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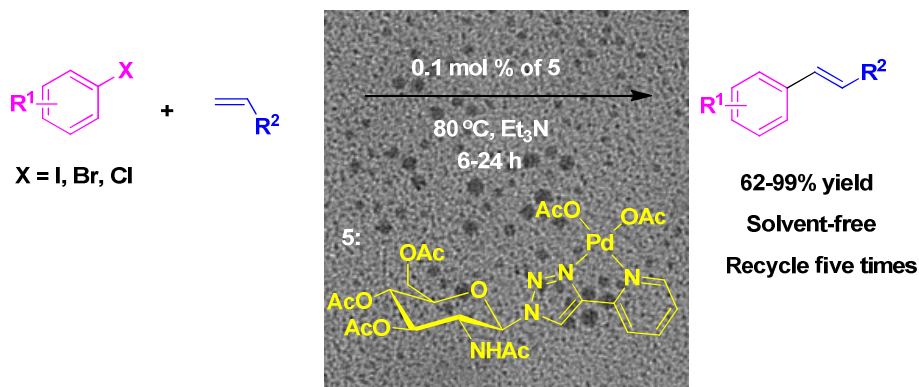
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Novel D-glucosamine-derived pyridyl-triazole@palladium catalyst for solvent-free Mizoroki-Heck reactions and its application in the synthesis of Axitinib

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A green method for the synthesis of D-glucosamine-derived triazole@palladium catalyst has been described. The synthesized catalyst containing a 2-pyridyl-1,2,3-triazole ligand was prepared *via* a click route in high yields and was explored in Heck cross-coupling reactions between different aryl halides and olefins under solvent-free conditions. The catalyst can be separated from the reaction mixture and reused at least six times with superior activity. In addition, by using this protocol, the marketed drug Axitinib (antitumor) could be synthesized easily.

Introduction

Palladium-catalyzed Mizoroki-Heck coupling reaction is one of the most powerful synthetic methods for the formation of C-C bonds between alkenes and aryl or alkyl halides.¹ The Mizoroki-Heck coupling products find good applications as intermediates in the preparation of materials, natural products, and bioactive compounds.² However, drawbacks like the high cost of palladium catalysts, harsh reaction conditions and low yields greatly hamper its large-scale practical applications, especially in the pharmaceutical industry.³ Attempts to overcome these boundaries include attempted syntheses of more efficient catalysts,⁴ performing coupling reactions in ionic liquids or water,⁵ the utilization of solvent-free reaction conditions and the application of non-classical energy sources such as microwave irradiation, ultrasonication or high pressure and mechanochemical techniques.⁶ Recently, interest in the exploration of catalytic reactions in solvent-free conditions is increasing dramatically due to the solvent-free organic syntheses are generally faster, selective, higher yielding with cleaner products, environmentally benign and involve simple operational procedure as compared to the classical reaction.⁷ Hence during the past years, many efforts

have been made to design novel ligands/catalysts to promote transformations under solvent-free conditions.⁸ While how to keep the activity of catalyst in solvent-free catalytic reaction was still a real challenge.

To date, numerous attempts have been made to prepare new heterogeneous metal catalysts for the coupling reactions, because of their reusability compared to homogeneous catalysts.⁹ The advantages of heterogeneous processes, ease of separation of product, reusability of catalyst and better steric control of the reaction intermediate, prompted researchers to immobilize a homogeneous catalytic site on various supports such as silica,¹⁰ zeolites,¹¹ magnetic materials,¹² and polymers.¹³ And from the published literatures, we also can know most of these catalysts are in nano-size. Among these heterogeneous metal catalysts, the biopolymers (such as starch, cellulose, chitosan or pectin) offers a unique set of environmentally benign properties such as biodegradability to harmless products, biocompatibility, stability to air and moisture, and cheapness.¹⁴ However, extensive progress in designing more sustainable chemical processes takes place if biopolymers themselves without any post-modification. On the other hand, one of the major reasons for poor recyclability is the aggregation and agglomeration of metal nanoparticles into less active large particles during the reaction due to the high surface energy of nanoparticles. Even for these systems using molecular catalysts, the aggregation and agglomeration still occurred because metal nanoclusters were formed as the reaction proceeded and all of these lead to the drastic decrease in activity of the reused catalysts. In this context, the development of highly active and easily recoverable catalysts which can be used not only in academic fields but also in industrial applications are full of significance.

