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Synthesis of Bis(hydroxylmethylfurfuryl)amine Monomers from 5-Hydroxymethylfurfural

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We report the synthesis of bis(hydroxylmethylfurfuryl)amine (BHMFA) from 5-hydroxymethylfurfural (5-HMF) by reacting 5-HMF with primary amines in the presence of homogeneous Ru^{II} catalysts having sterically strained ligands. BHMFA is a group of furan-based monomers that offer great potential to form functional biopolymers with tunable properties. A range of primary amines, such as aliphatic and benzyl amines, are readily converted with 5-HMF to form the corresponding BHMFA in good yields. The reaction proceeds through reductive amination of 5-HMF with primary amine to form secondary amine, followed by reductive amination of 5-HMF with in situ generated secondary amine to produce BHMFA.

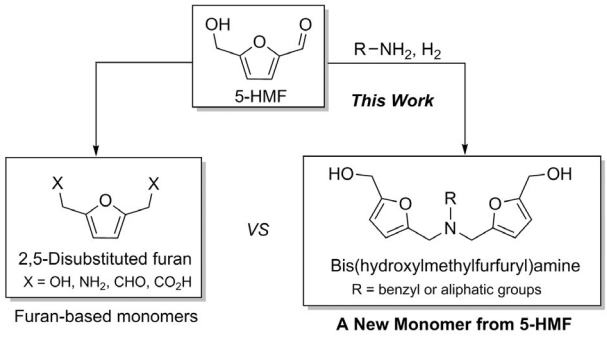

Figure 1. Furan-based monomers from 5-HMF.

Lignocellulosic biomass is the most abundant and renewable feedstock in nature. 5-Hydroxymethylfurfural (5-HMF), a versatile platform feedstock, is available from fructose, glucose, sucrose, starch, inulin, as well as cellulose.[1] 5-HMF is regarded as one of the most promising building blocks to produce valuable chemicals and fuels. Starting with 5-HMF, numerous important chemicals have become available.[2] For example, 2,5-dimethylfuran,[3] an important hydrogenation product from 5-HMF, was considered a suitable replacement for ethanol in gasoline–ethanol blends. Levulinic acid obtained from 5-HMF can be further converted to prepare fuel additives, dyestuffs, and pharmaceutical compounds.[4] The hydrogenative/hydrolytic product 1-hydroxyhexane-2,5-dione may serve as a new feedstock.[5] Aldol condensation of 5-HMF with acetone furnishes a precursor for biofuels.[6]

The recent rapid development of 5-HMF also offers numerous opportunities for the synthesis and exploration of new furan-based monomers and polymers (Figure 1). For example, 5-HMF can be converted to various 2,5-disubstituted furans, including 2,5-furandicarboxylicacid,[7] 2,5-furandicarbaldehyde,[8] 2,5-furandimethanol,[9] and 2,5-furandiamine.[10] These monomers show a high potential in step-growth and chain-growth polymerizations.[11] More specifically, 2,5-furandicarboxylic acid is an alternative to terephthalic and isophthalic acid;[12] 2,5-furandicarbaldehyde is a monomer to produce polyimines with high CO_2 adsorption capacity;[13] and 2,5-furandimethanol, an hydrogenation product of 5-HMF, was used to synthesize polyesters.[14] Some of the furan-based polymers were further converted by thermo reversible Diels–Alder (D-A) reactions with maleimide. These functional polymers may offer various interesting properties, such as recyclability, shape memory, soft–hard conversion, and healing ability. Although both the synthesis of 2,5-disubstituted furans and polymerization have been well developed so far, there are few studies regarding the synthesis of aminated furan-based monomers from 5-HMF.

In this paper, we report the synthesis of bis(hydroxylmethylfurfuryl)amines (BHMFAs) directly from 5-HMF (Figure 1). We anticipate BHMFAs to be a new group of inspiring furan-based monomers owing to some important features of BHMFAs: 1) they can be easily prepared from 5-HMF; 2) compared with 2,5-disubstituted furans, a large number of BHMFAs can be synthesized by varying the kinds of substituents; and 3) the properties of BHMFAs can be modified by different substituents, which make it possible to synthesize biopolymers, such as polyester and polyurethane, with self-healing ability and malleability.

