H NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer and are reported relative to DMSO–d_6 (δ2.50 ppm) or $CDCl_3$ (δ 7.27). Coupling constants *J* are reported in Hertz (Hz). Proton–decoupled ^{13}C NMR spectra were recorded at 100 MHz and reported relative to DMSO–d_6 (δ39.51 ppm) or $CDCl_3$ (δ 77.23 ppm). ATR–IR spectra were recorded on a Bruker ECO–ATR spectrophotometer from 600–4000 cm^{-1}. Elemental analyses were performed using a Perkin Elmer 2400 Series II CHN/S microanalyzer. The crystal data of **3b** were collected using an Agilent (formerly Oxford Diffraction) SuperNova A diffractometer that was fitted with an Atlas detector using monochromated Mo Kα radiation (0.71073 Å). A complete set of data was collected assuming the Friedel pairs were non–equivalent and an analytical absorption correction based on the shape of the crystal was performed [37]. The structure was solved by direct methods using SHELXS–2014 and refined by full–matrix least squares on F_2 for all data using SHELXL– 2014 [38]. Hydrogens

were added at calculated positions and were refined using a riding model. Anisotropic thermal displacement parameters were used for all non disordered non–hydrogen atoms. The crystallographic data has been deposited in the Cambridge Crystallographic Data Center; CCDC 1842020 contain the supplementary crystallographic data for **3b**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

2.2. *General synthetic route to 4–substituted phenylazides (2a–c)*

4–Substituted phenyl azides were synthesized following a reported procedure with minor modifications [39]. 4–Substituted aniline (15.0 mmol) was taken in water (25 mL) to which concentrated sulphuric acid (12.5 g) was added dropwise. The mixture was cooled in ice–cold water and a mixture of sodium nitrite (2.625g, 38 mmol) in water (16 mL) was added. Hexane (50 mL) was poured into the above mixture followed by a solution of sodium azide (2.3 g, 35 mmol) in minimum water. The mixture was allowed to stir in ice–cold condition for 3 h. The organic phase was then separated, dried over magnesium sulphate and filtered. The solvent was removed *in vacuo* to obtain pure **2a–c**.

2.2.1. *Synthesis of 4–bromophenylazide (2a)*

Compound **2a** was synthesized according to the general procedure using 4–bromoaniline (2.58 g, 15.0 mmol). Yield: 74%; Yellow liquid.

2.2.2. *Synthesis of 4–chlorophenylazide (2b)*

Compound **2b** was synthesized according to the general procedure using 4–chloroaniline (1.91 g, 15.0 mmol). Yield: 76%; Yellow liquid.

2.2.3. *Synthesis of 4–methylphenylazide (2c)*

Compound **2c** was synthesized according to the general procedure using 4–toluidine (1.60 g, 15.0 mmol). Yield: 69%; Yellow liquid.

2.3. *General synthetic route to access 1–(4–substitutedphenyl)–4–phenyl–1H–1,2,3–triazoles (3a–c)*

Compounds **3a–c** were synthesized following the reported procedure with slight modifications [40]. The previously synthesized 4–substituted phenylazides (**2a–c**) (1.0 mmol) were treated with phenylacetylene (0.12 g, 1.2 mmol) in the presence of bromotris(triphenylposphine)copper(I) catalyst (0.5 mol%) neat at room temperature for 1 h. The reaction mixture was then washed with hexane (3 x 10 mL) to obtain the corresponding 1–(4–substitutedphenyl)–4–phenyl–1*H*–1,2,3–triazoles **(3a–c)**.

2.3.1. *Synthesis of 1–(4–bromophenyl)–4–phenyl–1H–1,2,3–triazole (3a)*

Compound **3a** was synthesized following the general procedure using the previously synthesized compound **2a**. Yield: 81%; Off white solid; M. P.: 156–158 ˚C; ^{1}H NMR (δ ppm, DMSO–d_6, 400 MHz, ppm): 9.27 (s, 1H, C5), 7.91–7.89 (m, 4H, $CH_{Br–Phenyl}$), 7.82–7.80 (m, 2H, CH_{Phenyl}), 7.49–7.45 (m, 2H, CH_{Phenyl}), 7.38–7.34 (m, 1H, CH_{Phenyl}); ^{13}C NMR (δ ppm DMSO–d_6, 100 MHz, proton decoupled, ppm): 142.9 (C5), 136.2, 133.2, 130.5, 129.4, 128.7, 125.8, 122.3, 121.7, 120.1 (C_4 + $C_{Br–Phenyl}$ + C_{Phenyl}); ATR–IR (cm^{-1}): 3021.6 (w), 1610.5 (s), 1593.1 (m), 1228.7 (m), 1202.8 (m); Anal. Calc. for $C_{14}H_{10}N_3Br$: C, 56.02; H, 3.36; N, 14.00. Found: C, 55.99; H, 3.34; N, 14.11 %.

2.3.2. *Synthesis of 1–(4–chlorophenyl)–4–phenyl–1H–1,2,3–triazole (3b)*

Compound **3b** was synthesized following the general procedure using the previously synthesized **2b**. Yield: 79 %; Off white solid; M. P.: 157–159 ˚C; ^{1}H NMR (δ ppm, DMSO–d_6, 400 MHz, ppm): 9.48 (s, 1H, C5), 8.42–8.40 (m, 2H, $CH_{Cl–Phenyl}$), 8.23–8.21 (m, 2H, $CH_{Cl–Phenyl}$), 7.91–7.90 (m, 2H, CH_{Phenyl}), 7.47–7.43 (m, 2H, CH_{Phenyl}), 7.36–7.35 (m, 1H, CH_{Phenyl}); ^{13}C NMR (δ ppm DMSO–d_6, 100 MHz, proton decoupled, ppm): 142.7 (C5), 135.9, 133.4, 130.1, 129.5, 126.0, 125.9, 122.8, 120.9, 120.5 (C_4 + $C_{Cl–Phenyl}$ + C_{Phenyl}); ATR–

IR (cm^{-1}): 3011.1 (w), 1636.4 (s), 1573.9 (m), 1232.6 (m), 1212.6 (m); Anal. Calc. for $C_{14}H_{10}N_3Br$: C, 65.76; H, 3.94; N, 16.43. Found: C, 65.67; H, 3.78; N, 16.36 %.

2.3.3. ***Synthesis of 1–(4–tolyl)–4–phenyl–1H–1,2,3–triazole (3c)***

Compound **3c** was synthesized following the general procedure using the previously synthesized **2c**. Yield: 77%; Off white solid; M. P.: 162–163 ˚C; ^{1}H NMR (δ ppm, $CDCl_3$, 400 MHz, ppm): 8.19 (s, 1H, C5), 7.92–7.90 (m, 2H, CH_{Tolyl}), 7.66–7.64 (m, 2H, CH_{Tolyl}), 7.46–7.42 (m, 2H, CH_{Phenyl}), 7.37–7.24 (m, 3H, CH_{Phenyl}), 2.41 (s, 3H, CH_{3Tolyl}); ^{13}C NMR (δ ppm $CDCl_3$, 100 MHz, proton decoupled, ppm): 138.4 (C5), 136.2, 135.3, 134.8, 130.4, 128.8, 128.3, 126.9, 125.8, 120.4 (C_4 + C_{Tolyl}+ C_{Phenyl}), 21.06 (CH_{3Tolyl}); ATR–IR (cm^{-1}): 3032.1 (w), 1650.8 (s), 1542.7 (m), 1213.3 (m), 1201.4 (m); Anal. Calc. for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.52; H, 5.61; N, 17.83 %.