Following our interesting in carbohydrates as a source of highly efficient catalysts,¹⁵ we have recently reviewed that D-glucosamine as a cheap and readily available chiral scaffold for the synthesis of a series of novel ligands and organocatalysts.¹⁶ And our previous investigation and other groups' work revealed that support structure and functional groups grafted on the support played an important role in preventing the aggregation of metal nanoparticles into the less active large particles.^{14a,17} The

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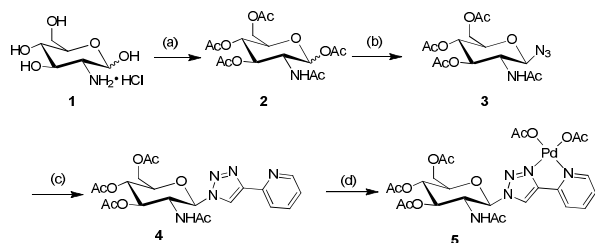
‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

hydrogen bonding interaction and special structure of the sugar ring may inhibit the motion of metal nanoparticles, thereby preventing the undesired aggregation and agglomeration.

Herein, we report an efficient method for the synthesis of D-glucosamine-derived triazole@palladium catalyst. The synthesized catalyst containing a 2-pyridyl-1,2,3-triazole ligand was prepared *via* a click route and was explored in Heck cross-coupling reactions between different aryl halides and olefins under solvent-free conditions. The catalyst can be separated from the reaction mixture and reused at least six times with superior activity. In addition, by using this protocol, the marketed drug Axitinib (antitumor) could be synthesized easily.

Results and discussion

Catalyst synthesis and characterization



Scheme 1 Synthesis of D-Glucosamine-derived triazole@Pd catalyst **5**. Reaction conditions: (a) AcONa/(AcO)₂O, 12 h; (b) TMSN₃, SnCl₄, CH₂Cl₂, rt; (c) 2-ethynylpyridine, CuSO₄/NaAsc, MeOH/H₂O, rt, 12 h; (d) Pd(OAc)₂, toluene, rt, 6h.

The synthetic pathway for chelating palladium complexes is depicted in Scheme 1. Acetylation of the free D-glucosamine using AcONa/(AcO)₂O to afford sugar substrate (**2**) and the azide group was introduced into **2** through a simple procedure and verified by the appearance of the N₃ band at 2118 cm⁻¹ in FT-IR spectra (Figure S1, ESI[†]). Then azide (**3**) underwent a click process with commercially available 2-ethynylpyridine in the presence of copper sulfate and sodium ascorbate in *tert*-butanol. The resulting D-glucosamine-derived triazole (**4**) was further treated with Pd(OAc)₂ in toluene to provide the desired solid catalyst (**5**).

Complex **5** is stable in air and moisture. They can be stored in air for a long period of time. They are characterized by ¹H, ¹³C NMR, 2D ROESY NMR spectrum, Infra-red analyses (FT-IR), Thermogravimetric analysis (TG) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). It was clear that the proton signals on pyridine and triazole rings of Pd(OAc)₂ in general were shifted downfield apparently (Fig. 1), which indicated that the palladium ion was coordinated with both units of the ligand and the triazole unit worked as a part of the bidentate chelator. Meanwhile, because the triazole ligand could bind with the palladium metal through either N2 or N3 atom, the

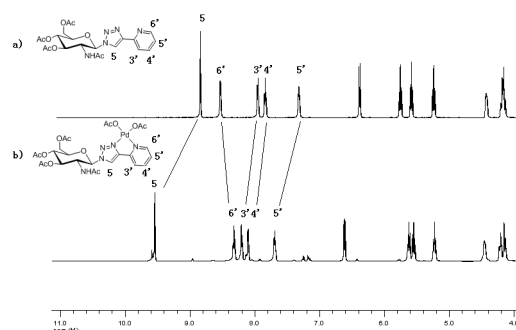


Figure 1 Partial ¹H NMR spectra (400 MHz, DMSO-*d*₆, 298 K) of (a) the ligand D-Glucosamine-derived triazoles **4**, (b) the palladium complex Pd@triazoles **5**.

spectra of PdL(OAc)₂ showed two sets of proton signals, the ratio of which was around 1:5. Hence the formation of six-membered chelate rings by binding with the N3 atom and the nitrogen atom of pyridine is considered to be the predominant structure. Then a two-dimensional ROESY NMR experiment was conducted, with the aim of examining the potential spatial proximities among the different protons of catalyst **5** (Figure S4, ESI[†]). From the spectrum, it turned out that no contacts were observed among the aromatic protons of triazole-pyridine and the sugar ring protons, implying that the functional group was not embraced in the hydrophobic cavity of the D-glucosamine.