The realm of BHMFAs has been the subject of very few investigations, beginning with Dunlop's pioneering work 30 years ago, which described the synthesis of bis(hydroxylmethylfurfuryl)butylamine[15] and bis(hydroxylmethylfurfuryl)methylamine[16] by Mannich-type reaction of furfuryl alcohol, amine, and formaldehyde. Although the products yields were not given in the patents, the yields of BHMFA are expected to be low as furfuryl alcohol is unstable in strong acidic solution and a complex procedure was adopted in the synthesis. Since 1980, using 5-HMF as a starting material to form BHMFAs has been rarely studied, and very few structures are reported so far.[17] Zhu and co-authors reported a one-pot reaction of

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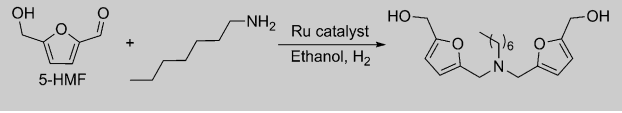
5-HMF and tryptamine with excess, costly $Na(CN)BH_3$ as a hydrogen source, which generated copious amounts of waste or toxic NaCN under humid conditions.[17]

Ru-catalyzed reductive amination is a powerful method to synthesize functional secondary and tertiary amines from aldehyde.[18] However, preparation of tertiary amines directly from aldehyde and primary amines has limited studies. Recently, we reported the Ru-catalyzed reductive amination of 5-HMF with different amines.[19] Hydroxylmethylfurfurylamines were obtained from a broad scope of primary and secondary amines. We hypothesized that BHMFAs could be synthesized from 5-HMF and primary amines by Ru-catalyzed direct reductive amination. To obtain BHMFAs as the major product, we applied an excess of 5-HMF, increased temperature, higher H_2 pressure, and more Ru catalyst (Table 1).

Table 1. Optimization of reaction conditions.[a]



Entry	Catalyst	T [°C]	Yield [%][b]
1	$Ru(Bipy)_2Cl_2$	110	71.3
2	$Ru(Dmbp)_2Cl_2$	110	85.4
3	$Ru(Phen)_2Cl_2$	110	23.1
4	$Ru(DMP)_2Cl_2$	110	90.3
5	$RuHCl(CO)(PPh_3)_3$	110	0
6	$Ru(DMP)_2Cl_2$	120	84.9
7	$Ru(DMP)_2Cl_2$	100	69.6

[a] Reaction conditions: Ru catalyst (1.0 mol% to amine), *n*-heptylamine (115.2 mg, 1.0 mmol), EtOH (2.0 mL), and 5-HMF (290.0 mg, 2.3 equiv. to *n*-heptylamine), under H_2 (20 bar = 2 MPa) for 12 h. [b] GC–MS yield.

Our initial studies began with the reaction of 5-HMF with *n*-heptylamine as a model reaction for proof-of-concept investigation, followed by further optimization of the reaction conditions (Table 1). Easily prepared and air-stable Ru^{II} complexes,[20] including $Ru^{II}(Bipy)_2Cl_2$ (Bipy = 2,2′-bipyridine), $Ru^{II}(Dmbp)_2Cl_2$ (Dmbp = 6,6′-dimethyl-2,2′-bipyridine), $Ru^{II}(Phen)_2Cl_2$ (Phen = 1,10-phenanthroline), $Ru^{II}(DMP)_2Cl_2$ (DMP = 2,9-dimethyl-1,10-phenanthroline), and $Ru^{II}(H)(Cl)(CO)(PPh_3)_3$ were tested for the reaction in ethanol (EtOH) solution (entries 1–5). Bidentate ligands seem to play an important role to control reaction selectivity. The Ru^{II} catalysts coordinated by sterically hindered ligands, such as Dmbp and DMP, exhibited good catalytic activity (entries 2 and 4 with yields of 85.4% and 90.3%, respectively), whereas Bipy- or Phen-based catalysts resulted in poor product yields (entries 1 and 3 with yields of 71.3% and 23.1%, respectively). It is likely that the Ru catalysts coordinated with sterically hindered ligands prefer *cis*-coordination mode,[21] which may be favorable for H_2 activation. The electron-donating methyl group may also enhance the hydrogenative ability of Ru^{II} complexes. Increasing temperature for the $Ru(DMP)_2Cl_2$ catalyst in EtOH from 110 °C (entry 4) to 120 °C was not found to further improve the product yield (entry 6). However, the product yield decreased sharply at 100 °C (entry 7). Under optimized conditions, subsequent synthesis of furan-based BHMFA monomers from 5-HMF and various amines was performed with $Ru(DMP)_2Cl_2$ as the catalyst in EtOH at 110 °C under a H_2 atmosphere (20 bar = 2 MPa).