2.4. ***General synthetic route to access 1–(4–substitutedphenyl)–3–methyl–4–phenyl 1,2,3–triazolium iodide salts (4a–c)***

The previously synthesized 1–(4–substituted–phenyl)–4–phenyl–1,2,3–triazoles (**3a–c**) (1.0 mmol) were treated with excess methyl iodide (10.0 mmol) in acetonitrile at 60 ˚C for 48 h with vigorous stirring. The white precipitate obtained was filtered and washed with acetonitrile (3 x 10 mL) and dried under vacuum to obtain the corresponding 1–(4–substitutedphenyl)–3–methyl–4–phenyl–1,2,3–triazolium iodide salts (**4a–c**).

2.4.1. ***Synthesis of 1–(4–bromophenyl)–3–methyl–4–phenyl–1,2,3–triazolium iodide (4a)***

Compound **4a** was synthesized according to the general procedure. Yield: 62%; White solid; M. P.: 160–163 ˚C; ^{1}H NMR (δ ppm, DMSO–d_6, 400 MHz, ppm): 9.84 (s, 1H, C5), 8.10–7.90 (m, 4H, $CH_{Br–Phenyl}$), 7.83–7.81 (m, 2H, CH_{Phenyl}), 7.70–7.68 (m, 3H, CH_{Phenyl}), 4.40 (s, 3H, $CH_{3Methyl}$); ^{13}C NMR (δ ppm DMSO–d_6, 100 MHz, proton decoupled, ppm): 143.6 (C5), 134.4, 133.9, 132.2, 129.9, 129.8, 128.0, 125.5, 123.9, 122.8 (C_4 + $C_{Br–Phenyl}$ + C_{Phenyl}); ATR–

IR (cm^{-1}): 3019.7 (w), 2782.1 (s), 1687.6 (s), 1559.2 (m), 1221.3 (m), 1198.9 (m); Anal. Calc. for $C_{15}H_{13}N_3BrI$: C, 40.75; H, 2.96; N, 9.50. Found: C, 40.58; H, 2.78; N, 9.65 %.

2.4.2. ***Synthesis of 1–(4–chlorophenyl)–3–methyl–4–phenyl–1,2,3–triazolium iodide (4b)***

Compound **4b** was synthesized according to the general procedure. Yield: 56%; White solid; M. P.: 161–163 ˚C; ^{1}H NMR (δ ppm, DMSO–d_6, 400 MHz, ppm): 9.82 (s, 1H, C5), 8.09–7.88 (m, 4H, $CH_{Cl–Phenyl}$), 7.80–7.77 (m, 2H, CH_{Phenyl}), 7.70–7.64 (m, 3H, CH_{Phenyl}), 4.42 (s, 3H, $CH_{3Methyl}$); ^{13}C NMR (δ ppm DMSO–d_6, 100 MHz, proton decoupled, ppm): 142.9 (C5), 133.4, 132.7, 132.1, 129.8, 129.2, 128.5, 124.1, 123.1, 121.3 (C_4 + $C_{Cl–Phenyl}$ + C_{Phenyl}); ATR–IR (cm^{-1}): 3028.5 (w), 2793.2 (s), 1671.4 (s), 1562.8 (m), 1234.9 (m), 1211.7 (m). Anal. Calc. for $C_{15}H_{13}N_3ClI$: C, 45.31; H, 3.35; N, 10.57. Found: C, 45.42; H, 3.41; N, 10.71 %.

2.4.3. ***Synthesis of 1–(4–tolyl)–3–methyl–4–phenyl–1,2,3–triazolium iodide (4c)***

Compound **4c** was synthesized according to the general procedure. Yield: 59%; White solid; M. P.: 164–165 ˚C; ^{1}H NMR (δ ppm, $CDCl_3$, 400 MHz, ppm): 9.61 (s, 1H, C5), 8.00–7.98 (m, 2H, $CH_{Br–Phenyl}$), 7.93–7.91 (m, 2H, $CH_{Br–Phenyl}$), 7.47–7.44 (m, 3H, CH_{Phenyl}), 7.31–7.25 (m, 2H, CH_{Phenyl}), 4.39 (s, 3H, $CH_{3Methyl}$), 2.38 (s, 3H, CH_{Tolyl}); ^{13}C NMR (δ ppm $CDCl_3$, 100 MHz, proton decoupled, ppm): 143.9 (C5), 142.5, 132.3, 131.8, 130.7, 130.0, 129.5, 127.0, 121.6, 121.4 (C_4 + C_{Tolyl} + C_{Phenyl}), 40.02 (C_{Methyl}), 21.32 (C_{Tolyl}); ATR–IR (cm^{-1}): 3025.2 (w), 2803.7 (s), 1652.1 (s), 1596.8 (m), 1236.5 (m), 1207.2 (m); Anal. Calc. for $C_{16}H_{16}N_3I$: C, 50.94; H, 4.28; N, 11.14. Found: C, 50.88; H, 4.35; N, 11.07 %.

2.5. ***Application of in situ generated 1–(4–phenyl)–3–methyl–4–phenyl–1,2,3–triazole based palladium(II) complexes in C–C cross coupling reactions***

The synthesized 1–(4–phenyl)–3–methyl–4–phenyl–1,2,3–triazolium iodide salts were treated with a palladium(II) sources in the presence of a base to catalyze C–C cross–coupling reactions.

2.5.1. ***General procedure for Suzuki–Miyaura cross–coupling reactions***

The synthesized 1–(4–substitutedphenyl)–3–methyl–4–phenyl–1,2,3–triazolium iodide salts (**4a–c**) (1.0 mol %), palladium(II) acetate (0.5 equiv), aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol) and potassium carbonate (0.30 g, 2.2 mmol) were placed in a round bottomed flask. To the reaction mixture, toluene (5 mL) was added and stirred at room temperature for designated time. The progress of the reaction was monitored by TLC. After completion of the reaction, water (10 mL) and ethyl acetate (10 mL) were added. The product was extracted to the ethyl acetate layer using a separating funnel and dried over magnesium sulphate. It was then concentrated *in vacuo* and the product was purified by column chromatography using hexane and ethyl acetate as eluents to access the corresponding products. As all the Suzuki–Miyaura cross–coupling products are known molecules, they were confirmed by comparing the purity and *R*–factors on TLC with authentic samples previously published [41].

2.5.2 ***General procedure for Heck–Mizoroki cross–coupling reactions***

The synthesized 1–(4–substituted–phenyl)–3–methyl–4–phenyl–1,2,3–triazolium iodide salts (**4a–c**) (1.0 mol %), palladium(II) acetate (0.5 equivalent), aryl halide (1.0 mmol), styrene (1.2 mmol) and sodium carbonate (0.23 g, 2.2 mmol) were placed in a round bottomed flask. To the reaction mixture, toluene (5 mL) was added and stirred at 80 °C for designated time. The progress of the reaction was monitored by TLC. After completion of the reaction, water (10 mL) and ethyl acetate (10 mL) were added. The product was extracted to the ethyl acetate layer using a separating funnel and dried over magnesium sulphate. It was then concentrated *in vacuo* and the product was purified by column chromatography using hexane and ethyl acetate as eluents to access the corresponding products. The Heck–Mizoroki cross–coupled products were confirmed by ^{1}H NMR spectroscopy.

