Palladium nanoparticles supported on titanium dioxide cellulose composite (PdNPs@TiO_2-Cell) for ligand-free carbon-carbon cross coupling reactions

Sanjay Jadhav[a], Ashutosh Jagdale[b], Santosh Kamble[c], Arjun Kumbhar[b]*, Rajshri Salunkhe[a]*

[a]*Department of Chemistry, Shivaji University, Kolhapur, 416004, M.S., India*

[b]*Department of Chemistry, Padmabhushan Dr. Vasantraodada Patil College, Tasgaon, (Sangli) Maharashtra, 416312, India*

[c]*Department of Chemistry, Yashvantrao Chavan Institute of Science, Satara, Maharashtra, 415001, India*

E-mail: arjun2win@yahoo.co.in

Supporting Information

Experimental section

Instrumentation and chemicals

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avon 300 MHz and 75 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal reference. Mass spectra were recorded on a Shimadzu QP2010 GCMS instrument. A JEOL (Tokyo, Japan) JSM-5200 scanning electron microscope was used for SEM observations and Energy dispersive X-ray spectroscopy (EDS) analysis. Elemental analysis was carried on EURO EA 3000 elemental analyzer. XPS of palladium was recorded on UG Multilab 2000-Thermo Scientific USA, Kα. A SDT Q600 V20.9 Build 20 was used for TGA-DTA analysis. Powder XRD patterns were collected on the Philips, PW 3710, Almelo, Holland diffractometer in the 2θ range 5-60° with the step size of 0.02° using CuKα radiation (λ=1.5406 Å). All the reagents were commercially sourced from Sigma Aldrich, Alpha Aser and Spectrochem companies and used as received. Solvents were dried and purified by slandered methods. The synthesis of titanium dioxide–cellulose composite (TiO_2-Cell) was carried out as described in the literature.[25]

Typical procedure for synthesis of PdNPs@TiO_2-Cell

In a small Schlenk tube TiO_2-Cell (5.0 g) was mixed with $Pd(OAc)_2$ (112.5 mg, 0.5 mmol) in ethanol (50 mL). The mixture was stirred at 50 °C temperature for 4 h. The solid product was filtered, washed with ethanol (3x10 mL) and acetone (3x10 mL) successively,

and dried under vacuum at room temperature for 8 h to afford gray colored palladium catalyst.

Typical experimental procedure for the Suzuki-Miyaura cross-coupling reaction

Aryl halide/arenediazonium salt/benzoyl chloride (1 mmol) and aryl boronic acid (1.1 mmol), catalyst (1 mol %) and base (1 mmol) were added to a Shlenk tube. The reaction mixture was allowed to stir at as specified temperature until completion of the reaction as monitored by TLC. The catalyst was separated by filtration/centrifugation and washed with ethyl acetate (3×5 mL) and water (3×5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the removal of solvent afforded crude product which was purified by column chromatography.

Typical experimental procedure for the Mizoroki-Heck and Heck-Matsuda cross-coupling reaction

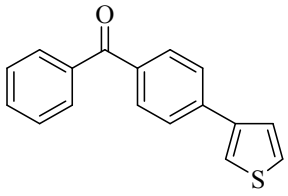
Aryl halide/arenediazonium salt (1 mmol) and olefin (1.1 mmol), catalyst (1 mol %) and base (1 mmol) were added to a Shlenk tube contains 5ml DMF/water. The reaction mixture was allowed to stir at as specified temperature until completion of the reaction as monitored by TLC. The catalyst was separated by filtration/centrifugation and washed with ethyl acetate (3×5 mL) and water (3×5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the removal of solvent afforded crude product which was purified by column chromatography.

Typical experimental procedure for the Sonogashira cross-coupling reaction

Aryl halide (1 mmol) and phenyl acetylene (1.1 mmol), catalyst (1 mol %) and base (1 mmol) were added to a Shlenk tube containing 5ml DMF. The reaction mixture was allowed to stir at as specified temperature until completion of the reaction as monitored by TLC. The catalyst was separated by filtration/centrifugation and washed with ethyl acetate (3×5 mL) and water (3×5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the removal of solvent afforded crude product which was purified by column chromatography.