The synthesis of furan-based monomers from 5-HMF and primary amines was performed under optimized conditions, and the results are shown in Figure 2. The reactions of aliphatic straight-chain amines such as ethyl, *n*-butyl, and *n*-dodecyl amine smoothly proceeded to generate the corresponding

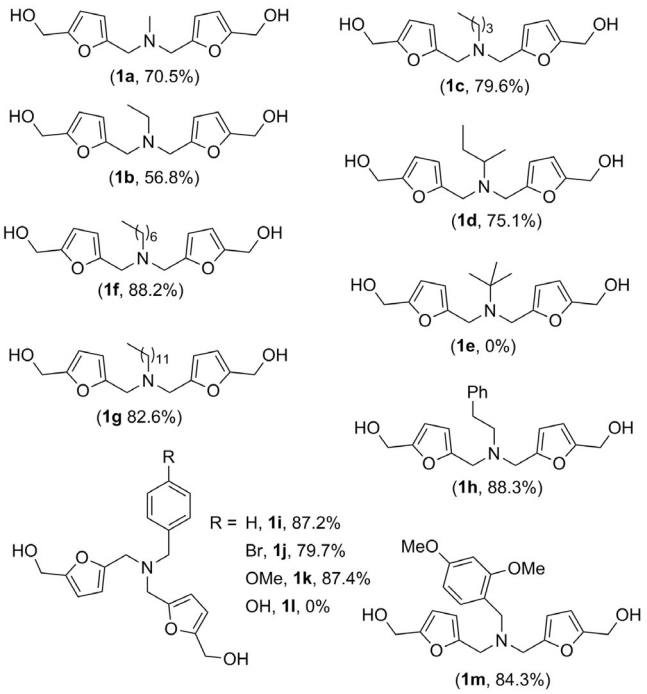


Figure 2. Synthesis of furan-based monomers from 5-HMF. Reaction conditions: $Ru(DMP)_2Cl_2$ (1.0 mol% to amine), amine (1.0 mmol), EtOH (2.0 mL), and 5-HMF (290.0 mg, 2.3 equiv. to amine), under H_2 (20 bar = 2 MPa) for 12 h. Isolated yield is given in the figure.

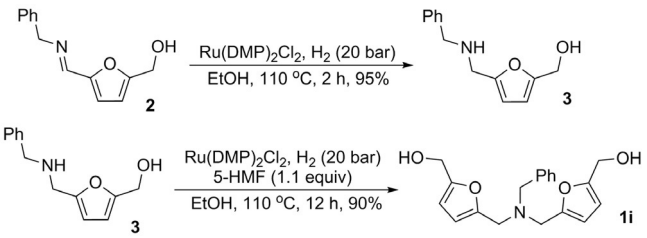
products **1b**, **1c**, and **1g** in good yields (56.8%, 79.6%, and 82.6%, respectively). An aqueous solution of ethylamine (65 wt%) was used. The lower yield of **1b** is a result of the influence of additional water, as water could suppress imine/iminium-ion formation. We also studied the reactivity of methylamine (25 wt%). Trace amounts of the corresponding product **1a** was observed from GC–MS analysis. As a more dilute aqueous solution of methylamine (25 wt%) was used, more water was introduced into the solution compared with ethylamine (65 wt%), suggesting that the reactivity of methylamine is lower than that of ethylamine. To increase the yield of **1a**, methylamine hydrochloride was used as a starting material.[22] The yield of **1a** was increased to 70.5% as the reaction was carried out in the absence of water. *iso*-Butylamine gave the product **1d** in 75.1% yield, whereas no product was obtained using *tert*-butylamine.[22] The sterically hindered *tert*-butyl group hindered the coordination of the corresponding imine with the Ru catalyst. Phenylethylamine gave the corresponding

