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Aluminium based binary catalytic system for the solvent free conversion of CO_2 to carbonates with high activity and selectivity†

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An easily prepared and low-cost aluminium based metal complex catalyst was prepared using kojic acid (Hkoj) as a ligand, and this developed oxo-coordinated $Al(koj)_3$ complex showed high activity and selectivity for the CO_2 fixation reaction with epoxides under mild conditions without any organic solvents. Various cyclic carbonates were obtained in excellent yields (up to 99%). This stable catalytically active $Al(koj)_3$ has strong Lewis acidity for the activation of epoxides, and meanwhile the hydroxy group in $Al(koj)_3$ may play a role in boosting the catalytic activity through possible hydrogen bonding interactions with the epoxide.

Introduction

Recent daily and weekly values of CO_2 concentration measured at Mauna Loa Observatory have remained above 400 parts per million.[1] This is a significant symbolic event in the global warming process, because part of global warming is attributed to increasing carbon dioxide levels in atmosphere, which is mainly caused by the combustion of huge amounts of fossil fuels (such as coal, petroleum, and natural gas). The rising CO_2 concentration may cause a pronounced change to our ecosystem because plant species are very sensitive to the increasing CO_2 concentration, as this will influence the behavior of stomata, the microscopic holes in leaves that allow leaves to take up CO_2, and as a result will cause changes to land plant photosynthesis. The existing fossil fuel reserves are limited and are being gradually depleted, and alternative resources such as CO_2 and biomass have received extensive attention.[2] In this context, the utilization of CO_2 as an inexpensive, ubiquitous, nontoxic, non-flammable, renewable, and green basic raw material has drawn wide attention in academia and industry.[3] Many useful fine chemical products, which have previously been derived from the limited fossil fuel resources, are currently produced using CO_2 as an alternative C1 building block, such as methanol, urea, carbonate, formamide and carboxylic acid.[4] However, just a fraction of the huge amount of CO_2 has been fixed into value-added products and the thermodynamic stability and kinetic inertness of CO_2 limits its conversion under mild conditions. A large energy input is required, such as higher CO_2 pressure and higher reaction temperatures, thus resulting in huge production costs. Therefore, development of high-efficiency, inexpensive, eco-friendly processes for CO_2 conversion and utilization are most urgently needed.[5]

One of the methods used to overcome the obstacles in CO_2 utilization is the use of high-energy small-membered ring compounds, *e.g.* epoxides, as the reactants with a negative Gibbs free energy for the reaction. Also, the addition of CO_2 to epoxides is a 100% atom-economical reaction, which is in accordance with the principles of green chemistry, and thus this method represents one of the most attractive routes for CO_2 utilization.[6] Cyclic carbonates and polycarbonate products have been studied with particular interest due to their widespread application in industry, *e.g.* as aprotic high-boiling polar solvents for organic synthesis (replacing DMF, DMSO, NMP and acetonitrile), electrolytes for lithium-ion batteries, monomers for polymeric materials (polycarbonates, and isocyanate-free polyurethanes), and intermediates in the synthesis of fine chemicals.[7] In the past few years, plenty of catalysts have been exploited for the synthesis of carbonates from CO_2 and epoxides, including metal-based catalysts (such as salen–metal compounds, porphyrin–metal compounds, metal oxides, metal–organic frameworks and so on), miscellaneous catalytic systems, ionic liquids, onium salts, and mono or binary metal-free catalysts.[8] Catalysts are used to activate the epoxide or/and CO_2 and reduce the activation energy of the transformation. The epoxide, activated by the catalyst, is liable to go through ring cleavage-addition with CO_2 upon nucleophilic attack by Br^- or I^-, to form an alkoxide anion, ultimately affording the corresponding cyclic carbonate (Scheme 1). Thus, electron-deficient metal catalysts are privileged for this reaction. In this respect, metal complexes based on porphyrins and metallosalen complexes have been widely investigated due to their unique

