

Check fo updates

C-C cross-coupling reactions of organosilanes with terminal alkenes and allylic acetates using Pd(II) catalyst supported on starch coated magnetic nanoparticles

Debabrata Patra,^[a] Subir Panja,^[b] and Amit Saha*^[a]

 [a] Dr. A. Saha, Mr. D. Patra Department of Chemistry Jadavpur University Kolkata 700032, India E-mail: amit.saha@jadavpuruniversity.in
 [b] Mr. S. Panja

School of Chemical Sciences Indian Association for the Cultivation of Science Kolkata 700032, India

Supporting information for this article is given via a link at the end of the document.

Abstract: Starch coated magnetic nanoparticles supported palladium catalyst has been explored to perform C-C cross coupling reactions, such as oxidative Heck coupling and Tsuji-Trost allylic coupling using organosilicon compounds as one of the coupling partners. The biopolymer coated magnetic catalyst was very easy to recover magnetically and was recycled efficiently in the subsequent batches. All the reactions were performed in air and thus necessity of air and moisture free reaction condition is avoided. The present protocols show wide substrate scope and good yields of the products.

Introduction

The pioneering route for constructing C-C bonds involves the cross-coupling reactions using various organometallic and organometalloid reagents. Heck coupling and Tsuji-Trost coupling are two important tools for C-C bond formations leading to total synthesis of many natural products and biologically active organic compounds.^[1] The oxidative Heck reaction has recently gained more attention mainly because of air and moisture insensitive reaction conditions using organoboron,^[2] organotin^[3] and organosilicon^[4] reagents as the coupling partners. Among common organometallic reagents organosilicon compounds are attractive due to their stability, low toxicity, lowcost and high natural abundance of silicon.^[5] Although, organosilicon compounds have been employed in oxidative Heck coupling reaction for a number of times,^[4] but the use of expensive non-recyclable homogeneous catalysts makes them economically less potent. In this report, we demonstrate the use of magnetic heterogeneous catalyst to carry out the oxidative Heck coupling reactions of organosilane compounds with terminal alkenes in aerial condition. Organosilanes have also been used in this study to perform Tsuji-Trost allylation reactions with allylic acetates in presence of magnetic nano-catalyst.

Heterogeneous magnetic catalysts⁽⁶⁾ have become popular due to easy magnetic separation of the catalyst from the reaction mixture. Additionally, the heterogeneous catalysts with good recyclability offer economic sustainability. Here, we have used the starch coated magnetic ferrite nanoparticles as the heterogeneous support of Pd(II) catalyst. The starch coated Fe₃O₄ nanoparticles^[7] have extensively been used in biomedical sciences for different purposes like drug delivery, tumor targeting, magnetic resonance imaging etc. We have explored the starch coated magnetic Fe_3O_4 nanoparticles to immobilize the Pd(II) catalyst on the surface of the nanoparticles. The synthesized magnetic palladium nano-catalyst has been tested to catalyze the C-C cross coupling reactions of organosilanes with alkenes and allylic acetates. Various terminal alkenes underwent smooth $C(sp^2)$ -H arylation by aryltrimethoxysilanes in presence of magnetic-Pd(II) catalyst, tetrabutylammonium fluoride (TBAF) and *p*-benzoquinone (BQ) as the oxidizing agent in open air condition (Scheme 1). C-C cross-coupling of allylic acetates were also performed with organosilanes using magnetic-Pd(II) catalyst and TBAF in aerial atmosphere (Scheme 1).



Scheme 1. Pd(II) catalyzed C-C cross coupling reactions of organosilanes with terminal alkenes and allylic acetates.