Spectral Data of Compounds:

phenyl(4-(thiophen-3-yl)phenyl)methanone (**Table 4, entry 2**):

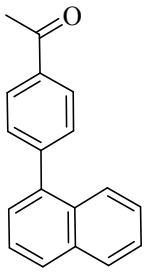


White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H (ppm):7.81 (*t*, 1H, J=6.4Hz), 7.75 (dd, 2H, *J*=1.6, 2.0 Hz), 7.69 (d, 2H, J=2.0 Hz), 7.66 (d, 2H, *J*=2.0 Hz), 7.64 (d, 2H, J=2.4 Hz) 7.53 (d, 1H, J=1.6 Hz), 7.51 (d, 1H, J=7.2 Hz), 7.20 (s, 1H). ^{13}C NMR ($CDCl_3$, 100MHz): δ_C (ppm)**,** 195.6, 137.1, 136.3, 131.6, 131.5, 129.9, 128.4, 127.5, 125.7, 124.4, 123.6, 119.5.

phenyl 1, 4 (4-dimethoxy phenyl) (**Table 4, entry 9**)**:**

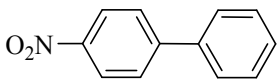
White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H (ppm): 3.88 (s, 6H) 6.96-7.49 (m, 4H) 7.51-7.66 (m, 4H), 7.81-7.96 (m, 4H) ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C (ppm): 147.1, 138.4, 132.7, 130.4, 128.2, 127.7, 55.3.

1-(4-(Naphthalen-1-yl)phenyl)ethanone (**Table 4, entry 4**):



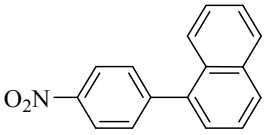
White solid, ^{1}H NMR: ($CDCl_3$, 400 MHz):δ_H (ppm): 2.67 (s, 3H), 7.40-7.56 (m, 4H), 7.62 (dd, 2H, *J*=6.3, 1.7 Hz), 7.82 (d, 1H, *J*=8.2 Hz), 7.91 (*t*, 2H, *J*= 1.4 Hz), 8.20 (dd, 2H, *J*= 6.2, 1.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C (ppm): 25.7, 126.3, 126.6, 127.0, 128.3, 129.9, 130.3, 131.3, 132.2, 134.2, 134.8, 137.1, 140.0, 146.8, 196.8.

4-Nitro-1,1'-biphenyl (**Table 5, entry 5**):



Yellow solid. ^{1}HNMR ($CDCl_3$, 400 MHz): δ_H (ppm): 7.40-7.51(m, 3H), 7.61-7.68 (m, 2H), 7.71 (dd, 2H, *J* = 7.1, 1.9 Hz), 8.23 (dd, 2H, *J*=8.3, 1.4 Hz). ^{13}CNMR ($CDCl_3$, 100 MHz): δ_C (ppm): 123.3, 128.4, 128.8, 129.9, 130.1, 139.6, 148.7.

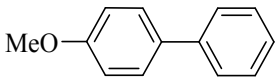
1-(4-Nitrophenyl)naphthalene (**Table 5, entry 7**):



White solid. ^{1}HNMR ($CDCl_3$, 400 MHz), δ_H (ppm): 7.43-7.55 (m, 2H), 7.49-7.63 (m, 2H), 7.66 (d, 2H, *J*=9.1 Hz), 7.91 (d, 2H, *J*=8.3 Hz), 8.39 (dd, 2H, *J*=8.8, 1.6 Hz). ^{13}CNMR

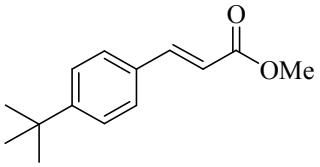
($CDCl_3$, 100 MHz): δ_C (ppm): 124.1, 125.5, 126.4, 127.3, 128.8, 129.3, 129.8, 130.9, 131.4, 132.8, 138.6, 148.3, 149.6.

4-Methoxybiphenyl (**Table 5, entry 8**):



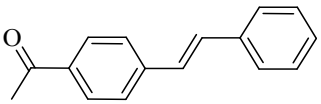
White solid. ^{1}HNMR ($CDCl_3$, 400 MHz), δ_H (ppm): 3.87 (s, 3H), 7.01(d, 2H, *J*=8.6 Hz), 7.31-7.36 (m, 1H), 7.45 (t, 2H, *J*=7.3 Hz), 7.55-7.60 (m, 4H). ^{13}CNMR ($CDCl_3$, 100 MHz): δ_C (ppm) 55.8, 114.3, 126.5, 129.3, 129.9, 134.9, 140.0, 158.5.