tertiary amine **1h** in 88.3% yield. The reactivity of benzyl amines was also studied. Good product yields of 79.7% and 87.4% were obtained when benzyl amine bore a bromo (**1j**) or a methoxy group (**1k**), respectively. However, when the phenyl ring is linked with a hydroxyl group, no desired product was detected. Coordination of the phenol group to the catalyst likely suppressed the reaction.

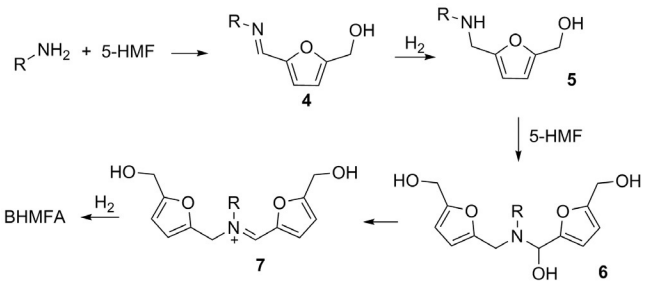
To test the practicability of this method, a gram-scale synthesis of **1f** was studied. **1f** could be obtained in 84% yield when 5-HMF (5.8 g) and *n*-heptylamine (2.3 g) were used.[22] We performed X-ray photoelectron spectroscopy (XPS) analysis of the catalyst residue after performing the hydrogenation.[22] No reduction of the Ru^{II} complex to Ru^0 metal was observed. We studied the reaction of 5-HMF with *n*-heptylamine in the presence of $Ru(DMP)_2Cl_2$ (0.5 mol%). The isolated yield of product was 43% at 24 h, and the turnover number (TON) was 86. Further work to improve the Ru catalyst for higher TON and turnover frequency (TOF) is in progress.

To investigate the reaction pathway, the hydrogenation of imine **2** was studied (Scheme 1), and 95% of secondary amine **3** was obtained. Amine **3** reacted with 5-HMF to produce tertiary amine **1i** with 90% yield. These results support our proposed mechanism (Scheme 2) that the synthesis of BHMFA from 5-HMF and primary amines proceeds through imine **4** formation, followed by hydrogenation of imine **4**. The in situ generated secondary amine **5** may further react with 5-HMF to form iminium ion intermediate **7** through intermediate **6**.[23] The final hydrogenation of **7** may form furan-based BHMFA.

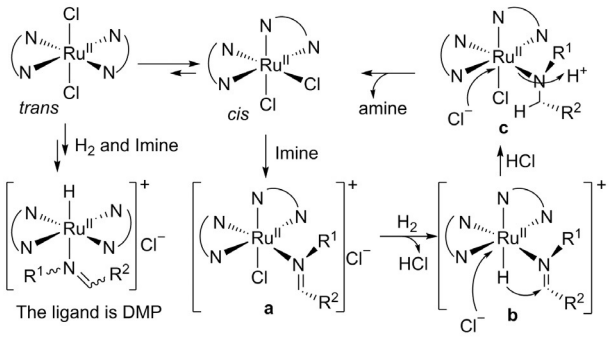
The mechanism of Ru-catalyzed hydrogenation is proposed as shown in Scheme 3. $Ru(DMP)_2Cl_2$ with a *trans*-coordination mode is not a favored structure, as the hydride atom and the imine group are on the *para*-position. $Ru(DMP)_2Cl_2$ with sterically hindered DMP ligand prefers *cis*-coordination mode.[21] *cis*-$Ru(DMP)_2Cl_2$ may undergo ligand exchange with imine to form intermediate **a**. The reaction of **a** with H_2 forms **b**. As the hydride atom and the imine group are on the *ortho*-position, **b** generates **c** through the intramolecular hydrogenation pathway. The reaction of **c** with acid produces amine and releases the Ru catalyst. Stericly strained amines (*tert*-butylamine) may influence the coordination chemistry of the corresponding imine–Ru complex, which may further lower the hydrogenation reactivity.