Results and Discussion

The starch coated magnetic ferrite nanoparticles were prepared following the similar methods reported earlier $^{[7a\makebox{-}7c]}$ The $\mbox{Fe}^{^{3+}}$ and Fe²⁺ salts were dissolved in an aqueous solution of starch by heating at 60 °C. Black colored starch coated Fe₃O₄ nanoparticles were started to appear upon addition of aqueous ammonia solution. The black nanoparticles were centrifuged, washed with acetone and dried under vacuum. The Pd(II) was immobilized on the surface of starch coated Fe₃O₄ nanoparticles by stirring the methanolic suspension of the nanoparticles with PdCl₂ at room temperature for 15 h. The sizes of the Pd(II) immobilized starch coated magnetic nanoparticles were checked by TEM (transmission electron microscopy) experiment and it was found to be 7 - 19 nm (Fig. 1). The surface morphology and the amount of palladium in the supported catalyst were determined by SEM (scanning electron microscope) (Fig. 2) along with the EDX (Energy Dispersive X-ray) (Fig. 3)

WILEY-VCH

experiments. The weight percentage of palladium in the supported magnetic catalyst is found to be 4.92 as per the EDX elemental compositional analysis (Fig. 3, elemental analysis table). The weight% of palladium was also verified by ICP-AES analysis and it was found to be 4.95 which is very close to the result as obtained from EDX experiment.



Figure 1. TEM image of the Pd(II) nano-catalyst [Fe₃O₄-starch-Pd(II)].



Figure 2. SEM image of the Pd(II) nano-catalyst [Fe₃O₄-starch-Pd(II)].



Figure 3. Energy Dispersive X-ray spectrum (EDX) and the elemental analysis table of the Pd(II) nano-catalyst [Fe₃O₄-starch-Pd(II)].

The BET (nitrogen adsorption isotherms) experiment shows, the specific surface area of the catalyst is 10 m²/gm (Figure is included in the Supporting Information). The thermal stability of the catalyst was examined by TGA analysis (Fig. 4) which reveals a gradual weight loss due to removal of physically adsorbed solvent molecules^[6i] below 200 °C. The weight loss around 300 - 350 °C may be due to the loss of surface hydroxyl groups.



Figure 4. TGA analysis of the catalyst [Fe₃O₄-starch-Pd(II)].

The oxidative Heck coupling reaction was performed by simple experimental procedure. The solution of terminal alkene and organosilane (1.5 equiv.) in THF solvent was stirred at 40 °C in presence of p-benzoquinone (BQ), tetrabutylammonium fluoride (TBAF) and Pd(II) magnetic catalyst (Fe₃O₄-starch-Pd(II)) under aerial atmosphere for a certain time period. Upon completion of reaction (monitored by TLC), the catalyst was separated magnetically and the desired product was obtained by usual work-up followed by column chromatographic purification.

The reaction condition was optimized by performing a set of reactions between butyl acrylate and phenyltrimethoxysilane with variation of different reaction parameters (Table 1). The coupling between butyl acrylate and phenyltrimethoxysilane was first tried using Fe₃O₄-starch-Pd(II) catalyst in presence of pbenzoquinone (BQ) and TBAF in DMF solvent (entry 1, Table 1). However, the yield was not satisfactory (48%). Other common solvents like DMSO, water, acetonitrile (entries 2 - 4, Table 1) were also not suitable for the coupling reaction. The reaction was found to proceed efficiently in presence of Fe₃O₄-starch-Pd(II) catalyst, p-benzoquinone oxidant and TBAF in THF medium under aerial condition at 40 °C to produce the desired product with 80% of yield in 12 h of reaction time period (entry 5, Table 1). The reaction remained incomplete within 10 h of time period (entry 7, Table 1). However, the yield of the reaction did not improve prolonging the reaction time period beyond 12 h. In presence of DDQ as the oxidizing agent, a complex reaction mixture was obtained with the formation of several unidentified side-products (entry 8, Table 1). The crucial role of pbenzoquinone oxidant in the coupling reaction of butyl acrylate and phenyltrimethoxysilane was established by the control experiment (entry 9, Table 1) which produces the desired product only in 26% of yield in absence of p-benzoquinone. The reaction did not initiate at all without the Pd-catalyst. Other magnetic palladium catalyst, such as Fe₃O₄-Dopamine-Pd(II)^[6a] was not found suitable for the reaction and produced the desired

WILEY-VCH

product only in 13% of yield (entry 10, Table 1). Some nonmagnetic heterogeneous catalysts (Cellulose-Pd^[8a], Pd/Al₂O₃^[8b]) were also found to be nonfunctional to catalyze the coupling reaction between butyl acrylate and phenyltrimethoxysilane (entries 11, 12, Table 1).