1. *(E)–1,2–diphenylethene* (Table 16, entries 1, 9 and 13): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.51–7.48 (m, 4H), 7.42–7.40 (m, 4H), 7.34–7.21 (m, 4H).

2. *(E)–1–methyl–4–styrylbenzene* (Table 16, entries 2 and 11): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.42–7.30 (m, 9H), 7.27–7.26 (m, 2H), 2.29 (s, 3H).

3. *(E)–1–methoxy–4–styrylbenzene* (Table 16, entries 3 and 12): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.55–7.53 (m, 5H), 6.88–6.66 (m, 6H), 3.76 (s, 3H).

4. *(E)–1–(4–styrylphenyl)ethanone* (Table 16, entries 4 and 15): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.42–7.40 (m, 4H), 7.34–7.31 (m, 5H), 7.27–7.26 (m, 2H), 2.56–2.55 (m, 3H).

5. *(E)–4–styrylbenzenamine* (Table 16, entries 5 and 14): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.42–7.40 (m, 3H), 7.34–7.31 (m, 3H), 7.27–7.22 (m, 5H), 5.26–5.23 (m, 2H).

6. *(E)–4–styrylphenol* (Table 16, entries 6 and 10): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.34–7.30 (m, 5H), 6.73–6.69 (m, 6H), 4.84 (s, 1H).

7. *(E)–1–(4–nitrostyryl)benzene* (Table 16, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.10–8.08 (m, 5H), 7.69–7.67 (m, 6H).

8. *(E)–1–tert–butyl–4–styrylbenzene* (Table 16, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.43–7.41 (m, 5H), 7.35–7.25 (m, 6H), 1.31 (s, 9H).

3. Results and discussion

3.1. *Chemistry*

1,3,4–Trisubstituted–1,2,3–triazole based palladium(II) complexes have attracted attention owing to their superior catalytic potential in a vast array of coupling reactions. In the present report, a set of three 1,3,4–trisubstituted–1,2,3–triazolium iodide salts **(4a–c)** are presented. The 1,3,4–trisubstituted–1,2,3–triazolium iodide salts **(4a–c)** were synthesized in good yields with excellent purity in a three step reaction sequence from economically available starting materials. They were nonhygroscopic and can be stored at room temperature.

3.2. *Synthesis*

The reported 1,4–disubstituted–1,2,3–triazoles (**3a–c**) were synthesized according to the reported protocol with minor modifications [31, 32]. Corresponding anilines (**1a–c**) were

treated with sodium azide and sodium nitrite in the presence of concentrated sulphuric acid in ice–cold conditions to access the corresponding azides (**2a–c**) in pure form in yields ranging from 69 to 76%. Compounds **2a–c** were then treated with phenyl acetylene and bromotris(triphenylphosphine)copper(I) catalyst in neat reaction condition at room temperature to access pure 1,4–disubstituted–1,2,3–triazoles (**3a–c**) in yields ranging from 77 to 81%. The 1,4–disubstituted–1,2,3–triazoles (**3a–c**) were converted to the 1,3,4–trisubstituted–1,2,3–triazolium iodide salts (**4a–c**) with 56–62% yields by treating them with excess methyl iodide in acetonitrile at 60 ^{0}C for 48 h (Scheme 1).

3.3. *Spectroscopic characterization*

The 1,4–disubstituted–1,2,3–triazoles (**3a–c**) were characterized by ^{1}H, ^{13}C NMR, ATR–IR spectroscopic techniques and elemental analysis. In the ^{1}H NMR spectra of **3a–c**, a distinct peak was observed between δ = 9.48 and 8.19 ppm corresponding to the carbene carbon. Peaks corresponding to the protons of the 4–substituted–phenyl ring appeared at δ = 8.42–7.64 ppm, followed by the protons of 1–substituted–phenyl ring which appeared at δ = 7.91–7.24. Further, the ^{13}C NMR spectra of **3a–c** revealed a distinct peak at δ = 142.9–138.4 ppm attributed to carbene carbon. The remaining carbons were at δ = 136.2–120.1 ppm. Formation of the compounds was confirmed by ATR–IR where the peaks corresponding to C–H, C=C and C–N bonds were seen at 3032–3011, 1650–1610 and 1232–1201 cm^{-1} respectively. Finally, the purities of **3a–c** were confirmed by elemental analysis.

1,3,4–Trisubstituted–1,2,3–triazoliumioidide salts (**4a–c**) were also characterized by ^{1}H and ^{13}C NMR and ATR–IR spectroscopic techniques and elemental analysis. In ^{1}H NMR spectra of **4a–c**, the peak attributed to carbene carbon was slightly deshielded as compared to the corresponding 1,4–disubstituted–1,2,3–triazoles (**3a–c**) and observed between δ = 9.84–9.61 ppm. The peaks corresponding to protons of the 4–substituted–phenyl ring appeared slightly

deshielded at δ = 8.10–7.90 ppm, while those of 1–substituted–phenyl ring appeared at δ = 7.83–7.47 ppm. The methyl protons appeared at δ = 4.42–4.39 ppm. The ^{13}C NMR spectra of **4a–c** revealed carbene carbon peaks at δ = 143.9–142.9 ppm. Similar to 1,4–disubstituted–1,2,3–triazoles (**3a–c**), the remaining carbons were observed at δ = 142.5–121.3 ppm. However, C_{methyl} peaks for **4a** and **4b** were masked by DMSO peaks but were observed at δ = 40.02 ppm for **4c**. Also, the formation of the compounds was confirmed by ATR–IR where the peaks corresponding to C–H, C=C and C–N bonds were seen at 3028–3019, 1687–1652and 1236–1198 cm^{-1}, respectively. Finally, the purities of **4a–c** were confirmed by elemental analyses.

3.4. *Single crystal X–ray diffraction analysis*

Single crystals suitable for X–ray diffraction analysis of 1–(4–chlorophenyl)–4–phenyl–1,2,3–triazole (**3b**) were grown by slow evaporation of saturated DMSO solution at room temperature. The crystal data and structure refinement details are given in Table 1. The molecular structure of **3b** is shown in Figure 1 and pertinent bond distances and angles are tabulated in Table 2. Compound **3b** crystallized in the triclinic space group *P–1* with two motifs in a unit cell. The asymmetric unit consists of one unit of (**3b**) and does not possess any lattice water molecules or organic solvent molecules. The internal ring angle of the 1,2,3–triazole core at C5 carbon center N(1)–C(7)–C(8) is $104.71(11)^0$ and the bond angles and distances are in agreement with those reported [30]. The molecules follow a linear arrangement where the intermolecular hydrogen bonds between H(7)–N(3), H(7)–N(2), H(2)–N(2) and Cl(1)–H(13) with distances 2.624 Å, 2.722 Å, 2.748 Å and 2.850 Å, respectively, frame a sheet like appearance (Figure 2).