Scheme 1. Reaction pathway studied.



Scheme 2. Proposed mechanism.



Scheme 3. Proposed Ru-catalyzed hydrogenation pathway.

In summary, a simple and efficient procedure to synthesize BHMFAs by direct hydrogenation of biomass-derived 5-HMF and primary amines was developed. Sterically unstrained aliphatic at α-C position and benzyl amines showed good reactivity and yield to form new furan-based diols. This represents an important addition to the suite of furan-based monomers from bio-based platform 5-HMF. Further improving of the catalyst efficiency and a homogeneous catalytic process for economic production of BHMFAs from 5-HMF, as well as production of bio-polymers from BHMFAs, are underway.

Experimental Section

Synthesis of BHMFA: To a solution of 5-HMF (290.0 mg, 2.3 mmol) in EtOH (2.0 mL) at room temperature was added Ru catalyst (1.0 mol% to amine) and amine (1.0 mmol). The high pressure reactor (10 mL) was purged with H_2 (20 bar = 2 MPa) three times, and was heated to the set temperature for 12 h until completion of the reaction. After removing the solvent, the crude residue was purified on a silica gel column to afford the product.

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Keywords: biomass · green chemistry · polymers · renewable resources · ruthenium

[1] a) S. P. Teong, G. Yi, Y. Zhang, *Green Chem.* **2014**, *16*, 2015; b) R. A. Sheldon, *Green Chem.* **2014**, *16*, 950; c) R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, *113*, 1499; d) M. E. Zakrzewska, E. Bogel-Łukasik, R. Bogel-Łukasik, *Chem.*

Rev. **2011**, *111*, 397; e) J. J. Bozell, G. R. Petersen, *Green Chem.* **2010**, *12*, 539; f) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411.

[2] a) S. Zhu, J. Wang, W. Fan, *Catal. Sci. Technol.* **2015**, *5*, 3845; b) D. (D. J.) Liu, E. Y.-X. Chen, *Green Chem.* **2014**, *16*, 964; c) Y. Nakagawa, M. Tamura, K. Tomishige, *ACS Catal.* **2013**, *3*, 2655; d) T. Buntara, S. Noel, P. H. Phua, I. Melián-Cabrera, J. G. de Vries, H. J. Heeres, *Angew. Chem. Int. Ed.* **2011**, *50*, 7083; *Angew. Chem.* **2011**, *123*, 7221.

[3] a) B. Saha, M. M. Abu-Omar, *ChemSusChem* **2015**, *8*, 1133; b) Y. Qian, L. Zhu, Y. Wang, X. Lu, *Renewable Sustainable Energy Rev.* **2015**, *41*, 633; c) L. Hu, L. Lin, S. Liu, *Ind. Eng. Chem. Res.* **2014**, *53*, 9969.

[4] a) A. Démolis, N. Essayem, F. Rataboul, *ACS Sustainable Chem. Eng.* **2014**, *2*, 1338; b) A. Caretto, A. Perosa, *ACS Sustainable Chem. Eng.* **2013**, *1*, 989; c) J. Zhang, S. Wu, B. Li, H. Zhang, *ChemCatChem* **2012**, *4*, 1230; d) W. R. H. Wright, R. Palkovits, *ChemSusChem* **2012**, *5*, 1657; e) X.-L. Du, L. He, S. Zhao, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, *Angew. Chem. Int. Ed.* **2011**, *50*, 7815; *Angew. Chem.* **2011**, *123*, 7961.