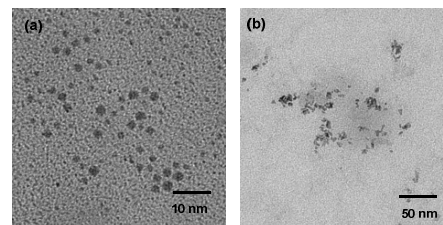


Figure 2 TEM images of (a) catalyst **5**, (b) recovered catalyst **5** after the sixth run.

The surface morphology of the synthesized catalyst **5** was also characterized by TEM. The TEM analysis showed that the average diameter of the catalysts' diameter was about 3–7 nm and the dispersion of the Pd particles was very well (Figure 1a). The TEM images also suggested that no palladium clusters were formed during the preparation.

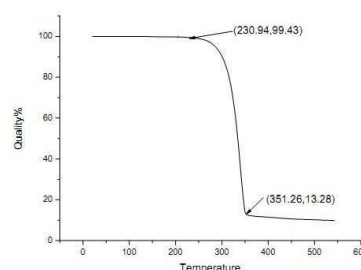


Figure 3 Thermogravimetric plots of D-glucosamine-derived triazoles@Pd catalyst **5**.

Entry	Solvent	Base	Catalyst (mol %)	Time (h)	Yield ^b (%)
1	DMSO	Et ₃ N	0.1	6	97
2	DMF	Et ₃ N	0.1	6	80
3	Toluene	Et ₃ N	0.1	6	55
4	Dioxane	Et ₃ N	0.1	6	61
5	H ₂ O	Et ₃ N	0.1	6	trace
6	Neat	Et ₃ N	0.1	6	99(95) ^c
7	Neat	NaOH	0.1	12	35
8	Neat	KOAc	0.1	12	35
9	Neat	K ₂ CO ₃	0.1	12	45
10	Neat	Cs ₂ CO ₃	0.1	12	61
11	Neat	K ₃ PO ₄	0.1	12	23
12	Neat	-	0.1	6	0
13	Neat	Et ₃ N	0.1	12	77 ^d
14	Neat	Et ₃ N	0.05	6	81

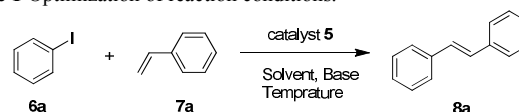
The catalysts was also characterized by TG to study its thermal behavior and stability at elevated temperatures and the TG shows that the catalyst **5** are stable up to 230.9 °C (Figure 3), suggesting that its high thermal stability allows it to be compatible with most organic reactions. The palladium amount of which measured by inductively coupled plasma atomic emission spectrometry (ICP-MS) was 1.41 mmol/ g⁻¹.

Catalytic studies

To evaluate the catalytic performance of catalyst, the model coupling reaction between iodobenzene **6a** and styrene **7a** in the presence of catalyst **5** was conducted to screen the optimal reaction conditions, including solvents, bases, temperature and catalyst loadings. Initially, considering that the solvent always plays important roles in Heck coupling reaction. Thus, we have studied the solvent effect, and the results were shown in Table 1. After much experimentation on optimizing solvent, it was found that the use of a high polar solvent like DMF and DMSO afforded product **3a** in high yields (Table 1, entries 1 and 2). In stark contrast, the coupling reaction proceeded less efficiently in nonpolar solvent such as dioxane and toluene (Table 1, entries 3

and 4). With H₂O as the solvent, no target product was obtained (Table 1, entry 5). Excellent yield was achieved under solvent-free conditions (Table 1, entry 6). In order to find a suitable base that would effect the desired reaction, we also screened several bases such as NaOH, KOAc, K₂CO₃, and K₃PO₄. All the reactions examined led to some conversion, albeit with quite different efficiencies (Table 1, entries 7-11), with Et₃N being the most reactive, allowing the reaction to be completed in 6 h. However the coupling reactions did not proceed in the absence of base (Table 1, entry 12). Lowering the reaction temperature to 60 °C decreased the yield to 77% even with a prolonged reaction time (Table 1, entry 13). When the amount of