3.5. *Catalytic activity*

3.5.1. *Suzuki–Miyaura cross–coupling reaction*

The Suzuki–Miyaura cross–coupling is one of the most versatile and utilized reactions for formation of carbon–carbon bonds, especially for the development of biaryl and heterobiaryl derivatives [32]. In the present work, the catalytic potentials of **4a–c** were assessed for Suzuki–Miyaura cross–coupling reactions. The Suzuki–Miyaura cross–coupling between bromobenzene and phenylboronic acid was chosen as the model reaction (Scheme 2). The reaction conditions were optimized by varying different parameters such as solvent, base, temperature, time, palladium(II) source and catalyst load (Tables 3–8) using **4a–c.** Reactions in toluene with potassium carbonate at room temperature for 1 h using 1 mol% of **4b** and 0.5 equivalent palladium(II) acetate as catalyst resulted in good to excellent yields.

The catalytic activity of **4b** was investigated in conjugation with palladium(II) acetate for Suzuki–Miyaura cross–coupling under the optimized reaction conditions between various aryl halides and phenylboronic acid (Table 9). Interestingly, the electron–donating or electron–withdrawing groups of the aryl halides studied did not affect the efficiency of the catalyst. However, significant changes in activity were observed when steric bulk of the aryl halides was considered. Additionally, aryl iodides proved to be the best as compared with aryl bromides and aryl chlorides due to the respective bond strengths. Blank experiments were conducted in the absence of palladium(II) acetate which resulted in trace yields. Selectivity of the catalytic system was examined by carrying out the reactions in the absence of aryl halides that yielded trace amounts of homo–coupled biaryl compounds exhibiting high selectivity.

Suzuki–Miyaura cross–coupling is the palladium–catalyzed cross–coupling between organoboronic acid and an organo–halide first reported by A. Suzuki *et al.* in 1979. The first

step is the oxidative addition of palladium(0) to the organo–halide followed by reaction with base to give an intermediate. Meanwhile, the boronic acid is converted to a boronate complex upon action by the base. The intermediate species previously formed undergoes transmetalation with the boronate complex to form an organo–palladium species. The desired cross–coupled product is obtained by reductive elimination and the original palladium catalyst is retained and the catalytic cycle is completed.

3.5.2. *Heck–Mizoroki cross–coupling reaction*

Encouraged by appreciable catalytic potential of the catalytic system toward Suzuki–Miyaura cross–coupling reactions, Heck–Mizoroki cross–coupling reactions were also assessed (Scheme 3). The reaction conditions were optimized by varying parameters such as solvent, base, temperature, time, palladium(II) source and catalyst load (Tables 10–15). It was observed that reactions in toluene with sodium carbonate for 5 h using 1 mol% of **4b** and 0.5 equivalent palladium(II) acetate as catalyst at 80 ^{0}C resulted in good yields.

The catalytic potential of **4b** was studied in conjunction with palladium(II) acetate for Heck–Mizoroki cross–coupling reactions under the optimized reaction conditions between various aryl halides and styrene (Table 16). Similar to Suzuki–Heck coupling, the electron–donating or electron–withdrawing groups of the aryl halides studied did not affect the efficiency of the catalyst and activity varied marginally when steric bulk of the aryl halides was considered. Again, aryl iodides performed better than aryl bromides and chlorides. Blank experiments conducted in the absence of palladium(II) acetate resulted in trace yields and that without aryl halides yielded trace amounts of homo–coupled biaryl compounds. Hence, the selected catalytic system possessed appreciable catalytic potential toward Heck–Mizoroki cross–coupling reactions with desirable selectivity.

Heck–Mizoroki cross–coupling reaction is the palladium–catalyzed cross coupling between an alkene and an organo–halide, first reported by T. Mizoroki *et al.* in 1971. The first step is the oxidative addition of palladium(0) to the organo–halide. Upon insertion of the alkene, palladium(II) forms a π complex. A β–hydride elimination follows to yield the desired cross–coupled product and the reductive elimination step retains the original palladium catalyst and the catalytic cycle is completed.

3.5.3. Comparison of catalytic activity

To understand the activity of 1,3,4–trisubstituted–1,2,3–triazoliumioidide salt (**4b**) with palladium(II) acetate, the yields obtained were compared with the yields reported for the Suzuki–Miyaura [42-46] and Heck–Mizoroki [42, 44, 47-50] cross–coupling reactions with similar kind of catalysts and the results were comparable. Some of the key benefits of **4b** with palladium(II) acetate are: (i) economical, (ii) good yields and (iii) fewer synthetic steps. Additionally, **4b** can be prepared using inexpensive chemicals under aerobic conditions, and does not require a sophisticated setup.

4. Conclusion

We report a series of 1,3,4–trisubstituted–1,2,3–triazoliumiodide salts (**4a–c**) that were characterized by ^{1}H and ^{13}C NMR, ATR–IR and elemental analysis. **4a–c** were evaluated for catalytic potential for Suzuki–Miyaura and Heck–Mizoroki cross–coupling reactions by *in situ* generation of the corresponding palladium(II) complexes. **4b** was chosen as the best candidate for both reactions after a thorough screening for optimized reaction conditions. The catalytic system yielded excellent results for Suzuki–Miyaura cross–coupling reactions, whereas those for Heck–Mizoroki cross–coupling reactions were moderate. However, the *in situ* palladium(II) complex generation route omits an additional synthesis of the palladium(II) complexes while still demonstrating satisfactory results. Additionally, the 1,3,4–trisubstituted–1,2,3–triazolium iodide salts (**4a–c**) can be stored for future use which makes the process more economical.

Supporting information

Additional Supporting Information may be found online in the supporting information tab for this article.

Acknowledgement

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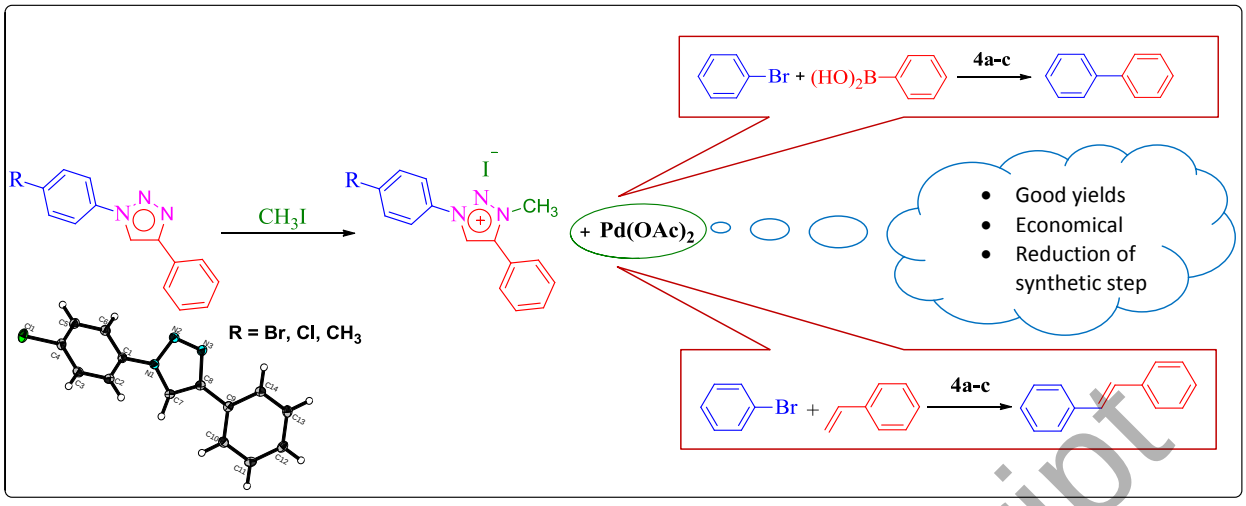
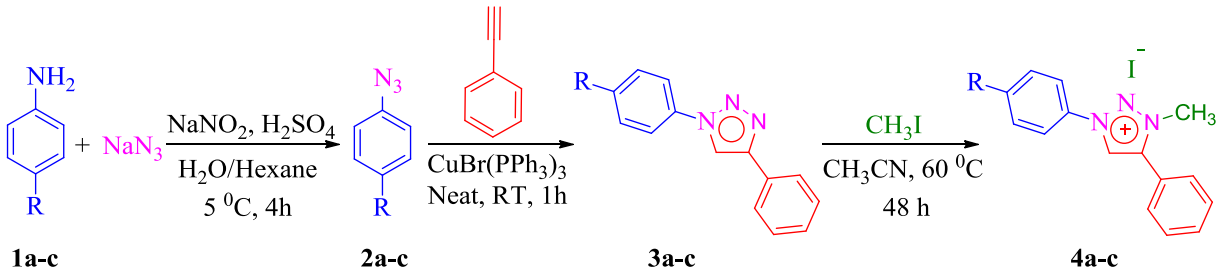
Graphical abstract