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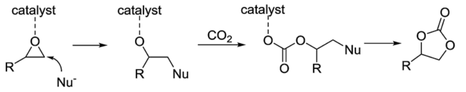
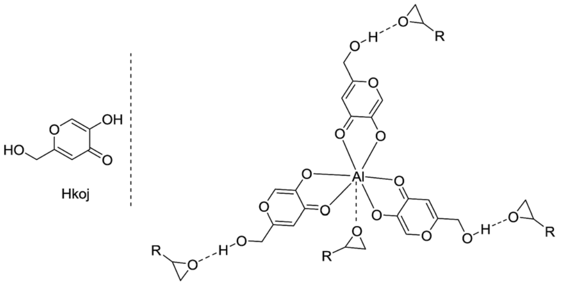


Scheme 1 Possible mechanism for the catalytic formation of cyclic carbonates.



Scheme 2 Multifunctional metal complexes used for the activation of epoxides in this work.

Table 1 Catalyst screening for the synthesis of styrene carbonate from styrene oxide with CO_2[a]

Entry	Cata./mol%	TBAI/mol%	Yield[b]/%
1	$Zn(koj)_2$/0.25	0.25	40
2	$Mn(koj)_2$/0.25	0.25	52
3	$Fe(koj)_3$/0.25	0.25	50
4	$Al(koj)_3$/0.25	0.25	69
5	—	0.25	21
6	Hkoj/0.75	0.25	43
7	—	—	0

[a] The reaction was carried out on a 5.0 mmol scale of styrene oxide at 100 °C under 1 MPa CO_2 (initial). [b] NMR yield using 1,1,2,2-tetrachloroethane as the internal standard.

Lewis acidities.[9] In addition, oxo-coordinated metal complexes also displayed high catalytic activity in the cycloaddition reaction of CO_2 with epoxides.[10] In our previous work, a tetraoxo-coordinated zinc complex, *i.e.* 2-hydroxypyridine N-oxide zinc(II), $Zn(OPO)_2$, was used and demonstrated remarkable turnover frequencies (up to 22 000 h^{-1}).[11] Therefore, we continued to consider highly active oxo-coordinated metal complexes for the synthesis of cyclic carbonates.

Kojic acid (5-hydroxy-2-(hydroxymethyl)-4-pyrone, Hkoj) is considered to be one of the safest food products and is widely used as a food additive to prevent enzymatic browning.[12] Hkoj has chelating activity and its metal complexes have reasonable hydrolytic stability, neutral charge and significant lipophilicity. Thus these kojic acid based metal complexes, *e.g.* $Al(koj)_3$, may have strong Lewis acidities for the activation of epoxides, and meanwhile the hydroxy group in $Al(koj)_3$ may play a role in boosting the catalytic activity through the possible hydrogen bonding interactions with the epoxide (Scheme 2). Hence, in this manuscript, we conducted a thorough investigation to explore the catalytic activity of these kojic acid based metal complexes, which are easy to prepare, low cost, multifunctional for the cycloaddition of CO_2 with epoxides.

Results and discussion

First, different kojic acid based metal complexes were prepared according to methods reported in the literatures[13] and the structures were confirmed using FT-IR and elemental analysis. The cycloaddition of styrene oxide with CO_2 was chosen as a benchmark reaction (Table 1). TBAI (tetrabutylammonium iodide) was used as a co-catalyst for this transformation due to its excellent nucleophilicity. The initial screening experiments were conducted at 100 °C, with 1 MPa CO_2 for 10 h with a catalyst loading of 0.25 mol%. The effect of different metal centers in the complexes was evaluated for the given reaction. $Zn(koj)_2$ and $Mn(koj)_2$, which have been reported as potential radioprotective agents,[12a] moderately promoted the reaction (40% and 52% yields, respectively, entries 1–2). An uncommon iron complex, $Fe(koj)_3$, also showed comparable reactivity (entry 3). Note that the reaction using $Al(koj)_3$ as a catalyst gave a good yield of 69% with the assistance of TBAI (entry 4). In the absence of $Al(koj)_3$, the yield dropped from 69% to 21% (entry 4 *vs.* 5). To clarify the role of the hydroxy group in $Al(koj)_3$, we also examined the reaction using Hkoj and a slightly higher yield of carbonate was obtained (entry 5 *vs.* 6). This result may indicate that the hydroxy group in $Al(koj)_3$ plays a role in boosting the catalytic activity through the possible hydrogen bonding interactions with the epoxide.[8d] No reaction occurred without any catalyst (entry 7).

