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Metal-free chemoselective oxidation of sulfides to sulfoxides catalyzed by immobilized L-aspartic acid and L-glutamic acid in an aqueous phase at room temperature†

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L-Aspartic acid and L-glutamic acid were immobilized on hybrid silica and characterized by FT-IR, XPS, contact angle measurements, TGA, SEM and XRD. Employed as heterogeneous catalysts in the selective oxidation of sulfides with 30% H_2O_2 at room temperature, 99% conversion and 97% selectivity were achieved with excellent substrate tolerance and recyclability.

Sulfoxides, which are important building blocks or intermediates in the construction of pharmaceuticals, agrochemicals, and other valuable fine chemicals, can usually be obtained through selective oxidation of the corresponding sulfides.[1–3] In this extremely useful transformation, a variety of oxidants can be employed such as molecular oxygen,[4–8] hydrogen peroxide,[9–16] cumene hydroperoxide,[17–20] *tert*-butyl hydroperoxide,[21–25] iodobenzene diacetate,[26–28] sodium hypochlorite[29–31] and oxone.[32] Among these oxidants, aqueous hydrogen peroxide is considered as an attractive choice, which is readily available, inexpensive, safely stored, easy to operate, and environmentally benign with harmless water as the only by-product generated in the reaction.[10,33,34] But without the presence of a catalyst, the oxidation of sulfides to sulfoxides employing aqueous hydrogen peroxide is a very slow process, especially at room temperature. Thus, in order to promote this chemical transformation, several catalytic systems have been developed, including proton acid catalysis,[33,35–38] organocatalyst catalysis,[11,39–43] transition metal complex catalysis,[44–50] metal oxide nanoparticle catalysis,[51–53] heteropoly acid catalysis,[14,54–57] and the heterogenization of the above catalytic systems.[34,58–62] Considering the separation and recovery of the expensive transition metal catalyst, inevitable transition metal residue contamination in the products, and the toxicity of transition metal complexes, the immobilization of proton acids and organocatalysts as heterogeneous catalysts seems to be much more attractive,[34,58] especially the immobilization of natural products owing to their excellent sustainable availability and biological compatibility from the perspective of green chemistry.

L-Aspartic acid and L-glutamic acid are two common natural amino acids with two carboxyl groups in their molecules, which can be obtained from the extraction of several biological organisms. Owing to the existence of two –COOH groups, L-aspartic acid and L-glutamic acid have the potential to function as proton-acid catalysts in the oxidation of sulfides to sulfoxides using aqueous hydrogen peroxide as the oxidant. In pursuit of the modifying groups for β-cyclodextrin to construct artificial enzymes,[63–65] especially oxidases, we have reported the chemoselective oxidation of sulfides to sulfoxides catalyzed by immobilized taurine and homotaurine in an aqueous phase at room temperature, and up to 99.9% conversion and 98.0% selectivity were achieved.[66] And a pH-dependence principle in the proton acid-catalyzed oxidation of sulfides to the corresponding sulfoxides with H_2O_2 as the oxidant was reported by our group too.[67] Based on the above research, the idea of immobilizing L-aspartic acid and L-glutamic acid onto suitable supports emerged in our minds. When immobilized L-aspartic acid and L-glutamic acid were applied to the oxidation of sulfides to sulfoxides, excellent yields and chemoselectivity were obtained. Thus, in this letter we have reported our work in the immobilization of L-aspartic acid and L-glutamic acid on the hybrid silica (Si@Cl), and their catalytic activity in the oxidation of sulfides to sulfoxides. To the best of our knowledge, our work is a very rare example in which immobilized L-aspartic acid and L-glutamic acid were employed as catalysts. And the advantages of our work are also very obvious, which include (1) biocompatible and sustainably available catalyst, (2) catalyst-separable and -recyclable, (3) metal-free, avoiding transition metal residue contamination of the products, (4) room temperature reaction, avoiding deep oxidation of sulfoxides to corresponding sulfones, and (5) high yield and chemoselectivity, selectivity of sulfoxides reaching up to 97.6% in 99.8% conversion.