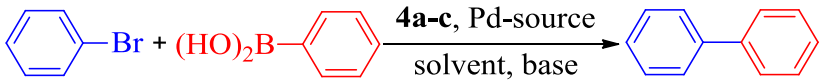
1a-c **2a-c** **3a-c** **4a-c**

1a, 2a, 3a, 4a = R= Br

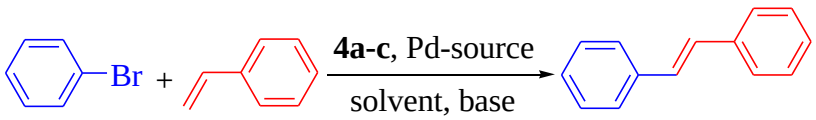
1b, 2b, 3b, 4b = R= Cl

1c, 2c, 3c, 4c = R= CH_3

Scheme 1. The synthesis of 1,3,4–trisubstituted–1,2,3–triazolium iodide salts (**4a–c**).



Scheme 2. General reaction scheme for Suzuki–Miyaura cross–coupling reaction.



Scheme 3. General reaction scheme for Heck–Mizoroki cross–coupling reactions.

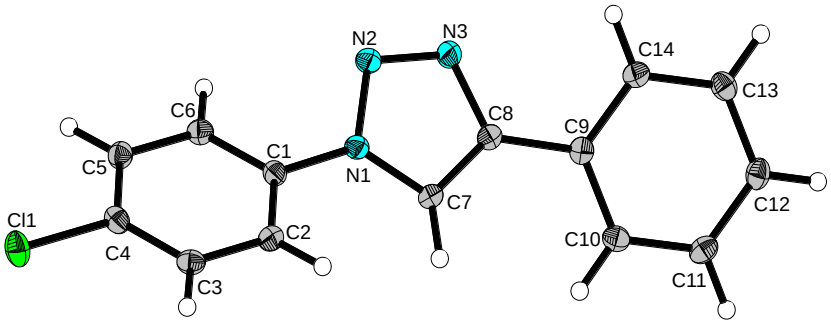


Figure 1. Molecular structure of **3b**. Thermal ellipsoids are drawn at the 50% level.

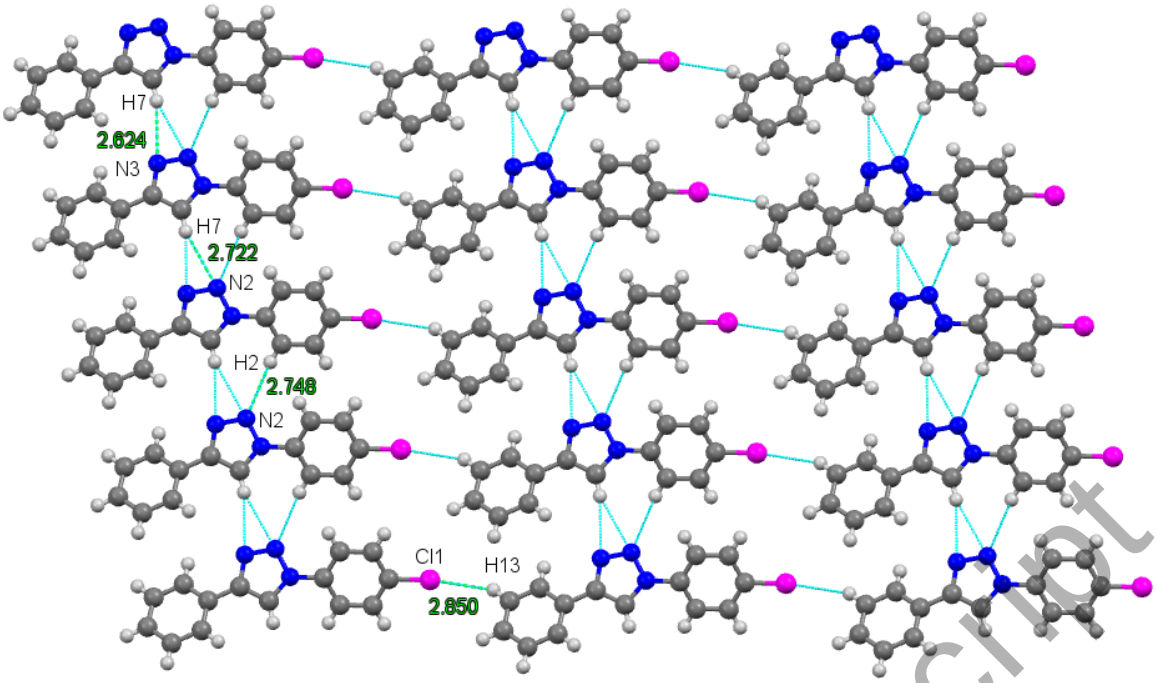


Figure 2. Molecular interactions of **3b**.

Table 1. Crystallographic data and the structure refinement details of **3b**.

Identification code	**3b**
Empirical formula	C_{14} H_{10} N_3 Cl
Formula weight	255.70
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	*P*–1 (#2)
Unit cell dimensions	a = 5.65213(8) Å α = 102.268(2)°.
	b = 7.2020(1) Å β = 98.486(1)°.
	c = 14.5498(2) Å γ = 90.119(1)°.
Volume	572.070(15) $Å^3$
Z	2
Density (calculated)	1.484 Mg/m^3
Absorption coefficient	2.805 mm^{-1}
F(000)	264
Crystal size	0.135 x 0.112 x 0.030 mm^3
Theta range for data collection	6.293 to 76.939°.
Index ranges	–7<=*h*<=7, –9<=*k*<=9, –18<=*l*<=18
Reflections collected	22625
Independent reflections	2393 [R(int) = 0.0329]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	0.923 and 0.745
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	2393 / 0 / 164
Goodness–of–fit on F^2	1.048
Final R indices [I>2sigma(I)]	R_1 = 0.0291, wR_2 = 0.0697
R indices (all data)	R_1 = 0.0327, wR_2 = 0.0720
Extinction coefficient	0.0025(4)
Largest diff. peak and hole	0.276 and –0.278 e.$Å^{-3}$

Table 2. Pertinent bond distances and angles of **3b**.