Table 1 Optimization of reaction conditions.^a



^aReaction conditions: iodobenzene (1 mmol), styrene (2 mmol), 0.1 mol% of **5**, base (3 mmol), solvent (3 mL) under air. ^bDetermined by GC-MS.

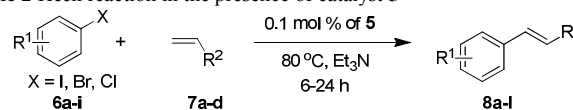
^cIsolated yield in parentheses. ^dUnder 60 °C.

catalyst was reduced to 0.05 mol%, the yields decreased obviously (Table 1, entry 14). Thus, we gained the optimal conditions: 1.0 mmol iodobenzene, 2.0 mmol styrene, 0.1 mol% catalyst **5**, 3.0 mmol Et₃N, at 80 °C under solvent-free conditions.

With optimal conditions determined, the scope of Heck coupling reactions of iodobenzene, bromobenzene and chlorobenzene with various olefins was investigated and the results are summarized in Table 2. Many valuable functional groups such as hydroxyl-, chloro-, acetyl and trifluoromethyl groups were well tolerated. We found substrate with electron-withdrawing group on the benzene ring performed better than those with electron-donating group. Furthermore, substituents at *meta*-, or *ortho*-positions of the benzene ring do not affect the efficiency of this transformation (Table 2, entries 10-12). This catalytic system was also applied for the bromobenzene and chlorobenzene. It is clear from Table 2 that aryl bromides containing electron donating, electron withdrawing, or electron neutral substituents are coupled in good yields (Table 2, entries 13-18). However, aryl chloride coupled with olefins in moderate yields within 24 h reaction times and also much higher temperature were needed (Table 2, entries 19-21).

The optimized conditions were also applied to Heck reactions between methyl acrylate and *t*-butyl acrylate with iodobenzene and bromobenzene, two olefins can give the products in excellent yield and the *t*-butyl acrylate acrylate substrate was the best (Table 2, entries 22-25).

Table 2 Heck reaction in the presence of catalyst **5**^a



^aUnless otherwise stated, the reaction were carried out using 1.0 mmol aryl halid, 2 mmol olefin, 3.0 mmol Et₃N, 0.1 mol% of **5**, at 80 °C under air. ^bIsolated yield. ^cUnder 120 °C.

Further experiments were performed to verify the catalyst recyclability using the reaction of iodobenzene with styrene as a model system. After the first use, the catalyst was recovered by simple filtration and reused in the next run after a simple workup. We were pleased to find that the recovered catalyst was successfully reused in the subsequent six cycles with a consistent catalytic activity, giving the products in excellent yields (84-94%). No Pd metal was detected in the solution by ICP analysis. Furthermore, the TEM image of the catalyst taken after the sixth cycle of the reaction does not show significant change in the morphology and the size of the catalyst (5-9 nm) (Figure 1b), which indicates the retention of the catalytic activity after recycling.

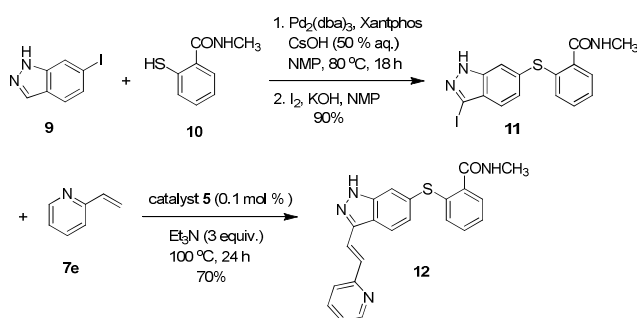
Run	1	2	3	4	5	6
Yield(%) ^b	94	90	90	88	85	84

Table 3. Catalyst recycling for solvent-free Mizoroki-Heck reactions.^a

^aReaction conditions: see Table 1, entry 6. The catalyst was recovered by simple filtration after reaction. ^b Isolated yield.

