Supporting Information

Bis(imino)acenaphthene (BIAN)-supported palladium(II) carbene complexes as effective C–C coupling catalysts and solvent effects in organic and aqueous media

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Experimental

General Procedures

All glassware was oven-dried before use. All reagents were obtained commercially and used without further purification. Toluene and THF were dried over sodium and freshly distilled prior to use. The dichloromethane was dried over calcium hydride and freshly distilled prior to use. The starting materials IMes(BIAN) imidazolium chloride and IPr(BIAN)[AgCl] were synthesized according to published procedures.

Physical Measurements

Low-resolution CI mass spectra were obtained on a Thermo Scientific TSQ Quantum GC mass spectrometer and high-resolution CI mass spectra were recorded on a magnetic sector Waters Autospec Ultima instrument. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 295 K in the indicated solvent on a Varian Unity 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) or a Varian AS400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz) immediately following sample preparation. Deuterated solvents were obtained from Cambridge Isotopes and stored over 4 Å molecular

sieves prior to use. ^{1}H and $^{13}C\{^{1}H\}$ chemical shift values are reported in parts per million (ppm) relative to $SiMe_4$ (δ 0.00), using solvent resonances as internal standards. Absorption spectra were recorded on a Varian Cary 6000i UV-VIS-NIR spectrophotometer with Starna Quartz fluorometer cells with a pathlength of 10 mm. Gas chromatography (GC) was performed on an Agilent 6850 gas chromatograph (HP-1 column, L = 30 m, I.D. = 0.32 mm) equipped with a flame ionization detector (FID). The GC oven temperature was held at 50 °C for 3 min, then increased to 300 °C at 30 °C min^{-1}. The internal standard mesitylene was used to aid in measuring reaction conversions.

Preparations

IMes(BIAN)[AgCl]. A 1:1 dichloromethane-THF solution (20 mL) was added to an aluminum foil covered 50 mL round bottom flask. IMes(BIAN) imidazolium chloride (0.2 g, 0.466 mmol) and Ag_2O (0.4 g, 1.724 mmol) were added to it. The reaction mixture was stirred at ambient temperature for 48 h under argon, following which it was filtered and the solvent stripped from the filtrate under reduced pressure to afford IMes(BIAN)[AgCl] as an analytically pure red/orange solid (0.233 g, 87.6%). MS (CI^+, CH_4): *m/z* $[M - Cl]^+$; ^{1}H NMR ($CDCl_3$): δ 2.33 (s, 12H, CH_3), 2.57 (s, 6H, CH_3), 7.22 (d, 2H, Naph-H), 7.41 (s, 4H, Ar-H), 7.58 (t, 2H, Naph-H), 7.93 (d, 2H, Naph-H); ^{13}C NMR ($CDCl_3$): δ 17.85, 21.21, 120.98, 125.17, 127.74, 128.33, 129.86, 130.58, 133.80, 134.47, 138.40, 139.89.

(IMes)$PdCl_2PPh_3$ (1). Toluene (5 mL) was added to an aluminum covered 50 mL round bottom flask that contained IMes(BIAN)[AgCl] (0.050 g, 0.0875 mmol) and $PdCl_2(PPh_3)_2$ (0.056 g, 0.0796 mmol). The reaction mixture was refluxed for 16 h. It was then cooled to ambient temperature and filtered over celite. The precipitate was extracted from the celite with

dichlormethane, followed by removal of the solvent. Recrystallization with ethanol afforded an analytically pure yellow solid (0.044 g, 58.3%). MS (CI^+, CH_4): *m/z* 831 $[M - Cl]^+$; ^1H NMR ($CDCl_3$): δ 2.39 (s, 12H, CH_3), 2.49 (s, 6H, CH_3), 7.00 (d, 2H, Naph-H), 7.12 (s, 4H, Ar-H), 7.21 (d, 2H, Naph-H), 7.29-7.39 (m, 11H, Naph-H, P*Ph*$_3$-H), 7.69 (d, 2H, Naph-H); ^{13}C NMR ($CDCl_3$): δ 138.67, 138.30, 137.78, 136.22, 135.98, 135.00, 134.87, 134.30, 134.16, 130.73, 130.14, 129.79, 129.64, 129.46, 129.25, 129.10, 128.02, 127.77, 127.67, 126.09, 125.89, 120.62, 120.29, 21.39, 19.18; ^{31}P NMR ($CDCl_3$): δ 20.99.