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In this work, the immobilized L-aspartic acid (Si@Asp) and L-glutamic acid (Si@Glu) were prepared following the route illustrated in the ESI† (Scheme S1). Firstly, the hybrid silica (Si@Cl) support was prepared through sol–gel hydrolysis–condensation of tetraethyl orthosilicate (TEOS) and (3-chloropropyl) triethoxysilane (CPTES) catalyzed by tetrabutylammonium fluoride,[68–71] and then the obtained hybrid silica support (Si@Cl) was dispersed in a mixture of triethanolamine and water ($V_{N(CH_2CH_2OH)_3} : V_{H_2O} = 1:1$). After L-aspartic acid or L-glutamic acid, and a catalytic amount of KI were added, the obtained reaction mixture was heated to 100 °C and vigorously stirred under a nitrogen atmosphere for 96 h. After cooling to room temperature, (Si@Asp) and (Si@Glu) were obtained as white powders through filtration under reduced pressure, after washing successively with ethanol and water, and acidification with 20% sulfuric acid solution (v/v).

Then, the immobilized L-aspartic acid and L-glutamic acid were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), contact angle measurements, thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM), and X-ray diffraction (XRD). In the FT-IR spectra of Si@Cl, Si@Asp and Si@Glu as shown in Fig. S1 in the ESI,† the strong peaks at around 1080 cm^{-1} are attributed to the Si–O–Si stretching vibrations, the broad peaks at around 3300 cm^{-1} belong to the symmetrical and asymmetrical stretching vibrations of SiO–H and C(O)O–H, and the broad peaks at around 3300 cm^{-1} become stronger as L-aspartic acid and L-glutamic acid were immobilized onto the hybrid silica due to the presence of –OH in L-aspartic acid and L-glutamic acid molecules, which is important evidence for the successful immobilization of L-aspartic acid and L-glutamic acid. The peaks at around 1650 cm^{-1}, which are attributed to the C=O stretching vibrations, appeared when L-aspartic acid and L-glutamic acid were immobilized onto the hybrid silica, which also is very important evidence for the successful immobilization. More powerful evidence for the successful immobilization were provided by the XPS spectra. XPS is a very helpful method for the investigation of the distribution and valence state of elements on the catalyst surface. Compared with Si@Cl, in the XPS spectra of Si@Asp and Si@Glu, nitrogen element and sulfur element are detected as shown in Fig. 1, and chlorine element disappears, which indicates that L-aspartic acid and L-glutamic acid were immobilized onto the hybrid silica successfully. The successful immobilization was also illustrated by the contact angle measurements. The surface of Si@Cl is hydrophobic, so the contact angle of water on it can reach up to 137.4°. But when water (6 μL) was dripped onto the surface of Si@Asp and Si@Glu, the water droplet seeped into Si@Asp and Si@Glu quickly (within 5 s) as shown in Fig. S5 (ESI†) due to the presence of hydrophilic –COOH groups. Other characterization data and spectra can be found in the ESI.†

With Si@Asp and Si@Glu in hand, we carried out the catalytic oxidation of sulfides at room temperature with 30% H_2O_2 as the oxidant. In a typical experiment, sulfide (1.0 mmol) was added to a solution of water (1.0 mL) and Si@Asp or Si@Glu; after stirring at 25 °C for 15 min, 30% H_2O_2 (1.15 mmol) was added. Then, the reaction mixture was kept stirred at 25 °C for 24.0 h or 48.0 h, and saturated aqueous Na_2SO_3 (2 mL) was added to stop deep oxidation. The obtained solution was extracted using ethyl acetate (3 × 2.0 mL), and the combined organic phase was washed with brine (2.0 mL) and dried over anhydrous Na_2SO_4, which was analyzed by GC or subjected to column chromatography (silica, eluent $V_{cyclohexane}/V_{ethyl\ acetate} = 6:4$) to determine the conversion and yield. Initially, in order to optimize the reaction conditions, the catalytic oxidation of methyl phenyl sulfide was chosen as the probe reaction and the effect of the catalyst amount on the probe reaction was evaluated systematically. As shown in Table 1 and Table S1 (ESI†), the amount of catalyst has a remarkable effect on the conversion, yield and selectivity. As the Si@Asp amount was increased from 0.0 mg to 86.9 mg, the conversion and yield of the probe reaction increased from 38.0% to 99.8% and 37.8% to 97.4% respectively, with a slight decrease in the selectivity, from 99.5% to 97.6%. All of the conversion, yield and selectivity are very satisfactory. Further increase in the Si@Asp amount led to no obvious effect on the conversion and yield. Thus, when the amount of methyl phenyl sulfide is 1.0 mmol, the more suitable amount of Si@Asp is