[5] a) Z. Xu, P. Yan, W. Xu, X. Liu, Z. Xia, B. Chung, S. Jia, Z. Conrad Zhang, *ACS Catal.* **2015**, *5*, 788; b) F. Liu, M. Audemar, K. De Oliveira Vigier, J.-M. Clacens, F. De Campo, F. Jérôme, *ChemSusChem* **2014**, *7*, 2089; c) F. Liu, M. Audemar, K. De Oliveira Vigier, J.-M. Clacens, F. De Campo, F. Jérôme, *Green Chem.* **2014**, *16*, 4110; d) J. Ohyama, R. Kanao, A. Esakia, A. Suatsuma, *Chem. Commun.* **2014**, *50*, 5633.

[6] a) A. D. Sutton, F. D. Waldie, R. Wu, M. Schlaf, L. A. 'Pete' Silks, III, J. C. Gordon, *Nat. Chem.* **2013**, *5*, 428; b) K. Pupovac, R. Palkovits, *ChemSusChem* **2013**, *6*, 2103; c) J. Julis, M. Hölscher, W. Leitner, *Green Chem.* **2010**, *12*, 1634.

[7] a) H. G. Cha, K.-S. Choi, *Nat. Chem.* **2015**, *7*, 328; b) J. Zhang, J. Li, Y. Tang, L. Lin, M. Long, *Carbohydr. Polym.* **2015**, *130*, 420; c) W. P. Dijkman, D. E. Groothuis, M. W. Fraaije, *Angew. Chem. Int. Ed.* **2014**, *53*, 6515; *Angew. Chem.* **2014**, *126*, 6633.

[8] a) N. Mittal, G. M. Nisola, J. G. Seo, S.-P. Lee, W.-J. Chung, *J. Mol. Catal. A* **2015**, *106*, 404; b) J. Artz, S. Mallmann, R. Palkovits, *ChemSusChem* **2015**, *8*, 672; c) C. A. Antonyraj, B. Kim, Y. Kim, S. Shin, K.-Y. Lee, I. Kim, J. K. Cho, *Catal. Commun.* **2014**, *57*, 64.

[9] a) G. Bottari, A. J. Kumalaputri, K. K. Krawczyk, B. L. Feringa, H. J. Heeres, K. Barta, *ChemSusChem* **2015**, *8*, 1323; b) T. Pasini, A. Lolli, S. Albonetti, F. Cavani, M. Mella, *J. Catal.* **2014**, *317*, 206; c) A. J. Kumalaputri, G. Bottari, P. M. Erne, H. J. Heeres, K. Barta, *ChemSusChem* **2014**, *7*, 2266; d) X. Kong, Y. Zhu, H. Zheng, F. Dong, Y. Zhu, Y.-W. Li, *RSC Adv.* **2014**, *4*, 60467.

[10] F. H. Isikgor, C. Remzi Becer, *Polym. Chem.* **2015**, *6*, 4497.

[11] E. Gubbels, L. Jasinska-Walc, C. E. Koning, *J. Polym. Sci. Part A* **2013**, *51*, 890.

[12] a) S. Rajendran, R. Raghunathan, I. Hevus, R. Krishnan, A. Ugrinov, M. P. Sibi, D. C. Webster, J. Sivaguru, *Angew. Chem. Int. Ed.* **2015**, *54*, 1159; *Angew. Chem.* **2015**, *127*, 1175; b) C. H. R. M. Wilsens, J. M. G. A. Verhoeven, B. A. J. Noordover, M. R. Hansen, D. Auhl, S. Rastogi, *Macromolecules* **2014**, *47*, 3306; c) J. Zhu, J. Cai, W. Xie, P.-H. Chen, M. Gazzano, M. Scandola, R. A. Gross, *Macromolecules* **2013**, *46*, 796; d) L. Wu, R. Mincheva, Y. Xu, J. Raquez, P. Dubois, *Biomacromolecules* **2012**, *13*, 2973; e) J. Ma, Y. Pang, M. Wang, J. Xu, H. Ma, X. Nie, *J. Mater. Chem.* **2012**, *22*, 3457; f) M. Jiang, Q. Zhang, C. Ye, G. Zhou, *J. Polym. Sci. Part A* **2012**, *50*, 1026; g) M. Gomes, A. Gandini, A. J. D. Silvestre, B. Reis, *J. Polym. Sci. Part A* **2011**, *49*, 3759; h) A. Gandini, A. J. D. Silvestre, C. P. Neto, A. F. Sousa, M. Gomes, *J. Polym. Sci. Part A* **2009**, *47*, 295.