 $\mbox{Table 1. Optimization of the reaction condition for oxidative Heck coupling reaction. <math display="inline">^{[a]}$

1		Catal	Catalyst			Ph CO ₂ Bu		
	00280	TBAF, oxida 40 °C	int, solven , air	t				
Entry	Amou PhSi(OMe)	nt of Catalyst : ₃ , (equiv.)	Solvent (Oxidant	Time (h)	Yield (%)		
1	1.5	Fe ₃ O ₄ -starch-Pd(II)	DMF	BQ	12	48		
2	1.5	Fe ₃ O ₄ -starch-Pd(II)	DMSO	BQ	12	39		
3	1.5	Fe ₃ O ₄ -starch-Pd(II)	H ₂ O	BQ	12	28		
4	1.5	Fe ₃ O ₄ -starch-Pd(II)	CH₃CN	BQ	12	16		
5	1.5	Fe ₃ O ₄ -starch-Pd(II)	THF	BQ	12	80		
6	1.2	Fe ₃ O ₄ -starch-Pd(II)	THF	BQ	12	60		
7	1.5	Fe ₃ O ₄ -starch-Pd(II)	THF	BQ	10	73		
8	1.5	Fe ₃ O ₄ -starch-Pd(II)	THF	DDQ	12	-		
9	1.5	Fe ₃ O ₄ -starch-Pd(II)	THF	-	12	26		
10	1.5	Fe ₃ O ₄ -Dopamine-Pd(II) ^{[6a}	^{a]} THF	BQ	12	13		
11	1.5	Cellulose-Pd ^[8a]	THF	BQ	12	-		
12	1.5	Pd/Al ₂ O ₃ ^[8b]	THF	BQ	12	<u> </u>		

[a] Reaction condition: Butyl acrylate (51 mg, 0.4 mmol), phenyl trimethoxysilane (120 mg, 0.6 mmol), catalyst (7 mg), BQ (64 mg, 0.6 mmol), TBAF (1 M Solution in THF, 0.6mL, 0.6 mmol) in THF (2 mL), at 40 $^\circ$ C for 12h.

The optimized reaction protocol (entry 5, Table 1) was explored to perform a series of oxidative coupling reactions (Table 2). Various electron deficient alkenes such as methyl acrylate, ethyl acrylate, butyl acrylate and acrylonitrile underwent oxidative C-H arylation reactions with the organosilicon compounds to produce the desired coupling products in good yields (**3a** - **3c**, **3e**, **3j**, Table 2). Styrene, 4-fluorostyrene, 3methylstyrene and 4-methylstyrene were also employed in the oxidative cross coupling reactions resulting the products **3d**, **3f** -**3h**, **3k** (Table 2) satisfactorily.

Under the similar reaction condition, allyl acetate produces 1,3-diphenyl propene (43%) along with trace amount of cinnamyl acetate in presence of 1.5 equivalent of phenyltrimethoxysilane in 14 h of time period (reaction 1, Scheme 2). However, the same reaction produces cinnamyl acetate (30%) and trace amount 1,3-diphenyl propene within 3 h of time period (reaction 2, Scheme 2). With time, the amount of 1,3-diphenyl propene gradually increases in the reaction mixture and the concentration of cinnamyl acetate decreases. Thus, allyl acetate participates in cascade oxidative coupling followed by Tsuji-Trost allylation reaction. In presence of large excess of phenyltrimethoxysilane (3 equivalent), exclusive formation of 1,3-diphenyl propene was obtained in good amount (69%) within 14 h of time period (entry 9, Table 2) *via* the cascade oxidative coupling and allyl-aryl cross coupling reactions.