With this methodology in hand, we turned our attention to the synthesis of Axitinib, an important anticancer agent of the vascular endothelial growth factor (VEGF)(Scheme 3).¹⁸ Axitinib has exhibited a tendency to retain palladium, a fact that likely is due to the indazole ring that may enable formation of a relatively stable complex with the metal. As a result, the separation of the Axitinib API from residual palladium has been a challenging task.^{19,20} So we planned to enable the palladium removal process using our system to reduce the residual Pd content. Firstly, a Pd₂(dba)₃-catalyzed Migita coupling reaction between commercially available 6-iodoindazole **9** and 2-mercapto-*N*-methylbenzamide **10** and iodination reactions afforded the iodoindazole intermediate **11** in 90% yield. Then the intermediate **11** was treated with 2-vinylpyridine **7e** (2 mmol) in the presence of 0.1 mol% of catalyst **5** and Et₃N (3.0 mmo) at 100 °C for 24 h, Axitinib was isolated in 70% yield.

Entry	R ¹	X	R ²	Time (h)	Yield ^b (%)
1	H	I	Ph	6	95(8a)
2	4-CH ₃ O	I	Ph	6	83(8b)
3	4-CH ₃	I	Ph	6	86(8c)
4	4-NO ₂	I	Ph	6	95(8d)
5	4-CF ₃	I	Ph	6	94(8e)
6	4-Cl	I	Ph	6	82(8f)
7	4-OH	I	Ph	12	71 ^c (8g)
8	4-CH ₃ CO	I	Ph	6	84(8h)
9	4-Ph	I	Ph	6	85(8i)
10	3-NO ₂	I	Ph	6	96(8j)
11	3-NO ₂	I	Pyridine	6	92(8k)
12	2-CH ₃	I	Ph	12	81(8l)
13	H	Br	Ph	12	82(8a)
14	4-CH ₃ O	Br	Ph	12	80(8b)
15	4-CH ₃	Br	Ph	12	83(8c)
16	4-NO ₂	Br	Ph	12	92(8d)
17	4-CF ₃	Br	Ph	12	90(8e)
18	4-Ph	Br	Ph	12	80(8i)
19	H	Cl	Ph	24	70 ^c (8a)
20	4-CH ₃ O	Cl	Ph	24	62 ^c (8b)
21	4-NO ₂	Cl	Ph	24	73 ^c (8k)
22	H	I	CO ₂ Me	6	93(8m)
23	H	Br	CO ₂ Me	6	85(8n)
24	H	I	CO ₂ <i>t</i> -Bu	6	95(8m)
25	H	Br	CO ₂ <i>t</i> -Bu	6	83(8n)



Scheme 2 Application of the catalyst **5** in the synthesis of Axitinib.

Such a heterogeneous catalysts not only gave the product in satisfying yield but also provided an efficient method for removal of residual palladium from Axitinib drug substance material. Residual Pd content in system was determined to be not more than 20 ppm by atomic absorption spectroscopy. Nextly the method was also successfully applied to the synthesis of novel fluoroquinolone derivatives (Scheme S1, ESI†).

Conclusions

In conclusion, we have prepared a new D-glucosamine-derived triazole@palladium catalyst via a “click” route and was explored in Heck cross-coupling reactions between different aryl halides and olefins under solvent-free conditions. The catalyst was very stable and could be easily separated from the products and reused at least six times with superior activity. The significantly enhanced recyclability may be attributed to the catalyst which could efficiently prevent the aggregation and agglomeration of Pd particles formed during the catalytic reaction into the less active large particles, as evidenced by TEM. In addition, by using this protocol, the marketed drug Axitinib (antitumor) could be synthesized easily and such an efficient process for removal of residual palladium from Axitinib drug was well provided. The applicability of the D-glucosamine-derived triazole@palladium catalyst in other fields of organic transformation is underway in our laboratory.