Bond distance (Å)	**Bond angle (°)**

C(1)–N(1)	1.4279(16)	C(7)–N(1)–N(2)	110.82(10)
N(1)–C(7)	1.3534(17)	C(7)–N(1)–C(1)	129.44(11)
N(1)–N(2)	1.3550(15)	N(2)–N(1)–C(1)	119.70(10)
N(2)–N(3)	1.3119(16)	N(3)–N(2)–N(1)	107.25(10)
N(3)–C(8)	1.3718(17)	N(2)–N(3)–C(8)	109.02(11)
C(7)–C(8)	1.3753(18)	N(1)–C(7)–C(8)	104.71(11)
C(8)–C(9)	1.4683(18)	N(3)–C(8)–C(7)	108.20(11)
C(4)–Cl(1)	1.7402(13)	N(3)–C(8)–C(9)	121.68(12)

Table 3. Optimization of solvent for Suzuki–Miyaura cross–coupling reactions[a].

Entry	Salt	Solvent	Yield (%)[b]
1	4a	THF	76
2	**4a**	**Toluene**	**88**
3	4a	Ethanol	78
4	4a	Ethanol–Methanol	85
5	4a	Ethanol–Water	80
6	4b	THF	70
7	**4b**	**Toluene**	**90**
8	4b	Ethanol	74
9	4b	Ethanol–Methanol	76
10	4b	Ethanol–Water	77
11	4c	THF	73
12	**4c**	**Toluene**	**89**
13	4c	Ethanol	77
14	4c	Ethanol–Methanol	81
15	4c	Ethanol–Water	74

[a]Reaction conditions: Bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium iodide (1.0 mol%), $Pd(OAc)_2$ (0.5 mol%), 50 ^{0}C, solvent (5 mL), 2 h in air. [b]Isolated yield after separation by column chromatography; average of two runs.

Table 4. Optimization of base for Suzuki–Miyaura cross–coupling reactions[a].

Entry	Salt	Base	Yield (%)[b]
1	**4a**	**K_2CO_3**	**90**
2	4a	Cs_2CO_3	84
3	4a	K_3PO_4	83
4	4a	KOH	trace
5	4a	NaO^tBu	trace
6	**4b**	**K_2CO_3**	**90**
7	4b	Cs_2CO_3	79
8	4b	K_3PO_4	84
9	4b	KOH	trace
10	4b	NaO^tBu	trace
11	**4c**	**K_2CO_3**	**89**
12	4c	Cs_2CO_3	77
13	4c	K_3PO_4	88
14	4c	KOH	trace
15	4c	NaO^tBu	trace

[a]Reaction conditions: Bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), base (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium iodide (1.0 mol%), $Pd(OAc)_2$ (0.5 mol%), 50 ^{0}C, toluene (5 mL), 2 h in air. [b]Isolated yield after separation by column chromatography; average of two runs.

Table 5. Optimization of temperature for Suzuki– Miyaura cross–coupling reactions[a].

Entry	Salt	Temperature (^{0}C)	Yield (%)[b]
1	**4a**	**RT**	**90**
2	4a	40	91
3	4a	50	89
4	4a	60	85
5	4a	70	89
6	**4b**	**RT**	**90**
7	4b	40	82
8	4b	50	89
9	4b	60	81
10	4b	70	80
11	**4c**	**RT**	**89**
12	4c	40	89
13	4c	50	87
14	4c	60	77
15	4c	70	78

[a]Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium iodide (1.0 mol%), $Pd(OAc)_2$ (0.5 mol%), toluene (5 mL), 2 h in air. [b]Isolated yield after separation by column chromatography; average of two runs.

Table 6. Optimization of time for Suzuki–Miyaura cross–coupling reactions[a].

Entry	Salt	Time (min)	Yield (%)[b]
1	4a	10	46
2	4a	20	65
3	4a	40	73
4	4a	60	85
5	**4a**	**90**	**90**
6	4a	120	90
7	4b	10	29
8	4b	20	43
9	4b	40	62
10	**4b**	**60**	**88**
11	4b	90	89
12	4b	120	91
13	4c	10	33
14	4c	20	52
15	4c	40	71
16	4c	60	81
17	**4c**	**90**	**88**
18	4c	120	83

[a]Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium ioidide (1.0 mol%), $Pd(OAc)_2$ (0.5 mol%), room temperature, toluene (5 mL) in air. [b]Isolated yield after separation by column chromatography; average of two runs.

Table 7. Optimization of palladium(II) source for Suzuki–Miyaura–cross–coupling reactions[a].

Entry	Salt	Pd(II) source	Yield (%)[b]
1	**4a**	**$Pd(OAc)_2$**	**90**
2	4a	$PdCl_2(CH_3CN)_2$	76
3	**4b**	**$Pd(OAc)_2$**	**88**
4	4b	$PdCl_2(CH_3CN)_2$	65
5	**4c**	**$Pd(OAc)_2$**	**87**
6	4c	$PdCl_2(CH_3CN)_2$	79

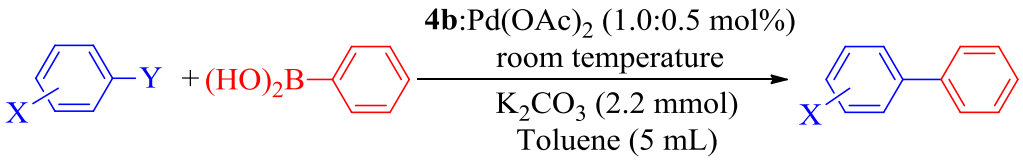
[a]Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium ioidide (1.0 mol%), Pd(II) source (0.5 mol%), room temperature, toluene (5 mL), 1.5 h in air. [b]Isolated yield after separation by column chromatography; average of two runs.