This result motivated us to explore the Pd-magnetic catalyst in organosilicon compound mediated Tsuji-Trost allylation^[9] reaction of cinnamyl acetate. It was found that cinnamyl acetate undergoes Tsuji-Trost cross-coupling reaction with phenyltrimethoxysilane efficiently to provide the desired coupling product, 1,3-diphenyl propene in good yield (84%) (entry 1, Table 3) in presence of Fe₃O₄-starch-Pd(II) catalyst and

Table 2. Oxidative Heck coupling using aryltrimethoxysilanes.^[a]

	Fe ₃ O ₄ -Starch-Pd(II)					
	1 1	2 E	3Q, TBAF air, 40	⁼, THI ° C	F 3	Z
Entry	y Z	Ar	Гime (h)		Product	Yield ^[b] (%)
1	CO ₂ Bu	Ph	12	Ph_	GO2Bu	80
2	CO ₂ Et	Ph	12	Ph 、	3b CO ₂ Et	77
3	CO ₂ Me	Ph	12	Ph 🔪	CO ₂ Me	76
4	Ph	Ph	13	Ph 、	3d Ph	74
5	CN	Ph	12	Ph 、	3e CN	78
6	р-F-С ₆ Н ₄	Ph	12	Ph 、	3f	76
7	<i>m</i> -CH ₃ -C ₆ H ₄	Ph	14	Ph 🔪	3g	72
8	<i>p</i> -CH ₃ -C ₆ H ₄	Ph	15	Ph 、	3h	68
9 ^[c]	CH ₂ OAc	Ph	14	Ph	3i Ph	69
10	CO ₂ Bu	<i>p</i> -CH ₃ -C ₆ H₂	14	p-Cł	H ₃ -C ₆ H ₄	70 CO ₂ Bu
11	Ph	<i>p</i> -OCH ₃ -C ₆ I	⊣ ₄ 14	<i>p</i> -O0	CH ₃ -C ₆ H ₄	68 Ph

[a] Reaction condition: alkene (0.4 mmol), aryltrimethoxysilane (0.6 mmol), Pdcatalyst (7 mg, 0.8 mol%), BQ (64 mg, 0.6 mmol), TBAF (1 M Solution in THF, 0.6 mL, 0.6 mmol) in THF (2 mL), at 40 °C for certain time period. [b] Yields are isolated yields. [c] The reaction was performed using 1.2 mmol (3 equiv.) of phenyltrimethoxysilane.



Scheme 2. Reactions of allyl acetate with phenyltrimethoxysilane.

TBAF in THF solvent at 60 °C under open aerial condition. Tsuji-Trost allylic couplings were performed with a series of cinnamyl acetate derivatives using various organosilane compounds (Table 3). The substituents like *o*-Me, *p*-Me, *o*-OMe, *m*-OMe, *p*-F,

p-Cl (entries 2 - 6, 8 - 10, Table 3) present in the aromatic ring of cinnamyl acetates remain unaltered under the present reaction condition. In case of *p*-chlorocinnamyl acetate, the $C(sp^2)$ -Cl functionality, did, not involve in C-C cross coupling with

condition. In case of *p*-chlorocinnamyl acetate, the C(sp²)-Cl functionality did not involve in C-C cross coupling with phenyltrimethoxysilane and selective allyl-aryl cross coupling occurred to provide the desired 1,3-diaryl propene (**5h**) product in good yield (86%) (entry 10, Table 3) under the present

Table 3. Tsuji-Trost allylic couplings using organosilane compounds.^[a]