(IPr)PdCl$_2$PPh$_3$ (2). Toluene (5 mL) was added to an aluminum covered 50 mL round bottom flask that contained IPr(BIAN)[AgCl] (0.0514 g, 0.0785 mmol) and $PdCl_2(PPh_3)_2$ (0.050 g, 0.0713 mmol). The reaction mixture was refluxed for 16 h. It was then cooled to ambient temperature and filtered over celite. The precipitate was extracted from the celite with dichloromethane, followed by removal of the solvent. Recrystallization with ethanol afforded an analytically pure yellow solid (0.046 g, 62.2%). MS (CI^+, CH_4): *m/z* 915 $[M - Cl]^+$; ^1H NMR ($CDCl_3$): δ 0.90 (d, 12H, CH_3), 1.26 (d, 12H, CH_3), 3.40 (sept, 4H, -C*H*$(CH_3)_2$), 6.86 (d, 2H, Naph-H), 7.17 (d, 6H, P*Ph*$_3$-H), 7028-7.37 (m, 11H, Naph-H, P*Ph*$_3$-H), 7.48 (d, 4H, *i*Pr-Ar-H), 7.65 (d/t, 4H, Naph-H, *i*Pr-Ar-H); ^{13}C NMR ($CDCl_3$): δ 146.94, 139.76, 134.59, 133.4, 130.35, 129.76, 129.21, 127.34, 127.16, 126.75, 125.88, 123.97, 121.57, 28.39, 35.40, 23.51; ^{31}P NMR ($CDCl_3$): δ 21.41.

General Procedure for Suzuki Cross-Coupling Reactions. Deionized water (3 mL) was added to a 20 mL scintillation vial containing aryl halide (0.267 mmol), phenylboronic acid (0.321 mmol), potassium carbonate (0.802 mmol), and the internal standard mesitylene (0.267 mmol). The scintillation vial was covered with a septum and wired down. The reaction mixture was heated to 40 °C while stirring. The catalyst concentration was determined by UV-Vis and

rapidly injected into the reaction mixture (0.1-2.0 mol% of **1** or **2**). The reaction was allowed to stir for twenty hours for all aryl iodides and bromides. The aryl chlorides required 48 hours to reach complete conversion. The reaction mixture was cooled to ambient temperature, filtered over celite, and washed with ether. The solvents were evaporated from the organic layer to produce the desired product. The reactions were monitored by GC and percent conversions were calculated based on the aryl halide. The product was determined by NMR to match literature results.