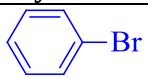
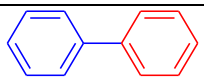
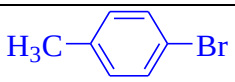
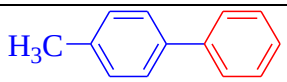
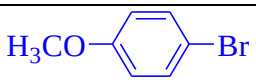
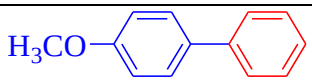
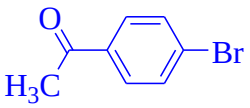
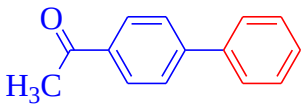
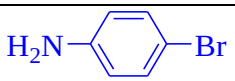
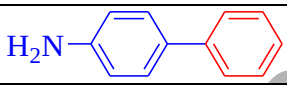
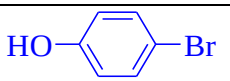
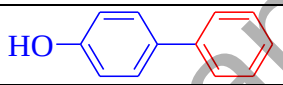
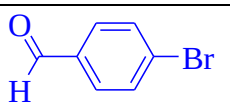
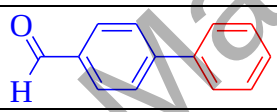
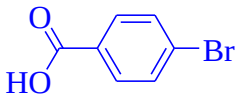
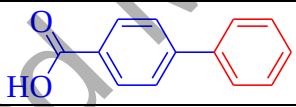
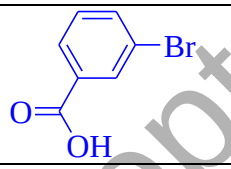
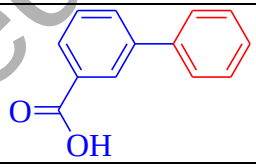
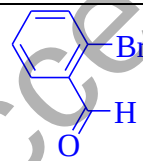
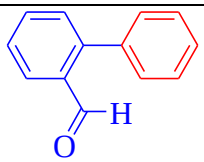
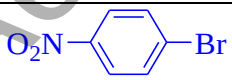
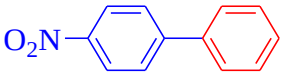
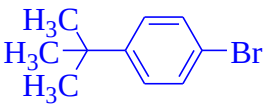
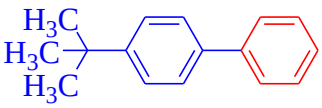
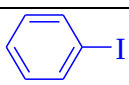
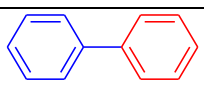
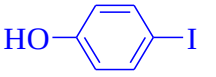
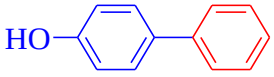
Table 8. Optimization of 1,3,4–trisubstituted–1,2,3–triazolium ioidide salt:palladium(II) acetate load for Suzuki–Miyaura cross–coupling reactions[a].

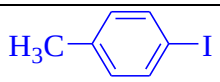
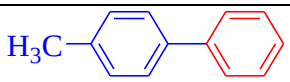
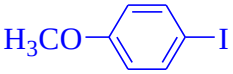
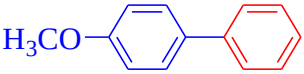
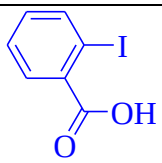
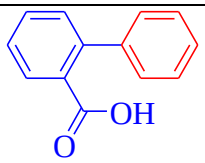
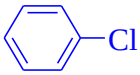
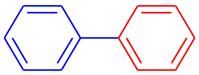
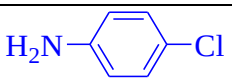
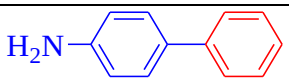
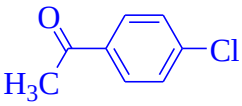
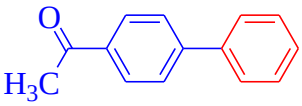
Entry	Salt	1,3,4–trisubstituted–1,2,3–triazolium ioidide salt:$Pd(OAc)_2$ ratio	Yield (%)[b]
1	4a	1.0 : 0.25	39
2	**4a**	**1.0 : 0.5**	**88**
3	4a	1.0 : 1.0	79
4	4b	1.0 : 0.25	41
5	**4b**	**1.0 : 0.5**	**89**
6	4b	1.0 : 1.0	82
7	4c	1.0 : 0.25	56
8	**4c**	**1.0 : 0.5**	**87**
9	4c	1.0 : 1.0	80

[a]Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), base (2.2 mmol), room temperature, toluene (5 mL), 1.5 h in air. [b]Isolated yield after separation by column chromatography; average of two runs.

Table 9. Suzuki–Miyaura cross–coupling reactions of different aryl halides with phenylboronic acid using the 1–(4–chlorophenyl)–3–methyl–4–phenyl–1,2,3–triazolium iodide (**4b**)[a].



Entry	Aryl halide	Product	Time (h)	Yield (%)[b]
1			1.0	88
2			0.5	83
3			2.0	71
4			1.0	79
5			1.5	72
6			1.0	81
7			1.5	Trace
8			1.5	73
9			1.5	62
10			3.0	Trace
11			1.0	81
12			2.0	71
13			0.5	87
14			1.0	84

15			0.5	88
16			1.0	77
17			1.0	60
18			1.5	63
19			2.0	51
20			2.0	67

[a]Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol). [b]Isolated yield after separation by column chromatography; average of two runs.

Table 10. Optimization of solvent for Heck–Mizoroki cross–coupling reactions[a].

Entry	Salt	Solvent	Yield (%)[b]
1	4a	THF	55
2	**4a**	**Toluene**	**57**
3	4a	Ethanol	56
4	4a	Ethanol–Methanol	51
5	4a	Ethanol–Water	45
6	4b	THF	49
7	**4b**	**Toluene**	**59**
8	4b	Ethanol	56
9	4b	Ethanol–Methanol	48
10	4b	Ethanol–Water	50
11	4c	THF	50
12	**4c**	**Toluene**	**51**
13	4c	Ethanol	49
14	4c	Ethanol–Methanol	41
15	4c	Ethanol–Water	44

[a]Reaction conditions: bromobenzene (1.0 mmol), styrene (1.2 mmol), Na_2CO_3 (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium ioidide (1.0 mol%), $Pd(OAc)_2$ (0.5 mol%), 60 ^{0}C, solvent (5 mL), 4 h in air. [b]Isolated yield after separation by column chromatography; average of two runs.

Table 11. Optimization of base for Heck–Mizoroki cross–coupling reactions[a].

Entry	Salt	Base	Yield (%)[b]
1	4a	K_2CO_3	58
2	**4a**	**Na_2CO_3**	**63**
3	4a	Cs_2CO_3	60
4	4a	K_3PO_4	47
5	4a	KOH	trace
6	4b	K_2CO_3	60
7	**4b**	**Na_2CO_3**	**64**
8	4b	Cs_2CO_3	58
9	4b	K_3PO_4	41
10	4b	KOH	trace
11	4c	K_2CO_3	49
12	4c	Na_2CO_3	51
13	**4c**	**Cs_2CO_3**	**56**
14	4c	K_3PO_4	53
15	4c	KOH	trace

[a]Reaction conditions: bromobenzene (1.0 mmol), styrene (1.2 mmol), base (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium ioidide (1.0 mol%), $Pd(OAc)_2$ (0.5 mol%), 60 ^{0}C, toluene (5 mL), 4 h in air. [b]Isolated yield after separation by column chromatography; average of two runs.

Table 12. Optimization of temperature for Heck–Mizoroki cross–coupling reactions[a].

Entry	Salt	Temperature (^{0}C)	Yield[b]
1	4a	RT	trace
2	4a	50	47
3	4a	70	67
4	**4a**	**80**	**69**
5	4a	90	68
6	4b	RT	trace
7	4b	50	51
8	4b	70	65
9	**4b**	**80**	**71**
10	4b	90	72
11	4c*	RT	trace
12	4c*	50	51
13	**4c***	**70**	**59**
14	4c*	80	60
15	4c*	90	59

[a]Reaction conditions: bromobenzene (1.0 mmol), styrene (1.2 mmol), Na_2CO_3 (2.2 mmol), *Cs_2CO_3 (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium ioidide (1.0 mol%), $Pd(OAc)_2$ (0.5 mol%), toluene (5 mL), 4 h in air. [b]Isolated yield after separation by column chromatography; average of two runs.

Table 13. Optimization of time for Heck–Mizoroki cross–coupling reactions[a].