	-12-		Fe ₃ O ₄ -Starch	n-Pd(II)		
	R^{-} OAc + $R^{2}S$	a(OMe) ₃ 2	TBAF, THF 60° C	, air		
Enti	y allylic acetate	R ²	time(h)	Proc	luct	Yield ^[b] (%)
1	Ph	Ph	4	Ph	3i Ph	84
2	o-CH ₃ -C ₆ H ₄ OAc	Ph	4 (o-CH₃-C ₆ H₄ ✓	5a Ph	70
3	p-CH ₃ -C ₆ H ₄ OAc	Ph	4.5 /	≻-CH ₃ -C ₆ H ₄	Ph 5b	76
4	<i>p</i> -CH ₃ -C ₆ H ₄ OAc	р-СН ₃ -(C ₆ H₄ 6 ⊮	o-CH₃-C ₆ H₄ ✓	5c	60
5	o-OMe-C ₆ H ₄ OAc	Ph	5 0	-OMe-C ₆ H ₄	5d Ph	68
6	m-OMe-C ₆ H ₄	Ph	4.5 ^m -	OMe-C ₆ H ₄	5e Ph	78
7	Ph	Ph	4	Ph	3i Ph	82
8	<i>p</i> -F-C ₆ H ₄ OAc	Ph	4	<i>p</i> -F-C ₆ H ₄	Sf Ph	89
9	p-F-C ₆ H ₄	р-СН ₃ -(C ₆ H₄ 4.5	<i>p</i> - F -C ₆ H₄ √	50	74
10	<i>p</i> -CI-C ₆ H ₄ OAc	Ph	4.5	<i>p</i> -CI-C ₆ H₄ ✓	5h Ph	86
11	Ph	C ₂ H ₃	4.5	Ph	5i	74

[a] Reaction condition: allylic acetate (0.4 mmol), organosilicon compound (0.6 mmol), Pd-catalyst (7 mg, 0.8 mol%), TBAF (1 M Solution in THF, 0.6mL, 0.6 mmol) in THF (2 mL), at 60 °C for certain time period. [b] Yields are isolated yields.

reaction condition. The vinyltrimethoxysilane was also found reactive to transfer the vinyl group resulting the formation of 1,4diene product (**5i**) in 74% yield (entry 11, Table 3). Interestingly, the *cis*-cinnamyl acetate undergoes Tsuji-Trost coupling with phenyltrimethoxysilane (entry 7, Table 3) to provide *trans*-1,3diphenylpropene (**3i**) exclusively. This result suggests the formation of $\eta 3$ - π -allyl complex of palladium (**A**) as the key intermediate (Scheme 3) which equilibrates with its *trans*-



Scheme 3. Formation of *trans*-1,3-diphenylpropene from *cis*-cinnamyl acetate *via* η 3- π -allyl complex.

geometry (**C**), *via* the well-known η 1- σ -alkyl complex (**B**)^[10] and reductive elimination from the more stable *trans*-intermediate (**C**) produces *trans*-1,3-diphenylpropene (**3i**) as the sole product.

The allylic coupling reaction between cinnamyl acetate and phenyltrimethoxysilane (entry 1, Table 3) was chosen to perform the hot filtration test for checking the heterogeneity of the magnetic catalyst during the course of the reaction. The reaction was observed to be arrested completely upon removal of the magnetic catalyst after an intermediate time period (1 h) and it proves the absence of palladium in the solution phase of the reaction mixture. Thus, starch binds the palladium firmly on the surface of the magnetic nanoparticles and prevents the leaching of palladium into the solution.

Upon completion of the reaction, the magnetic palladium catalyst can be recovered easily from the reaction mixture with the aid of an external magnet (Fig. 5). After washing the catalyst with acetone and drying under vacuum, the catalyst was used in the next batch of reaction efficiently.



Figure 5. Magnetic separation of Fe_3O_4 -starch-Pd(II) catalyst by an external magnet.