Experimental section

The starting materials were commercially available and were used without further purification except solvents. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 °C) and ethyl acetate. Melting points were determined on an X-5 Data microscopic melting point apparatus. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature with CDCl₃ or DMSO-*d*₆ as solvent unless otherwise noted and tetramethylsilane (TMS) as the internal standard. ¹H NMR data were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet,

m = multiplet and br = broad), coupling constant (*J* values, Hz). Mass spectra (EI-MS) were acquired on an Agilent 5975 spectrometer. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates. The sugar substrates were prepared according to our previous reports.¹⁵ All compounds were characterized by ¹H NMR and mass spectroscopy, which are consistent with those reported in the literature.¹⁻³

General procedure for solvent-free Mizoroki-Heck reaction.

To a flask, a mixture of D-glucosamine-derived triazole @ palladium catalyst **5** (0.1 mol%), aryl halide (1 mmol), olefins (2 mmol) and Et₃N (3 mmol) were added and heated at 80 °C under solvent-free conditions. After completion of the reaction, ethylacetate (10 mL) was added to the flask. The catalyst was separated by simple filtration. Water (3 × 15 mL) was added to the ethylacetate phase and decanted. The organic layer was dried over anhydrous Na₂SO₄. After evaporation of the solvent, the resulted crude products was purified by column chromatography (hexane/ethylacetate) giving the pure products in excellent yields.

General procedure for recycling of the catalyst in solvent-free Mizoroki-Heck reaction.

After completion of the reaction at the first run, the reaction mixture was cooled down to room temperature and ethylacetate (5 mL) was added to the reaction mixture to extract organics. The ethylacetate phase was sucked from the vial by a syringe and the catalyst was dried under vacuum. After complete drying, the catalyst was reused for the similar reaction. This process was repeated for six runs.

General procedure for synthesis of Axitinib under solvent-free condition.

To a flask, a mixture of intermediate **11** (1 mmol), 2-vinylpyridine **7e** (2 mmol), Et₃N (3 mmol) and D-glucosamine-derived triazole @palladium catalyst **5** (0.1 mol%) were added and heated at 100 °C under solvent-free conditions. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was allowed to cool to room temperature, ethylacetate (10 mL) was added to the flask. The catalyst was separated by simple filtration and the aqueous phase was extracted with CH₂Cl₂ for 3 times (3 × 2 mL). Then the combined organic layers were dried over anhydrous Na₂SO₄, concentrated under vacuum and purified by column chromatography (hexane/ethyl acetate 10:1) to afford the desired product. Residual Pd content in solvent was determined to be not more than 20 ppm by atomic absorption spectroscopy.