[13] a) T. Xiang, X. Liu, P. Yi, M. Guo, Y. Chen, C. Wesdemiotis, J. Xu, Y. Pang, *Polym. Int.* **2013**, *62*, 1517; b) J. Ma, M. Wang, Z. Du, C. Chen, J. Gao, J. Xu, *Polym. Chem.* **2012**, *3*, 2346.

[14] a) Y. Jiang, A. J. J. Woortman, G. O. R. Alberda van Ekenstein, D. M. Petrović, K. Loos, *Biomacromolecules* **2014**, *15*, 2482; b) P. Gopalakrishnan, S. Narayan-Sarathy, T. Ghosh, K. Mahajan, M. N. Belgacem, *J. Polym. Res.* **2014**, *21*, 340; c) T. Ikezaki, R. Matsuoka, K. Hatanaka, N. Yoshie, *J. Polym. Sci. Part A* **2014**, *52*, 216; d) C. Zeng, H. Seino, J. Ren, K. Hatanaka, N. Yoshie, *Polymer* **2013**, *54*, 5351; e) C. Zeng, H. Seino, J. Ren, K. Hatanaka, N. Yoshie, *Macromolecules* **2013**, *46*, 1794.

[15] A. P. Dunlop, US 4219485, **1980**.

[16] A. P. Dunlop, US 4219486, **1980**.

[17] D. Zhu, J. Zuo, S. Qu, W. Duan, G. Wang, C. Tan, P. He, F. Ji, C. Sun, X. Yao, WO 2011127833, **2011**.

[18] a) K. Beydoun, G. Ghattas, K. Thenert, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2014**, *53*, 11010; *Angew. Chem.* **2014**, *126*, 11190; b) S. Zhu, X. Lu, Y. Luo, W. Zhang, H. Jiang, M. Yan, W. Zeng, *Org. Lett.* **2013**, *15*, 1440; c) M. Vaquero, A. Suárez, S. Vargas, G. Bottari, E. Álvarez, A. Pizzano, *Chem. Eur. J.* **2012**, *18*, 15586; d) F. Chen, Z. Ding, J. Qin, T. Wang, Y. He, Q.-H. Fan, *Org. Lett.* **2011**, *13*, 4348; e) C. P. Casey, G. A. Bikzhanova, I. A. Guzei, *J. Am. Chem. Soc.* **2006**, *128*, 2286.

[19] Z. Xu, P. Yan, W. Xu, S. Jia, Z. Xia, B. Chung, Z. Conrad Zhang, *RSC Adv.* **2014**, *4*, 59083.

[20] a) S. Thota, M. Imran, M. Udugula, S. S. Karki, N. Kanjarla, R. Yerra, J. Balzarini, E. De Clercq, *J. Coord. Chem.* **2012**, *65*, 823; b) Sk. Jasimuddin, D. G. Thakurata, *Transition Met. Chem.* **2009**, *34*, 937; c) J. E. Collins, J. J. S. Lamba, J. C. Love, J. E. McAlvin, C. Ng, B. P. Peters, X. Wu, C. L. Fraser, *Inorg. Chem.* **1999**, *38*, 2020; d) A. S. Goldstein, R. H. Beer, R. S. Drago, *J. Am. Chem. Soc.* **1994**, *116*, 2424.

[21] J. P. Collin, J. P. Sauvage, *Inorg. Chem.* **1986**, *25*, 135.

[22] See SI for more information.

[23] a) H. Guan, M. Iimura, M. P. Magee, J. R. Norton, G. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 7805; b) M. P. Magee, J. R. Norton, *J. Am. Chem. Soc.* **2001**, *123*, 1778; c) M. J. Earle, R. A. Fairhurst, H. Heaney, G. Papageorgiou, R. F. Wilkins, *Tetrahedron Lett.* **1990**, *31*, 4229.

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