In the cross-coupling reaction of butyl acrylate with phenyltrimethoxysilane, the magnetic catalyst was recycled efficiently for 4 times without much loss of catalytic activity. The yield of desired product, **3a** was 78% at the 4th cycle of reaction (Fig. 6). However, the yield gradually decreases beyond 4th cycle and it was 68% at 6th cycle of reaction (Fig. 6).



Figure 6. The catalyst recyclability chart.

Conclusions

In conclusion, efficient protocols for C-C cross coupling reactions such as oxidative Heck coupling and Tsuji-Trost allylation have been developed using organosilicon compounds as aryl donors and heterogeneous magnetic palladium catalyst. The biopolymer (starch) coated magnetic nanoparticles were used as the heterogeneous support for palladium catalyst which is easy to recover and shows good recyclability. The catalyst allows the reactions to proceed under open aerial condition and thus avoids the necessity of moisture and oxygen free inert atmosphere. Catalyst reusability, air compatibility and good yields of the products make the protocols economically sustainable.

Experimental Section

General experimental procedures:

Representative experimental procedure for oxidative-Heck coupling reaction of *n*-butyl acrylate with phenyl trimethoxysilane (entry 1, Table 2). A mixture of *n*-butyl acrylate (0.051 g, 0.4 mmol), phenyltrimethoxysilane (0.120 g, 0.6 mmol), Pd-catalyst (7 mg, 0.8 mol%), TBAF (1M solution in THF, 0.6 mL, 0.6 mmol), and BQ (0.064 g, 0.6 mmol), in THF (2 ml), was stirred at 40 °C for 12 h under aerial atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction the Pd-catalyst was separated by an external magnet and the crude product was obtained by usual work- up using EtOAc. The crude product was purified by column chromatography over silica gel using petroleum ether-ethyl acetate (97:3) solvent mixture. The desired product, *n*-butyl cinnamate (**3a**) was obtained as colorless oil (65 mg, 80%).

This procedure is followed for preparation of other compounds (**3b** - **3k**) listed in Table 2.

Representative experimental procedure for Tsuji-Trost coupling of cinnamyl acetate with phenyltrimethoxysilane (entry 1, Table 3). A mixture of cinnamyl acetate (0.070 g, 0.4 mmol), phenyltrimethoxysilane (0.120 g, 0.6 mmol), Pd- catalyst (7 mg, 0.8 mol%) and TBAF (1 M solution in THF, 0.6 mL, 0.6 mmol) in THF (2 mL) was stirred at 60 °C for 4 h under air atmosphere. The reaction was monitored by TLC. After catalyst separation by external magnet, the reaction mixture was worked-up by usual procedure using ethyl acetate. The crude product was purified by column chromatography over silica gel using petroleum ether-ethyl acetate (99:1) solvent mixture to get the desired product, 1,3-diphenyl propene (**3i**) as a colorless oil (65.4 mg, 84%).

This procedure is followed for preparation of other compounds (**5a** - **5i**) listed in Table 3.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgements

Debabrata Patra is thankful to CSIR-India for his JRF fellowship. We are pleased to acknowledge UGC-BSR Start-up grant (FD Diary No.4855; Dated: 24.09.2018) for the financial support. We also acknowledge RUSA 2.0 research grant from Jadavpur University, UGC-CAS program in Chemistry, Jadavpur University and the DST-PURSE Program at Jadavpur University.

Keywords: Magnetic palladium catalyst • Oxidative Heck coupling • Tsuji-Trost allylic coupling • Organosilicon compounds • Recyclable catalyst

a) A. B. Dounay, L. E. Overman, *Chem. Rev.* 2003, *103*, 2945 – 2964;
b) A. Bianco, C. Cavarischia, M. Guiso, *Natural Product Research*, 2006, *20*, 93–97;
c) A. Madin, C. J. O'Donnell, T. Oh, D. W. Old, L. E. Overman, M. J. Sharp, *J. Am. Chem. Soc.* 2005, *127*, 18054 - 18065;
d) B. M. Trost, M. L. Crawley, *Chem. Rev.* 2003, *103*, 2921 – 2944;
e) B. M. Trost, *Tetrahedron* 2015, *71*, 5708–5733;
f) Y. Zhang, H. -C. Shen, Y. -Y. Li, Y. –S. Huang, Z. –Y. Han, X. Wu, *Chem. Commun.* 2019, *55*, 3769 – 3772.