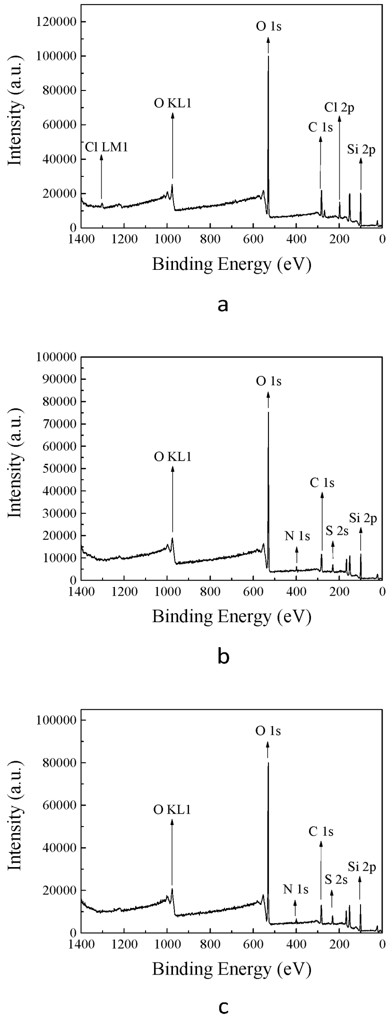

Fig. 1 XPS spectra of (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.

Table 1 Effect of Si@Asp amount on the oxidation of methyl phenyl sulfide with H_2O_2[a]

Entry	Si@Asp amount (mg)	Conversion[b] (%)	Yield[b] (%)	Selectivity (%)
1	0.0	38.0	37.8	99.5
2	12.4	57.2	56.9	99.5
3	24.8	63.3	63.0	99.5
4	37.3	76.5	75.9	99.2
5	49.7	81.7	80.0	97.9
6	62.1	86.1	84.2	97.8
7	74.5	94.7	92.7	97.9
8	86.9	99.8	97.4	97.6
9	99.4	99.8	97.6	97.8
10	111.8	99.7	96.9	97.2
11	124.2	99.8	96.5	96.7

[a] Reaction conditions: substrate (1.0 mmol, 124.2 mg), 30% H_2O_2 (1.15 mmol, 130 μL), solvent (1.0 mL H_2O), 25 °C, 24.0 h. [b] Conversion and selectivity were determined by GC with *p*-xylene as the internal standard, product was determined by comparison with the authentic sample.

86.9 mg, and in these conditions, the mass ratio of Si@Asp to methyl phenyl sulfide is 0.7 : 1.0. For Si@Glu, excellent conversion (99.5%), yield (97.4%) and selectivity (97.9%) are also obtained when the mass ratio of Si@Glu to methyl phenyl sulfide is 0.7 : 1.0. Thus, it can be concluded that both Si@Asp and Si@Glu are very effective catalysts in the catalytic oxidation of methyl phenyl sulfide at room temperature with 30% H_2O_2 as the oxidant. And it should be mentioned that the HSO_4^- in Si@Asp and Si@Glu also plays an indispensable role in the catalytic oxidation of methyl phenyl sulfide. The combination of Si@Cl, L-aspartic acid or L-glutamic acid and H_2SO_4 can not only realize the immobilization of L-aspartic acid or L-glutamic acid onto Si@Cl, but also results in the immobilization of H_2SO_4.

When the optimized reaction conditions were obtained (Table 1, entry 8 and Table S1, entry 8, ESI†), the substrate scope was extended to a series of structurally diverse sulfides such as methyl 4-methoxylphenyl sulfide (Table S2, entry 3, ESI†), ethyl phenyl sulfide (Table S2, entry 6, ESI†), 2-chloroethyl phenyl sulfide (entry 9), dibutyl sulfide (entry 15) and diphenyl sulfide (entry 10). As shown in Table S2 (ESI†), Si@Asp exhibits an excellent tolerance to a wide range of sulfides. Most of the sulfides can be oxidized to the corresponding sulfoxides with more than 95% conversion and selectivity, especially the liquid sulfides (Table S2, entries 1–6 and 13–15, ESI†) because of their excellent dispersion in water. For some solid sulfides (Table S2, entries 7–12, ESI†), 0.5 mL acetonitrile was added to enhance their dispersion in water, and acceptable conversion and selectivity were obtained. It is very clear in Table S2 (ESI†) that Si@Asp is a very effective catalyst for the catalytic oxidation of sulfides at room temperature with 30% H_2O_2 as the oxidant, no matter the substrates are aromatic sulfides or aliphatic sulfides.