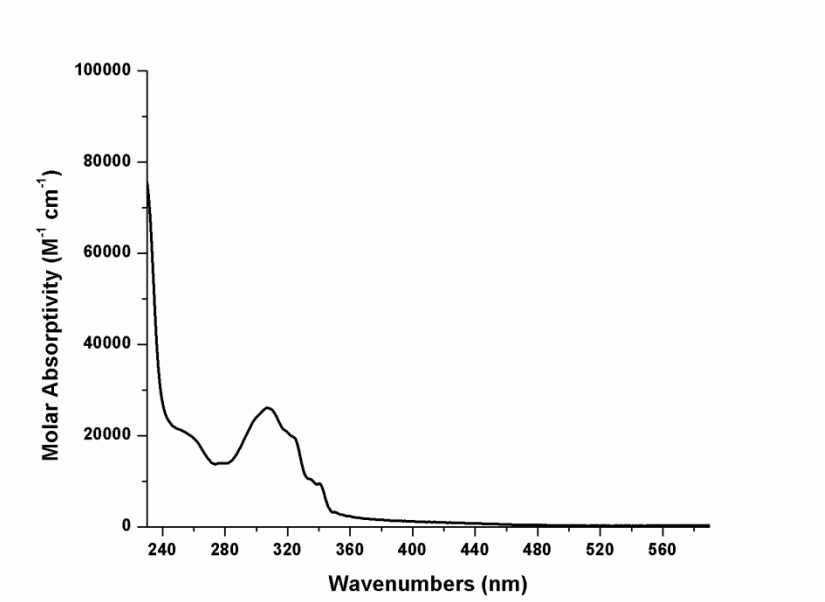

Figure S1. The absorption spectrum of **1** in dichloromethane with λ_{max} = 308 nm. Beer's law was used to determine the molar absorptivity from a calibration curve created with ten data points in 10 μL increments ranging 10-100 μL (ε = 29,646 M^{-1} cm^{-1}, R^2 = 0.9918).

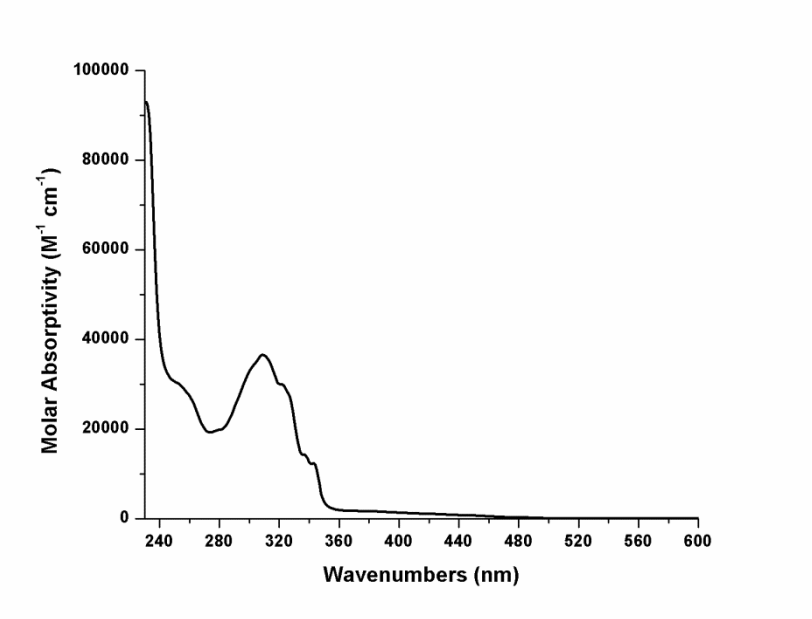

Figure S2. The absorption spectrum of **2** in dichloromethane with λ_{max} = 309 nm. Beer's law was used to determine the molar absorptivity from a calibration curve created with ten data points in 10 μL increments ranging 10-100 μL (ε = 36,868 M^{-1} cm^{-1}, R^2 = 0.9997).

General Procedure for Suzuki Cross-Coupling Kinetic Experiments. Deionized water (15 mL) was added to a 20 mL scintillation vial containing aryl halide (3.24 mmol), phenylboronic acid (3.89 mmol), potassium carbonate (9.73 mmol), and the internal standard mesitylene (3.24 mmol). The scintillation vial was covered with a septum and wired down. The reaction mixture was heated to 40 °C (unless otherwise noted) while stirring. The catalyst concentration was determined by UV-Vis (CH_2Cl_2) and rapidly injected into the reaction mixture. Aliquots were taken at desired reaction times by removing 0.6 mL of the system, filtering over celite, and washed with ether (1.0 mL). The extracted organic layer was injected into the GC. The percent conversions were calculated based on the aryl halide.