[2] a) Y. Li, Z. Qi, H. Wang, X. Fu, C. Duan, J. Org. Chem. 2012, 77, 2053–2057; b) A. -L. Lee, Org. Biomol. Chem. 2016, 14, 5357 – 5366.

[3] J. P. Parrish, Y. C. Jung, S. Il Shin, K. W. Jung, J. Org. Chem. 2002, 67, 7127 – 7130.

- [4] a) T. Koike, X. Du, T. Sanada, Y. Danda, A. Mori, *Angew. Chem. Int. Ed.* 2003, *42*, 89 92; b) K. Hirabayashi, J. –i. Ando, J. Kawashima, Y. Nishihara, A. Mori, T. Hiyama, *Bull. Chem. Soc. Jpn.* 2000, *73*, 1409 1417; c) A. Mori, Y. Danda, T. Fujii, K. Hirabayashi, K. Osakada, *J. Am. Chem. Soc.* 2001, *123*, 10774 10775; d) Z. Ye, F. Chen, F. Luo, W. Wang, B. Lin, X. Jia, J. Cheng, *Synlett* 2009, *13*, 2198–2200; e) T. Mino, M. Shibuya, S. Suzuki, K. Hirai, M. Sakamoto, T. Fujita, *Tetrahedron* 2012, *68*, 429 432; f) K. Hirabayashi, Y. Nishihara, A. Mori, T. Hiyama, *Tetrahedron Lett.* 1998, *39*, 7893-7896.
- [5] Y. Nakao, T. Hiyama, Chem. Soc. Rev. 2011, 40, 4893–4901.
- a) A. Saha, J. Leazer, R. S. Varma, Green Chem. 2012, 14, 67 71; b) [6] B. R. Vaddula, A. Saha, J. Leazer, R. S. Varma, Green Chem. 2012, 14, 2133 - 2136; c) Q. Zhang, X. Yang, J. Guan, ACS Appl. Nano Mater. 2019, 2, 4681-4697; d) H. M. Tanuraghaja, M. Farahi, RSC Adv. 2018, 8, 27818-27824; e) M. -N. Chen, L. -P. Mo, Z. -S. Cui, Z. -H. Zhang, Current Opinion in Green and Sustainable Chemistry, 2019, 15, 27-37; f) R. B. N. Baig, R. S. Varma, Chem. Commun. 2013, 49, 752 - 770; g) Z. B. Shifrina, L. M. Bronstein, Front. Chem. 2018, 6, 298; h) V. Polshettiwar, R. Lugue, A. Fihri, H. Zhu, M. Bouhrara, J. -M. Basset, Chem. Rev. 2011, 111, 3036 - 3075; i) B. -L. Li, M. Zhang, H. -C. Hu, X. Du, Z. -H. Zhang, New J. Chem. 2014, 38, 2435 - 2442; j) M. V. Parmekar, A. V. Salker, J. Nanopart. Res. 2019, 21, 220; k) M. P. Lati, M. I. Naeem, M. A. - Asli, F. Shirini, M. A. Rezvani, B. Åkermark, E. V. Johnston, O. Verho, ChemistrySelect 2018, 3, 7970-7975; I) M. Nasrollahzadeh, Z. Issaabadi, R. S. Varma, ACS Omega 2019, 4, 14234-14241; m) Z. Shahamat, F. Nemati, A. Elhampour, J. Porous Mater. 2019, https://doi.org/10.1007/s10934-019-00795-x.
- [7] a) N. H. Abdullah, K. Shameli, E. C. Abdullah, L. C. Abdullah, *Chinese Chemical Letters* 2017, *28*, 1590 1596; b) J. –S. Jiang, Z. –F. Gan, Y. Yang, B. Du, M. Qian, P. Zhang, *J. Nanopart. Res.* 2009, *11*, 1321 1330; c) M. Zheng, J. Lu, D. Zhao, *Science of the Total Environment* 2018, *622 623*, 930 941; d) A. J. Cole, A. E. David, J. Wang, C. J. Galbán, H. L. Hill, V. C. Yang, *Biomaterials* 2011, *32*, 2183 2193. e) D. K. Kim, M. Mikhaylova, F. H. Wang, J. Kehr, B. Bjelke, Y. Zhang, T.