An important purpose in the immobilization of L-aspartic acid and L-glutamic acid on hybrid silica in our research is to recycle Si@Asp and Si@Glu easily. Thus, the recyclability of Si@Asp was investigated in the catalytic oxidation of methyl phenyl sulfide. After the first catalytic run, Si@Asp was separated by centrifugation at 4500 rpm, washed with ethyl acetate (3 × 2.0 mL) and dried at 50 °C under vacuum. And then the obtained Si@Asp was subjected to the second run under the same reaction conditions. As shown in Fig. S6 (ESI†), Si@Asp demonstrated remarkably excellent recyclability. After six successive runs, the conversion, yield and selectivity could still be maintained at 85.1%, 83.6% and 98.2% respectively, without significant decrease, especially in the selectivity. The decrease in conversion and yield could be attributed to the dissociation of H_2SO_4 from Si@Asp and the loss of L-aspartic acid on Si@Asp particles because of the fracture of the Si@Asp particles. These results suggest that Si@Asp is a very suitable catalyst for the catalytic oxidation of various sulfides in aqueous phase at room temperature with 30% H_2O_2 as the oxidant.

In conclusion, we have immobilized L-aspartic acid and L-glutamic acid on a hybrid silica support successfully, and the obtained Si@Asp and Si@Glu were employed as heterogeneous catalysts in the catalytic oxidation of various sulfides at room temperature with 30% H_2O_2 as oxidants. Both Si@Asp and Si@Glu show high catalytic activity, selectivity and a good tolerance to a wide range of sulfides. Up to 97% conversion and 95% selectivity were achieved for several sulfides. And the heterogeneous catalysts can be recycled up to 6 times through centrifugation easily without a significant decrease in catalytic performance, which makes them as promising catalysts in practical and large-scale applications for the oxidation of various sulfides. The advantages of this protocol can be summarized as biocompatible and sustainably available catalysts, eco-friendly and cheap oxidants, high conversion and chemoselectivity, mild reaction conditions, and satisfactory recyclability. And the combination of Si@Cl, L-aspartic acid or L-glutamic acid and H_2SO_4 is the cause of the satisfactory catalytic activity. Finally, to the best of our knowledge, our research is a very rare example in the application of immobilized natural products L-aspartic acid and L-glutamic acid as catalysts in organic synthesis, and the attempt to apply Si@Asp and Si@Glu to other catalytic systems is currently in progress.

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Notes and references

1 I. Fernandez and N. Khiar, *Chem. Rev.*, 2003, **103**, 3651.
2 K. Kaczorowska, Z. Kolarska, K. Mitka and P. Kowalski, *Tetrahedron*, 2005, **61**, 8315.
3 K. A. Stingl and S. B. Tsogoeva, *Tetrahedron: Asymmetry*, 2010, **21**, 1055.