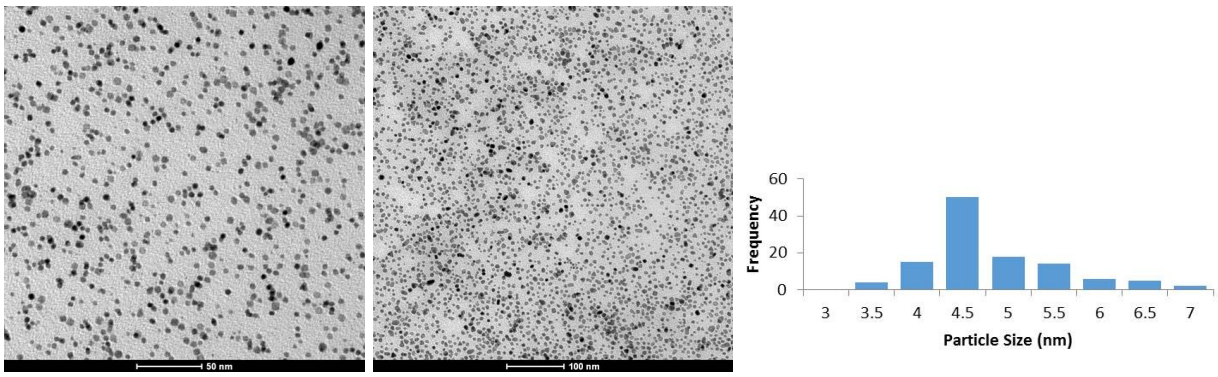

Figure S3. TEM images and histogram of Pd-PVP nanoparticles (left: 50 nm scale, right: 100 nm scale).

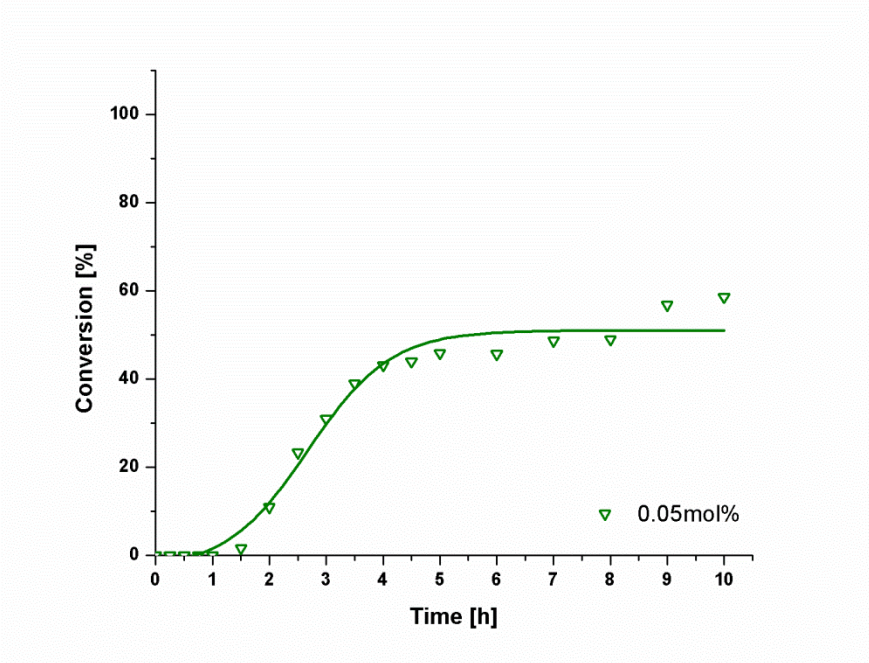

Figure S4. Conversion of *p*-bromobenzaldehyde with phenylboronic acid as a function of time in Suzuki-Miyaura coupling by catalyst **2** at 40˚C with 0.05 mol% catalyst loading ($k^2 = 0.8427$).