WILEY-VCH

Tsakalakos, M. Muhammed, *Chem. Mater.* **2003**, *15*, 4343-4351; f) T. T. Dung , T. M. Danh , L. T. M. Hoa , D. M. Chien, N. H. Duc, *Journal of Experimental Nanoscience* **2009**, *4*, 259 – 267; g) C. Jin, Z. Haiyan, L. Liping, Z. Li, *Digest Journal of Nanomaterials and Biostructures* **2014**, *9*, 143 – 149; h) C. Saikia, A. Hussain, A. Ramteke, H. K. Sharma, T. K. Maji, *Starch/Stärke* **2014**, *66*, 760 – 771.

- a) B. R. Vaddula, A. Saha, R. S. Varma, J. Leazer, *Eur. J. Org. Chem.* 2012, 6707–6709; b) N. S. Babu, N. Lingaiah, R. Gopinath, P. S. S. Reddy, P. S. S. Prasad, J. Phys. Chem. 2007, 111, 6447 6453.
- [9] a) H. Matsuhashi, S. Asai, K. Hirabayashi, Y. Hatanaka, A. Mori, T. Hiyama, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1943 1952; b) A. A. Zemtsov, V. V. Levin, A. D. Dilman, M. I. Struchkova, P. A. Belyakov, V. A. Tartakovsky, J. Hu, *Eur. J. Org. Chem.* **2010**, 6779–6785; c) Y. Tsuji, N. Yamada, S. Tanaka, *J. Org. Chem.* **1993**, *58*, 16-17; d) M. –R. Brescia, P. DeShong, *J. Org. Chem.* **1998**, *63*, 3156-3157; e) M. E. Hoke, M. –R. Brescia, S. Bogaczyk, P. DeShong, *J. Org. Chem.* **2002**, *67*, 327 335; f) G. W. Kabalka, G. Dong, B. Venkataiah, C. Chen, *J. Org. Chem.* **2005**, *70*, 9207-9210; g) R. Dey, K. Chattopadhyay, B. C. Ranu, *J. Org. Chem.* **2008**, *73*, 9461–9464; h) H. Matsuhashi, Y. Hatanaka, M. Kuroboshi, T. Hiyama, *Tetrahedron Lett.* **1995**, *36*, 1539–1540.
- [10] a) A. Saha, B. C. Ranu, *Org. Biomol. Chem.* 2011, *9*, 1763 1767; b) A. Ariafard, Z. Lin, *Organometallics* 2005, *24*, 3800 3806; c) B. Wucher, M. Moser, S. A. Schumacher, F. Rominger, D. Kunz, *Angew. Chem. Int. Ed.* 2009, *48*, 4417 4421.

WILEY-VCH

Entry for the Table of Contents

Key Topic: Magnetic Pd-Catalyst

COMMUNICATION



Magnetically retrievable palladium nano-catalyst has been used in Oxidative Heck coupling and Tsuji-Trost allylic coupling reactions using organosilicon compounds as the aryl donors under open aerial condition. The magnetic catalyst is easily recovered and recycled efficiently. Wide substrate scope and good yields of the products were obtained in both the cases.