4 V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammdpoor-Baltork, H. Kargar and M. Araghi, *Appl. Catal., A*, 2009, **353**, 61.
5 A. Rezaeifard and M. Jafarpour, *Catal. Sci. Technol.*, 2014, **4**, 1960.
6 Y. L. Hu, D. Fang and R. Xing, *RSC Adv.*, 2014, **4**, 63005.
7 Z. J. Wang, S. Ghasimi, K. Landfester and K. A. I. Zhang, *Chem. Commun.*, 2014, **50**, 8177.
8 J. A. Johnson, X. Zhang, T. C. Reeson, Y. S. Chen and J. Zhang, *J. Am. Chem. Soc.*, 2014, **136**, 15881.
9 P. Le Maux and G. Simonneaux, *Chem. Commun.*, 2011, **47**, 6957.
10 S. M. Islam, A. S. Roy, P. Mondal, K. Tuhina, M. Mobarak and J. Mondal, *Tetrahedron Lett.*, 2012, **53**, 127.
11 F. Secci, A. Frongia and P. P. Piras, *Tetrahedron Lett.*, 2014, **55**, 603.
12 P. Gogoi, M. Kalita, T. Bhattacharjee and P. Barman, *Tetrahedron Lett.*, 2014, **55**, 1028.
13 Y. Kon, T. Yokoi, M. Yoshioka, S. Tanaka, Y. Uesaka, T. Mochizuki, K. Sato and T. Tatsumi, *Tetrahedron*, 2014, **70**, 7584.
14 L. Huang, S. S. Wang, J. W. Zhao, L. Cheng and G. Y. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 7637.
15 J. Sturala, S. Bohacova, J. Chudoba, R. Metelkova and R. Cibulka, *J. Org. Chem.*, 2015, **80**, 2676.
16 A. Pourjavadi, M. Nazari-Chamazkoti and S. H. Hosseini, *New J. Chem.*, 2015, **39**, 1348.
17 J. H. Gao, H. C. Guo, S. Z. Liu and M. Wang, *Tetrahedron Lett.*, 2007, **48**, 8453.
18 A. Pordea, M. Creus, J. Panek, C. Duboc, D. Mathis, M. Novic and T. R. Ward, *J. Am. Chem. Soc.*, 2008, **130**, 8085.
19 M. Mba, L. J. Prins, C. Zonta, M. Cametti, A. Valkonen, K. Rissanen and G. Licini, *Dalton Trans.*, 2010, **39**, 7384.
20 G. Romanowski, *J. Mol. Catal. A: Chem.*, 2013, **368**, 137.
21 R. Das and D. Chakraborty, *Tetrahedron Lett.*, 2010, **51**, 6255.
22 J. Oble, B. Riflade, A. Noel, M. Malacria, S. Thorimbert, B. Hasenknopf and E. Lacote, *Org. Lett.*, 2011, **13**, 5990.
23 A. Rezaeifard, P. Farshid, M. Jafarpour and G. K. Moghaddam, *RSC Adv.*, 2014, **4**, 9189.
24 J. Orive, E. S. Larrea, R. F. de Luis, M. Iglesias, J. L. Mesa, T. Rojo and M. I. Arriortua, *Dalton Trans.*, 2013, **42**, 4500.
25 M. Mandal and D. Chakraborty, *RSC Adv.*, 2015, **5**, 12111.
26 M. Jaccob, P. Comba, M. Maurer, P. Vadivelu and P. Venuvanalingam, *Dalton Trans.*, 2011, **40**, 11276.
27 T. H. Chen, Z. B. Yuan, A. Carver and R. Zhang, *Appl. Catal., A*, 2014, **478**, 275.
28 B. Yu, C. X. Guo, C. L. Zhong, Z. F. Diao and L. N. He, *Tetrahedron Lett.*, 2014, **55**, 1818.
29 J. M. Khurana and B. Nand, *Can. J. Chem.*, 2010, **88**, 906.
30 J. Y. Huang, S. J. Li and Y. G. Wang, *Tetrahedron Lett.*, 2006, **47**, 5637.
31 M. J. Alcon, A. Corma, M. Iglesias and F. Sanchez, *J. Mol. Catal. A: Chem.*, 2002, **178**, 253.
32 B. Yu, A. H. Liu, L. N. He, B. Li, Z. F. Diao and Y. N. Li, *Green Chem.*, 2012, **14**, 957.
33 A. Rostami and J. Akradi, *Tetrahedron Lett.*, 2010, **51**, 3501.
34 A. Rostami, B. Tahmasbi, F. Abedi and Z. Shokri, *J. Mol. Catal. A: Chem.*, 2013, **378**, 200.
35 H. Firouzabadi, N. Iranpoor, A. A. Jafari and E. Riazymontazer, *Adv. Synth. Catal.*, 2006, **348**, 434.
36 H. Jafari, A. Rostami, F. Ahmad-Jangi and A. Ghorbani-Choghamarani, *Synth. Commun.*, 2012, **42**, 3150.
37 M. Mokhtary, M. Qandalee and M. R. Niaki, *E-J. Chem.*, 2012, **9**, 863.