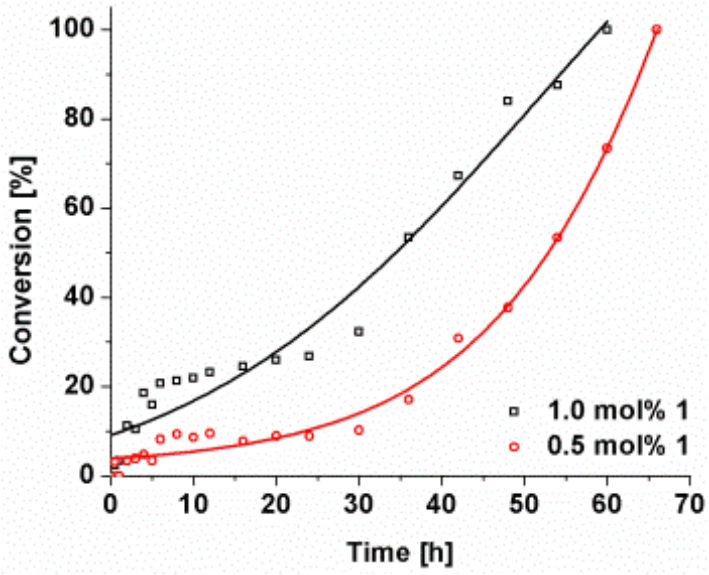

Figure S5. Reaction of *p*-chlorobenzaldehyde with phenylboronic acid as a function of time in the Suzuki-Miyaura coupling at 40 ℃ with 0.5 and 1.0 mol% of **1** in H_2O

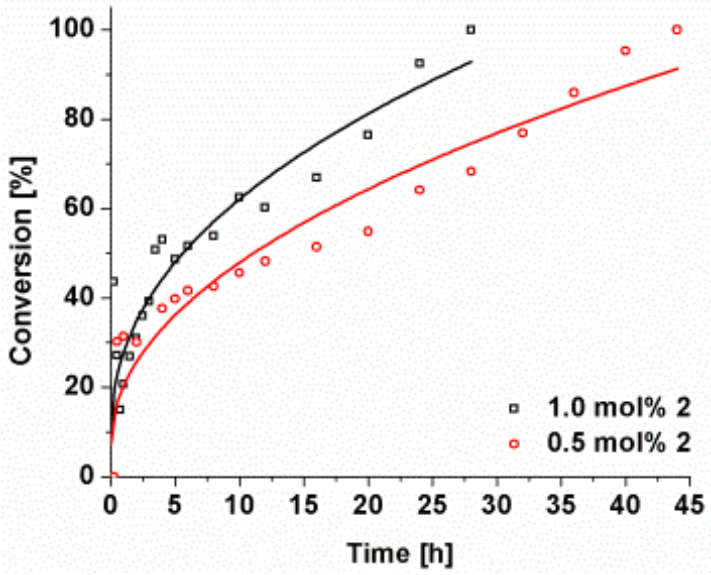

Figure S6. Reaction of *p*-chlorobenzaldehyde with phenylboronic acid as a function of time in the Suzuki-Miyaura coupling at 40 ℃ with 0.5 and 1.0 mol% of **2** in H_2O

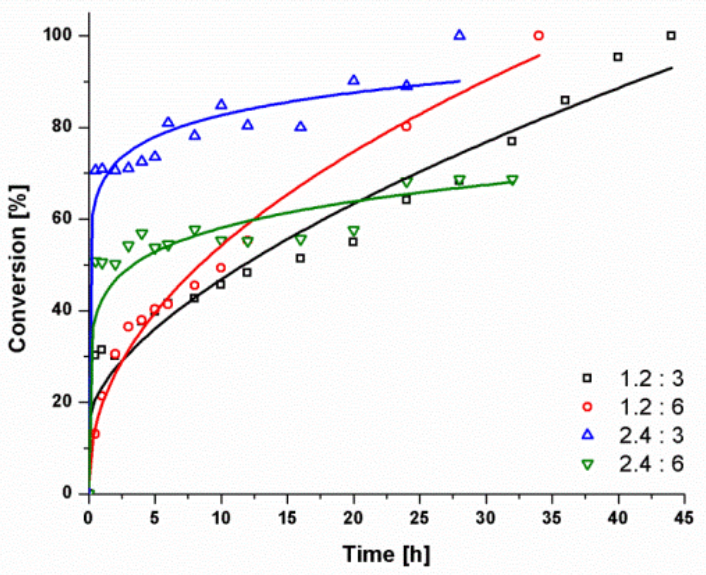

Figure S7. Conversion of *p*-chlorobenzaldehyde as a function of time in Suzuki-Miyaura coupling at 40 ℃ in H_2O with 0.5 mol% of **2** under varying conditions of phenylboronic acid and K_2CO_3 (legend denotes stoichiometric equivalents of phenylboronic acid : K_2CO_3).