(*E*)-methyl 3-(4-tert-butylphenyl)acrylate (**Table 6, entry 4**):



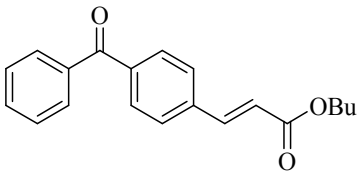
Yellow colored liquid, ^{1}HNMR ($CDCl_3$, 300 MHz) δ_H(ppm): 3.86 (s, 3H), 6.58 (d, 1H, *J*= 16.2 Hz), 7.68 (d, 2H), 7.74 (d, 1H, *J*=16.2 Hz), 8.27 (d, 2H, *J*=8.7 Hz,).^{13}CNMR (75MHz, $CDCl_3$): δ_C (ppm): 52.08, 122.0, 124.1, 128.6, 140.4, 141.9, 148.5, 166.4.

(*E*)-1-(4-Styrylphenyl)ethanone (**Table 6, entry 8**):



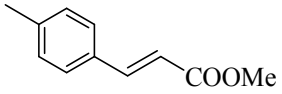
Yellow solid. 1H NMR ($CDCl_3$ 400 MHz) δH(ppm): 2.60 (s, 3H), 7.22 (d, 1H, *J*=16.0 Hz), 7.31-7.42 (m, 3H), 7.56-7.59 (m, 2H), 7.67(d, 2H, *J*=8.3 Hz), 7.96 (d, 1H, *J*=16.1 Hz), 7.98 (d, 2H, *J*=8.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δC (ppm): 26.4, 126.7, 127.6, 128.4, 129.3, 130.4, 131.8, 132.3, 136.7, 138.6, 140.0, 196.5.

(*E*)-Butyl-3-(4-benzophenonyl)acrylate (**Table 6, entry 10**):



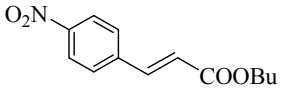
White solid. ^{1}HNMR ($CDCl_3$, 400 MHz); δH(ppm): 0.98 (*t*, 3H, *J*=7.4 Hz), 1.44-1.51 (m, 2H), 1.65-1.71 (m, 2H), 4.26 (*t*, 2H, *J*=6.7Hz), 6.57 (d, 1H, *J*=16.0 Hz), 7.48-7.55 (m, 2H), 7.61-7.67 (m, 3H), 7.75 (d, 1H, *J*=15.9 Hz), 7.81-7.85 (m, 4H). ^{13}CNMR (100 MHz, $CDCl_3$)δC: 13.6, 18.1, 31.6, 65.2, 121.7, 127.6, 128.4, 130.3, 130.7, 130.9, 131.6, 132.9, 138.4, 139.4, 139.7, 142.1, 165.6, 198.8 ppm.

(*E*)-Methyl-3-*p*-tolylacrylate (**Table 7, entry 3**)**:**



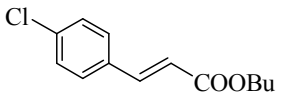
Yellow liquid. ^{1}HNMR ($CDCl_3$, 400 MHz) δ_H(ppm): 2.37 (s, 2H), 3.80 (s, 3H), 6.44 (d, 1H, *J*= 16.0 Hz), 7.22 (d, 2H, *J*=7.9 Hz), 7.34-7.46 (m, 2H), 7.70 (d, 1H, *J*=16.0 Hz). ^{13}CNMR (100 MHz, $CDCl_3$): δ_C (ppm)**:** 22.4, 55.6, 127.1, 129.4, 130.5, 131.6, 132.1, 133.7, 141.7, 166.6 ppm.

(*E*)-Butyl-3-(4-nitrophenyl)acrylate (**Table 7, entry 4**):



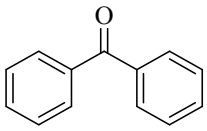
Yellow colored solid, ^{1}HNMR ($CDCl_3$, 400 MHz) δ_H(ppm): 0.99 (t, 3H, *J*=7.3 Hz,), 1.42-1.48 (m, 2H), 1.67-1.77 (m, 2H), 4.22 (t, 2H, *J*=6.5 Hz), 6.58 (d, 1H, *J*= 16.0 Hz), 7.66 (d, 2H, J=8.6 Hz), 7.72 (d, 1H, *J*= 15.9 Hz), 8.28 (d, 2H, *J*=8.8 Hz),. ^{13}CNMR (100 MHz, $CDCl_3$): δ_C (ppm): 13.8, 18.1, 31.2, 65.8, 121.6, 123.2, 127.4, 141.2, 143.5, 165.1.