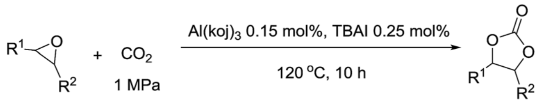
We continued our investigations by optimizing the reaction parameters using $Al(koj)_3$ as the catalyst (Table 2). Remarkably, with increasing temperature from 100 °C to 120 °C, the yield of styrene carbonate increased significantly from 69% to 93% (entry 1 *vs.* 2). The yield decreased sharply when the reaction was conducted at 80 °C, which thus suggested that 120 °C was the appropriate temperature for the cycloaddition reaction (entry 2 *vs.* 3). From a thermodynamics point of view, the cycloaddition of epoxides with CO_2 is an exothermic reaction and 120 °C is an easy operation temperature for industrial

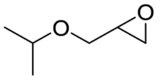
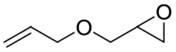
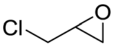
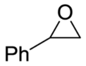
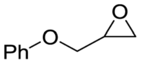
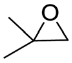
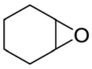
Table 2 Further optimization reaction conditions for the cycloaddition reaction[a]

Entry	Cata./mol%	T/°C	Yield[b]/%
1	$Al(koj)_3$/0.25	120	95
2	$Al(koj)_3$/0.25	100	69
3	$Al(koj)_3$/0.25	80	13
4	$Al(koj)_3$/0.15	120	94
5	$Al(koj)_3$/0.1	120	72
6	$Al(koj)_3$/0.05	120	66

[a] Reaction conditions: styrene oxide (5.0 mmol), TBAI (0.25 mol%), and 1 MPa CO_2 (initial). [b] NMR yield with 1,1,2,2-tetrachloroethane as the internal standard.

Table 3 Conversion of CO_2 to functionalized carbonate catalyzed with Al(koj)$_3$/TBAI[a]



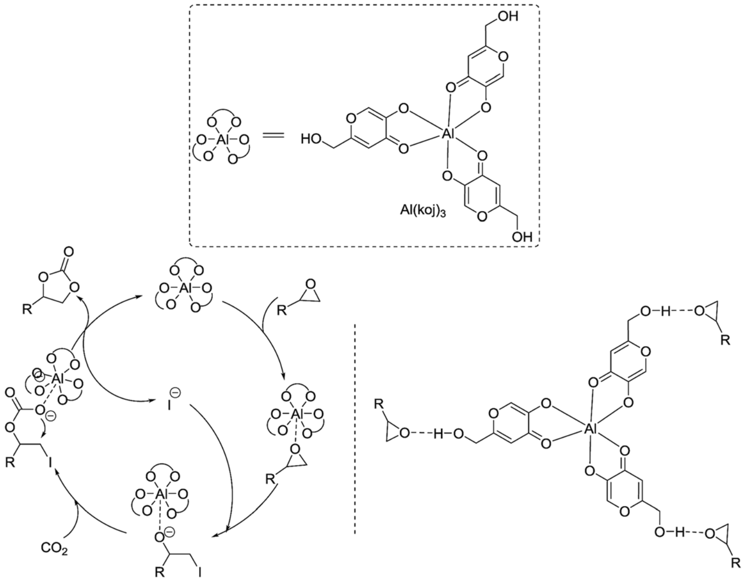
Entry	Substrate	Yield[b]/%
1		99(94), 94(91)[c], 96(95)[d]
2		95(91)
3		91(89)
4		90(88)
5		94(91)
6		95(90)
7[e]		42(40)
8[e]		37(34)