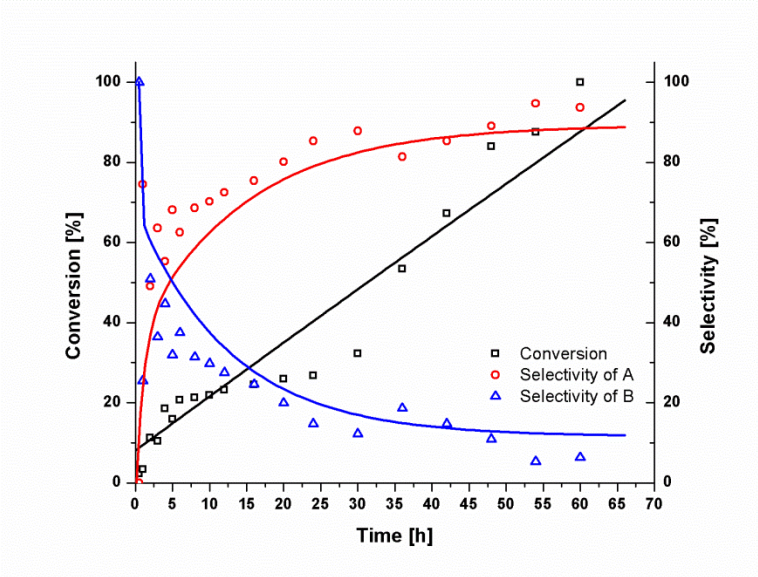

Figure S8. Conversion and selectivity of *p*-chlorobenzaldehyde with phenylboronic acid as a function of time in Suzuki-Miyaura coupling at 40˚C with 1.0 mol% of catalyst **1.**

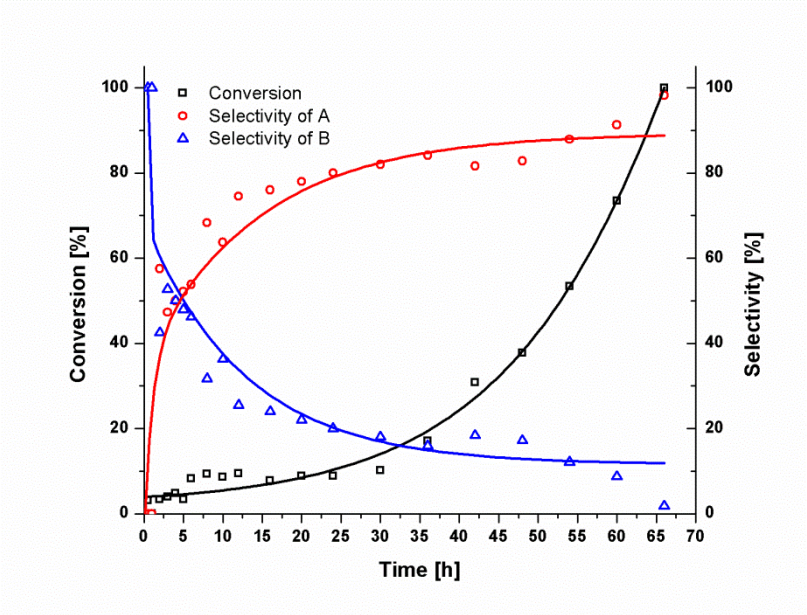

Figure S9. Conversion and selectivity of *p*-chlorobenzaldehyde with phenylboronic acid as a function of time in Suzuki-Miyaura coupling at 40˚C with 0.5 mol% of catalyst **1.**