Entry	Salt	Time (h)	Yield (%)[b]
1	4a	1	trace
2	4a	2	47
3	4a	4	59
4	4a	4	64
5	**4a**	**5**	**70**
6	4a	6	71
7	4b	1	trace
8	4b	2	51
9	4b	3	65
10	**4b**	**4**	**71**
11	4b	5	71
12	4b	6	73
13	4c*	1	trace
14	4c*	2	trace
15	4c*	3	38
16	4c*	4	46
17	**4c***	**5**	**59**
18	4c*	6	60

[a]Reaction conditions: bromobenzene (1.0 mmol), styrene (1.2 mmol), Na_2CO_3 (2.2 mmol), *Cs_2CO_3 (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium ioidide (1 mol%), $Pd(OAc)_2$ (0.5 mol%), 80 ^{0}C, toluene (5 mL), in air. [b]Isolated yield after separation by column chromatography; average of two runs.

Table 14. Optimization of palladium(II) source for Heck–Mizoroki cross–coupling reactions[a].

Entry	Salt	Pd(II) source	Yield (%)[b]
1	**4a**	**$Pd(OAc)_2$**	**69**
2	4a	$PdCl_2(CH_3CN)_2$	52
3	**4b**	**$Pd(OAc)_2$**	**72**
4	4b	$PdCl_2(CH_3CN)_2$	66
5	**4c***	**$Pd(OAc)_2$**	**58**
6	4c*	$PdCl_2(CH_3CN)_2$	45

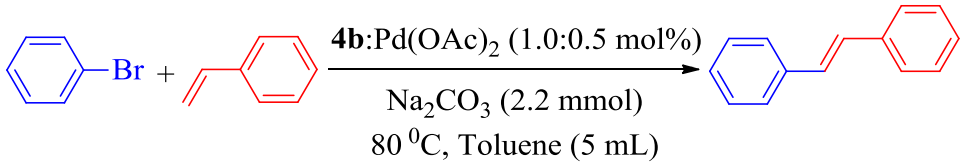
[a]Reaction conditions: bromobenzene (1.0 mmol), styrene (1.2 mmol), Na_2CO_3 (2.2 mmol), *Cs_2CO_3 (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium ioidide (1.0 mol%), $Pd(OAc)_2$ (0.5 mol%), 80 ^{0}C, toluene (5 mL), 5 h in air. [b]Isolated yield after separation by column chromatography; average of two runs.

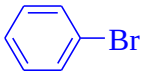
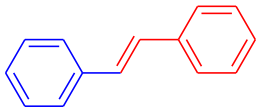
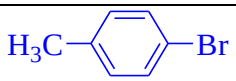
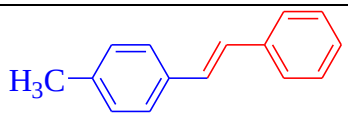
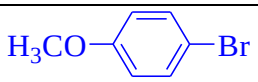
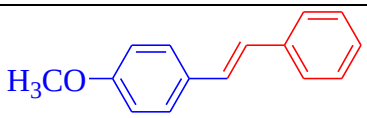
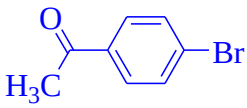
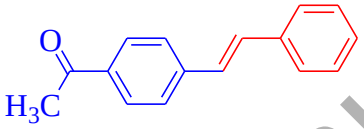
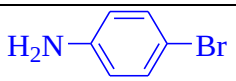
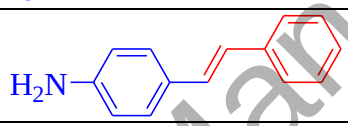
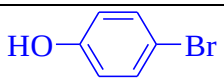
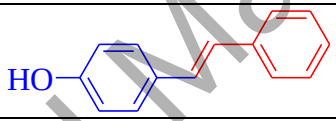
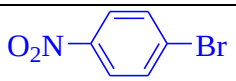
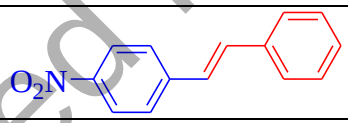
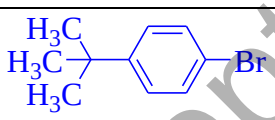
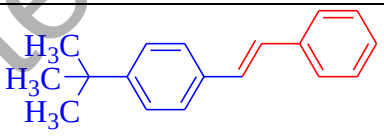
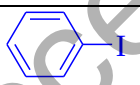
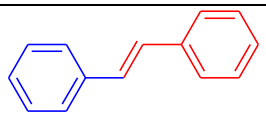
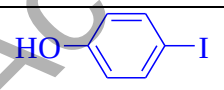
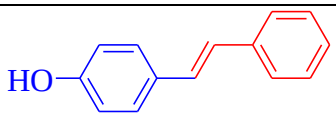
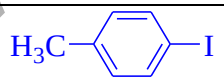
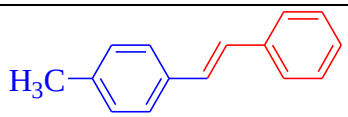
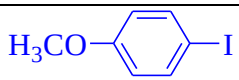
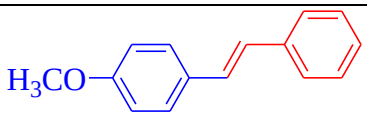
Table 15. Optimization of catalyst load for Heck–Mizoroki cross–coupling reactions[a].

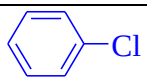
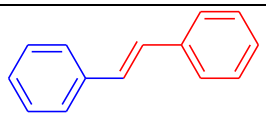
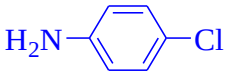
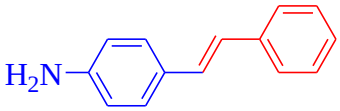
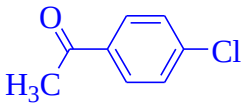
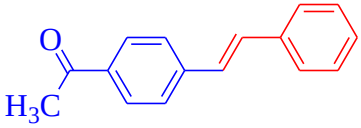
Entry	Salt	Salt : $Pd(OAc)_2$ ratio	Yield (%)[b]
1	4a	1.0 : 0.25	33
2	**4a**	**1.0 : 0.5**	**68**
3	4a	1.0 : 1.0	67
4	4b	1.0 : 0.25	37
5	**4b**	**1.0 : 0.5**	**70**
6	4b	1.0 : 1.0	67
7	4c	1.0 : 0.25	Trace
8	**4c**	**1.0 : 0.5**	**59**
9	4c	1.0 : 1.0	58

Reaction conditions: bromobenzene (1.0 mmol), styrene (1.2 mmol), Na_2CO_3 (2.2 mmol), *Cs_2CO_3 (2.2 mmol), 1,3,4–trisubstituted–1,2,3–triazolium ioidide (1.0 mol%), $Pd(OAc)_2$ (0.5 mol%), 80 ^{0}C, toluene (5 mL), 5 h in air. [b]Isolated yield after separation by column chromatography; average of two runs.

Table 16. Heck–Mizoroki cross–coupling reactions of different aryl halides with styrene using **4b**[a].



Entry	Aryl halide	Product	Time (h)	Yield (%)[b]
1			5	69
2			8	61
3			9	65
4			7	67
5			8	63
6			9	71
7			9	59
8			8	65
9			5	76
10			7	76
11			8	68
12			8	67

13			7	61
14			10	51
15			10	56

[a]Reaction conditions: aryl halide (1.0 mmol), styrene (1.2 mmol), in air. [b]Isolated yield after separation by column chromatography; average of two runs