(*E*)-Butyl-3-(4-chlorophenyl)acrylate (**Table 7, entry 5**):



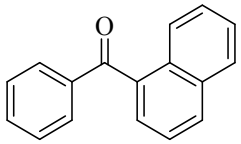
Yellow colored liquid, ^{1}HNMR ($CDCl_3$, 400 MHz) δ_H(ppm): 0.96 (t, 3H, *J*=7.6 Hz,), 1.39-1.51 (m, 2H), 1.64-1.75 (m, 2H), 4.21 (t, 2H, *J*=6.8 Hz), 6.41 (d, 1H, *J*= 16.0 Hz), 7.33-7.37 (m, 2H), 7.44 (d, 2H, *J*=8.3 Hz), 7.64 (d, 1H, *J*= 15.9 Hz,). ^{13}CNMR (100 MHz, $CDCl_3$): δ_C (ppm): 14.9, 19.2, 32.7, 64.7, 119.9, 129.8, 130.1, 131.9, 137.1, 144.0, 166.3.

Benzophenone (**Table 8, entry 1**):



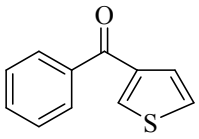
White solid. ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.77-7.82 (m, 4H), 7.55-7.60 (m, 2H), 7.45-7.51 (m, 4H); ^{13}C NMR (100 Mz, $CDCl_3$): δ 127.1, 130.1, 133.2, 138.2, 195.3.

(Naphthalen-1yl)(phenyl)methanone (**Table 8, entry 2**)**:**



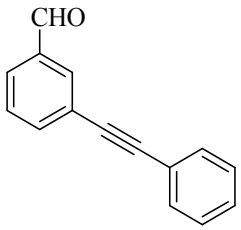
Low melting solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H (ppm): 7.46-7.57 (m, 4H), 7.62 (d, 2H, *J*= 6.8 Hz), 7.88 (d, 2H, *J*=7.4 Hz), 7.94-7.98 (m, 1H), 8.1 (d, 1H, *J*=8.2Hz), 8.12 (d, 1H, *J*= 9.2 Hz). ^{13}C NMR ($CDCl_3$), 100 MHz) δ_C (ppm): 125.3, 126.3, 127.2, 128.2, 129.8, 130.3, 130.4, 131.2, 132.7, 134.3, 136.5, 138.4, 139.4, 140.2, 196.2.

2-Benzoylthiophene (**Table 8, entry 7**):



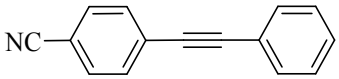
White solid, 1H NMR (400 Mz, $CDCl_3$): δ 7.84-7.88 (m, 2H), 7.72-7.75 (m, 1H), 7.63-7.65 (m,1H), 7.56-7.60 (m, 1H), 7.47-7.50 (m, 2H), 7.16-7.20 (m, 1H). ^{13}C NMR (100 Mz, $CDCl_3$): δ 126.9, 127.8, 128.0, 129.3, 131.2, 133.3, 137.5, 143.5, 189.1.

3-(2-Phenylethyl)benzaldehyde (**Table 9, entry 5**):



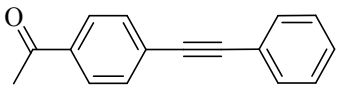
White Solid. ^1H NMR ($CDCl_3$, 400 MHz); δ_H(ppm): 7.37 (*t*, 3H, *J*= 3.4 Hz), 7.53-7.58 (m, 3H), 7.80-7.87 (m, 2H), 8.14 (s, 1H), 10.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) $_H\delta$(ppm): 88.8, 91.9, 123.5, 125.5, 129.4, 130.4, 130.9, 132.1, 133.7, 135.1, 138.2, 139.1, 192.2.

4-(2-*p*-Tolylethynyl)benzonitrile (**Table 9, entry 7**):



White Solid, ^1H NMR ($CDCl_3$, 400 MHz); δ_H(ppm): 2.40 (s, 3H), 7.19 (d, 4H, *J*=8.2Hz), 7.45 (d, 4H, *J*=8.4Hz). ^{13}C NMR (100 MHz, $CDCl_3$)δ: 22.3, 76.3, 83.3, 117.8, 128.3, 133.4, 137.1.

1-(4-(2-Phenylethynyl)phenyl)ethanone (Table 9, entry 9):



Yellow Solid. ^1H NMR ($CDCl_3$, 400 MHz); δ_H(ppm): 2.71 (s, 3H), 7.44 (*t*, 3H, *J*= 3.3 Hz), 7.52-7.57 (m, 2H), 7.64 (d, 2H, *J*= 8.8 Hz,), 7.94 (d, 2H, *J*= 8.7 Hz). ^{13}C NMR (100MHz, $CDCl_3$)δ: 28.7, 88.5, 92.2, 123.5, 127.3, 128.5, 129.7, 130.1, 131.9, 133.3, 137.3, 196.4.