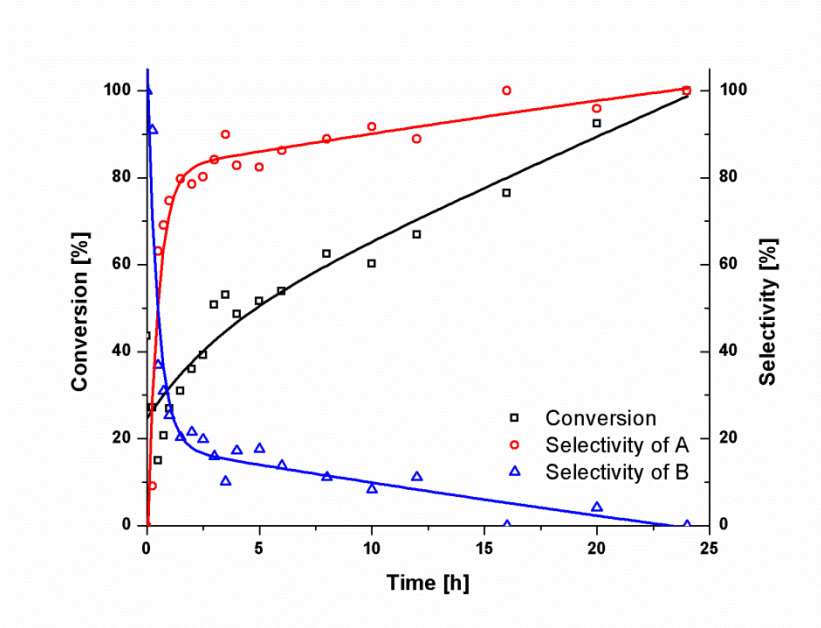

Figure S10. Conversion and selectivity of *p*-chlorobenzaldehyde with phenylboronic acid as a function of time in Suzuki-Miyaura coupling at 40˚C with 1.0 mol% of catalyst **2.**

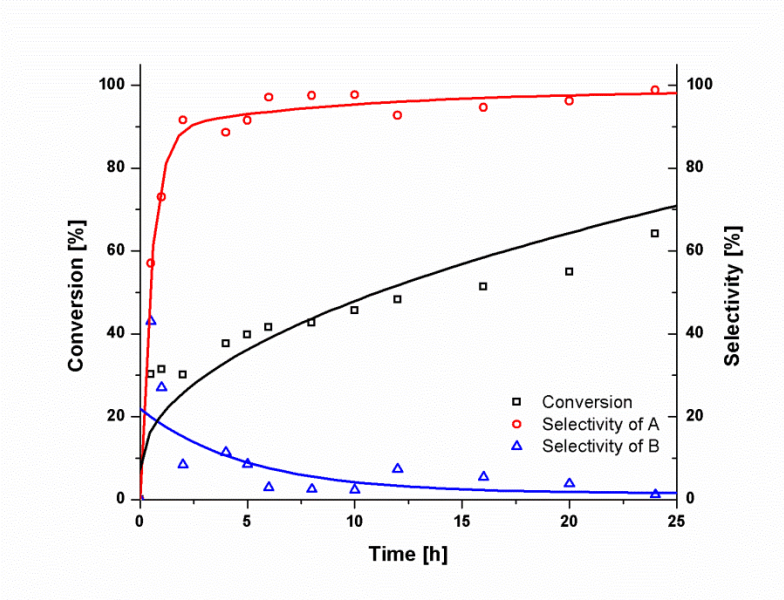

Figure S11. Conversion and selectivity of *p*-chlorobenzaldehyde with phenylboronic acid as a function of time in Suzuki-Miyaura coupling at 40˚C with 0.5 mol% of catalyst **2.**