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Notes and references

- (a) J. Ruan and J. Xiao, *Acc. Chem. Res.*, 2011, **44**, 614; (b) A. Balanta, C. Godard and C. Claver, *Chem. Soc. Rev.*, 2011, **40**, 4973; (c) C. A. Fleckenstein and H. Pleni, *Chem. Soc. Rev.*, 2010, **39**, 694.
- N. Marion and S. P. Nolan, *Acc. Chem. Res.*, 2008, **41**, 1440.
- J. Magano and J. R. Dunetz, *Chem. Rev.*, 2011, **111**, 2177.
- T. Nishikata, Y. Noda, R. Fujimoto and T. Sakashita, *J. Am. Chem. Soc.*, 2013, **135**, 16372.
- (a) H. Yang, X. Han, G. Li, and Y. Wang, *Green Chem.*, 2009, **11**, 1184; (b) R. Wang, B. Twamley and J. M. Shreeve, *J. Org. Chem.*, 2006, **71**, 426; (c) S. G. Babu, N. Neelakandeswari, N. Dharmaraj, S. D. Jackson and R. Karvembu, *RSC Adv.*, 2013, **3**, 7774.
- W. Susanto, C. Y. Chu, W. J. Ang, T. C. Chou, L. C. Lo, and Y. Lam, *J. Org. Chem.*, 2012, **77**, 2729.
- (a) Y. N. Zhao, Jian Li, C. J. Li, K. Yin, D. Y. Ye and X. S. Jia, *Green Chem.*, 2010, **12**, 1370; (b) A. G. Ying, L. Liu, G. F. Wu, G. Chen, X. Z. Chen and W. D. Ye, *Tetrahedron Lett.*, 2009, **50**, 1653. (c) A. Sakakura, K. Kawajiri, T. Ohkubo, Y. Kosugi, and K. Ishihara, *J. Am. Chem. Soc.*, 2007, **129**, 14775.
- (a) M. Tamura, S. M. A. H. Siddiki and K. Shimizu, *Green Chem.*, 2013, **15**, 1641; (b) M. Hosseini-Sarvari and F. Moeini, *New J. Chem.*, 2014, **38**, 624; (c) Z. N. Siddiqui and T. Khan, *Catal. Sci. Technol.*, 2013, **3**, 2032.
- L. Yin and J. Leibescher, *Chem. Rev.*, 2007, **107**, 133.
- B. Li, M. Li, C. H. Yao, Y. F. Shi, D. R. Ye, J. Wu and D. Y. Zhao, *J. Mater. Chem.*, 2013, **1**, 6742.
- (a) L. Gu, D. Ma, S. Yao, C. Wang, W. Shen and X. Bao, *Chem. Commun.*, 2010, **46**, 1733; (b) M. Iwasaki and H. Shinjoh, *Chem. Commun.*, 2011, **47**, 3966; (c) Y. Zhu, Z. Hua, X. Zhou, Y. Song, Y. Gong, J. Zhou, J. Zhao and J. Shi, *RSC Adv.*, 2013, **3**, 4193.
- (a) V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara and J. M. Basset, *Chem. Rev.*, 2011, **111**, 3036; (b) R. B. N. Baig and R. S. Varma, *Chem. Commun.*, 2012, **48**, 2582.
- J. Zhang, D. Han, H. Zhang, M. Chaker, Y. Zhao and D. Ma, *Chem. Commun.*, 2012, **48**, 11510.
- (a) C. Shen, J. Xu, W. B. Yu and P. F. Zhang, *Green Chem.* 2014, **16**, 3007. (b) Y. H. Yang, J. H. Cui, M. T. Zheng, C. F. Hu, S. Z. Tan, Y. Xiao, Q. Yang and Y. L. Liu, *Chem. Commun.*, 2012, **48**, 380; (c) A. E. Kadib, K. Molvinger, M. Bousmina, and D. Brunel, *Org. Lett.*, 2010, **12**, 948; (d) B. C. E. Makhubela, A. Jardine and G. S. Smith, *Green Chem.*, 2012, **14**, 338.
- (a) C. Shen, P. F. Zhang and X. Z. Chen, *Helv. Chim. Acta.*, 2010, **93**, 2433; (b) C. Shen, H. J. Xia, H. Zheng, P. F. Zhang and X. Z. Chen, *Tetrahedron: Asymmetry*, 2010, **21**, 1936; (c) C. Shen, F. Y. Shen, H. J. Xia, P. F. Zhang and X. Z. Chen, *Tetrahedron: Asymmetry*, 2011, **22**, 708; (d) C. Shen, F. Y. Shen, G. B. Zhou, H. J. Xia, X. Z. Chen, X. G. Liu and P. F. Zhang, *Catal. Commun.*, 2012, **26**, 6; (e) C. Shen, H. X. Liao, F. Y. Shen and P. F. Zhang, *Catal. Commun.*, 2013, **41**, 106.
- C. Shen and P. F. Zhang, *Curr. Org. Chem.*, 2013, **17**, 1507.
- J. E. Camp, J. J. Dunsford, E. P. Cannons, W. J. Restorick, A. Gadzhieva, M. W. Fay and R. J. Smith *ACS Sustainable Chem. Eng.*, 2014, **2**, 500.
- E. J. Flahive, B. L. Ewanicki, N. W. Sach, S. A. O'Neill-Slawecki, N.

S. Stankovic, S. Yu, S. M. Guinness and J. Dunn, *Org. Process Res.*

Dev., 2008, **12**, 637.

19. Y. Xiang, P. Y. Caron, P. Y. Lillie and R. Vaidyanathan, *Org. Process*

Res. Dev., 2008, **12**, 116.

s 20. B. P. Chekal, S. M. Guinness, B. M. Lillie, R. W. McLaughlin, C. W.

Palmer, R. J. Post, J. E. Sieser, R. A. Singer, G. W. Sluggett, R. Vaidy-

anathan and G. J. Withbroe, *Org. Process Res. Dev.*, 2014, **18**, 266.