38 H. Golchoubian and F. Hosseinpoor, *Molecules*, 2007, **12**, 304.
39 P. Menova, F. Kafka, H. Dvorakova, S. Gunnoo, M. Sanda and R. Cibulka, *Adv. Synth. Catal.*, 2011, **353**, 865.
40 J. Zurek, R. Cibulka, H. Dvorakova and J. Svoboda, *Tetrahedron Lett.*, 2010, **51**, 1083.
41 B. J. Marsh and D. R. Carbery, *Tetrahedron Lett.*, 2010, **51**, 2362.
42 R. Jurok, R. Cibulka, H. Dvorakova, F. Hampl and J. Hodacova, *Eur. J. Org. Chem.*, 2010, 5217.
43 Y. Imada, T. Kitagawa, S. Iwata, N. Komiya and T. Naota, *Tetrahedron*, 2014, **70**, 495.
44 Y. C. Jeong, Y. D. Huang, S. Choi and K. H. Ahn, *Tetrahedron: Asymmetry*, 2005, **16**, 3497.
45 A. E. Aydin, *Tetrahedron: Asymmetry*, 2013, **24**, 444.
46 G. Romanowski and T. Lis, *Inorg. Chim. Acta*, 2013, **394**, 627.
47 P. Adao, F. Avecilla, M. Bonchio, M. Carraro, J. C. Pessoa and I. Correia, *Eur. J. Inorg. Chem.*, 2010, 5568.
48 I. Nigel-Etinger, A. Mahammed and Z. Gross, *Catal. Sci. Technol.*, 2011, **1**, 578.
49 A. Stephen and K. Hashmi, *Gold Bull.*, 2004, **37**, 51.
50 A. Stephen and K. Hashmi, *Chem. Rev.*, 2007, **107**, 3180.
51 M. Rahimizadeh, G. Rajabzadeh, S. M. Khatami, H. Eshghi and A. Shiri, *J. Mol. Catal. A: Chem.*, 2010, **323**, 59.
52 P. Veerakumar, Z. Z. Lu, M. Velayudham, K. L. Lu and S. Rajagopal, *J. Mol. Catal. A: Chem.*, 2010, **332**, 128.
53 F. Rajabi, S. Naserian, A. Primo and R. Luque, *Adv. Synth. Catal.*, 2011, **353**, 2060.
54 P. Tundo, G. P. Romanelli, P. G. Vazquez and F. Arico, *Catal. Commun.*, 2010, **11**, 1181.
55 B. G. Donoeva, T. A. Trubitsina, G. M. Maksimov, R. I. Maksimovskaya and O. A. Kholdeeva, *Eur. J. Inorg. Chem.*, 2009, 5142.
56 R. Ezzat and N. Narges, *J. Mol. Catal. A: Chem.*, 2015, **398**, 17.
57 S. Meninno, A. Parrella, G. Brancatelli, S. Geremia, C. Gaeta, C. Talotta, P. Neri and A. Lattanzi, *Org. Lett.*, 2015, **17**, 5100.
58 A. Shaabani and A. H. Rezayan, *Catal. Commun.*, 2007, **8**, 1112.
59 A. Rostami, Y. Navasi, D. Moradi and A. Ghorbani-Choghamarani, *Catal. Commun.*, 2014, **43**, 16.
60 S. M. Islam, A. S. Roy, P. Mondal, N. Salam and S. Paul, *Catal. Lett.*, 2013, **143**, 225.
61 R. K. Sharma, A. Pandey and S. Gulati, *Polyhedron*, 2012, **45**, 86.
62 Z. R. Tshentu, C. Togo and R. S. Walmsley, *J. Mol. Catal. A: Chem.*, 2010, **318**, 30.
63 H. M. Shen and H. B. Ji, *Carbohydr. Res.*, 2012, **354**, 49.
64 H. M. Shen and H. B. Ji, *Tetrahedron Lett.*, 2012, **53**, 3541.
65 H. M. Shen and H. B. Ji, *Tetrahedron*, 2013, **69**, 8360.

66 H. M. Shen, W. J. Zhou, H. K. Wu, W. B. Yu, N. Ai, H. B. Ji, H. X. Shi and Y. B. She, *Tetrahedron Lett.*, 2015, **56**, 4494.

67 H. M. Shen, W. J. Zhou, X. Ma, H. K. Wu, W. B. Yu, N. Ai, H. B. Ji, H. X. Shi and Y. B. She, *Molecules*, 2015, **20**, 16709.

68 A. G. Stamatis, D. Giasafaki, K. C. Christoforidis, Y. Deligiannakis and M. Louloudi, *J. Mol. Catal. A: Chem.*, 2010, **319**, 58.

69 G. Borja, A. Monge-Marcet, R. Pleixats, T. Parella, X. Cattoen and M. W. C. Man, *Eur. J. Org. Chem.*, 2012, 3625.

70 W. S. Guo, A. Monge-Marcet, X. Cattoen, A. Shafir and R. Pleixats, *React. Funct. Polym.*, 2013, **73**, 192.

71 H. M. Shen, G. Y. Zhu, W. B. Yu, H. K. Wu, H. B. Ji, H. X. Shi, Y. F. Zheng and Y. B. She, *RSC Adv.*, 2015, **5**, 84410.