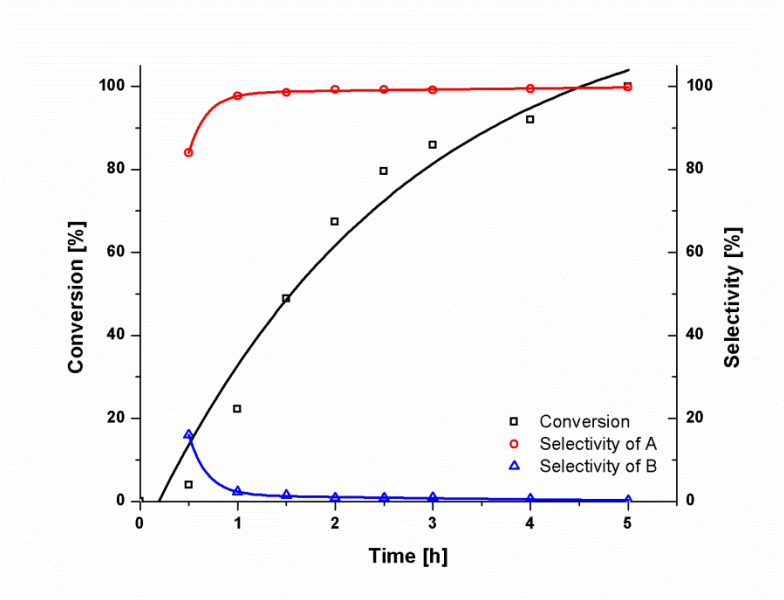

Figure S12. Conversion and selectivity of *p*-chlorobenzaldehyde with phenylboronic acid as a function of time in Suzuki-Miyaura coupling at 35˚C with 0.25 mol% of catalyst **2.**

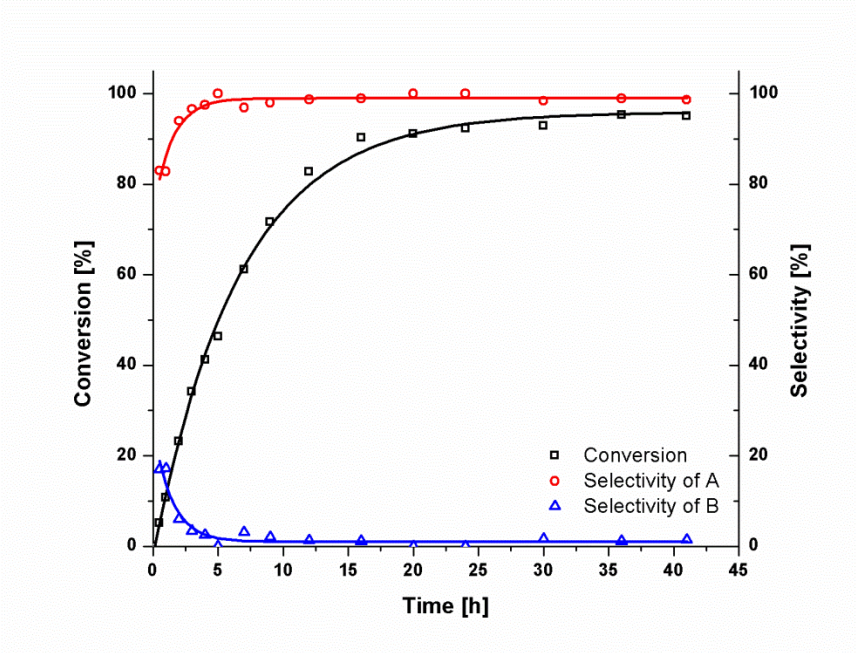

Figure S13. Conversion and selectivity of *p*-chlorobenzaldehyde with phenylboronic acid as a function of time in Suzuki-Miyaura coupling at 30˚C with 0.25 mol% of catalyst **2.**

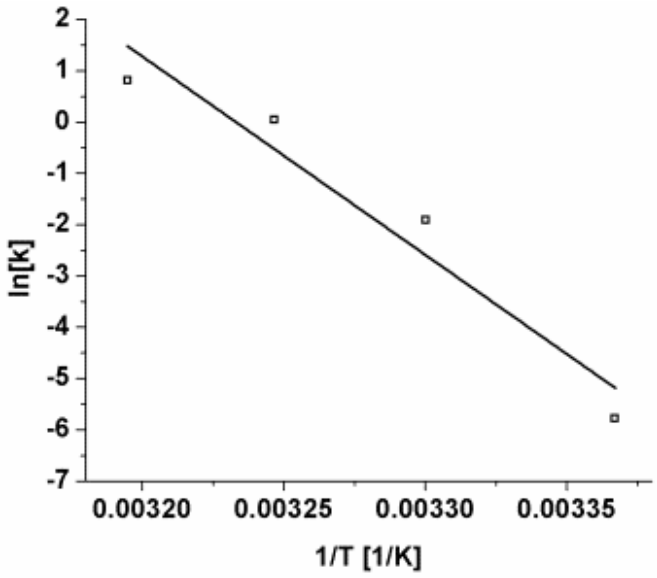

Figure S14. Arrhenius plot for the activation of *p*-chlorobenzaldehyde by **2** in H_2O