[a] Conditions: epoxide (5 mmol), Al(koj)$_3$ (0.15 mol%), TBAI (0.25 mol%), 1 MPa CO_2, 120 °C, and 10 h. [b] NMR yield with 1,1,2,2-tetrachloroethane as the internal standard. The yield in parentheses is the isolated yield. [c] TBAB instead of TBAI. [d] After three cycles using Al(koj)$_3$/TBAI. [e] Al(koj)$_3$ (0.25 mol%), 2 MPa CO_2, and 15 h.

production. Then, the effect of catalyst loading on the reaction was studied. A quantitative yield was obtained even after decreasing the catalyst loading from 0.25 mol% to 0.15 mol% (entry 4). Even at a loading of 0.05 mol%, a yield of 66% was achieved (entries 5–6). Thus, we defined the optimal reaction conditions for the cycloaddition as 0.15 mol% Al(koj)$_3$ at 120 °C with 1 MPa CO_2 under solvent-free conditions.

In order to evaluate the efficiency and general applicability of this oxo-coordinated Al(koj)$_3$ complex, a series of epoxides (terminal and internal) was examined for the synthesis of carbonates using CO_2 in the presence of Al(koj)$_3$ (Table 3). Propylene carbonate is widely used as an electrolyte and alternative green solvent in organic syntheses. An excellent yield of up to 99% was obtained using this developed catalyst system (entry 1). Using TBAB (tetrabutylammonium bromide) instead of TBAI also gave a quantitative yield of propylene carbonate. Furthermore, the reusability of the Al(koj)$_3$/TBAI system was examined for the synthesis of propylene carbonate, and no significant loss in its catalytic activity was observed after three successive runs (entry 1). The results achieved mark this protocol as an attractive method for potential future industrial applications. Other terminal epoxides smoothly converted to the corresponding cyclic carbonates in high yields and with excellent selectivities (entries 2–6). As for disubstituted epoxides, *e.g.* isobutylene oxide and cyclohexene oxide, these showed inferior activity even under harsh conditions (longer reaction times and increased amount of catalyst) compared with terminal counterparts, due to the increased steric hindrance (entries 7–8).[8c]

Based on previous studies[14] and the above experiments, a plausible mechanism for this Al(koj)$_3$ catalyzed coupling of CO_2 with epoxides was proposed and depicted in Scheme 3. Lewis acid metal catalyst activates the epoxide, followed by nucleophilic attack of the iodine anion from TBAI, to form the metal-coordinated iodo alkoxide. Then, the addition of CO_2



Scheme 3 Plausible reaction pathway for the coupling of epoxides with CO_2 catalyzed by Al(koj)$_3$/TBAI.

leads to the formation of the cyclic carbonate and regeneration of the catalyst. Notably, the hydroxy group in Al(koj)$_3$ may also play a role in boosting the catalytic activity through possible hydrogen bonding interactions with the epoxide.

Conclusions

In summary, oxo-coordinated Al(koj)$_3$ was developed as an efficient catalyst for the synthesis of carbonates from epoxides with CO_2 under mild conditions without any solvent. A series of terminal epoxides were converted to the corresponding carbonates in yields of up to 99%. Moreover, this developed catalyst system can be reused at least three times with no significant decrease in the propylene carbonate yield. This developed catalyst system shows great potential for industrialization due to the fact that it is easily prepared, inexpensive, has stable catalytic activity and requires reaction conditions that are easily realized.

Experimental

General information

TBAI and epoxides were purchased from Alfa Aesar, Aladdin, and J&K Chemical and were used without further treatment. Kojic acid, $Zn(OAc)_2$, $Mn(OAc)_2 \cdot 2H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $Al(NO_3)_3$ were from Energy Chemical. CO_2 with a purity of 99.99% was commercially available. The products were characterized in $CDCl_3$ using a Varian Bruker 400 spectrometer.

Synthesis and characterization of the kojic acid metal complexes[13]

Zn(koj)$_2$. IR data (KBr, cm^{-1}): 1622, 1568 (C═O); 1517 (C═C); 1277, 1219 (C–O). Elemental analysis: [calcd for $C_{12}H_{10}O_8Zn \cdot 1/2H_2O$], calc.: C, 41.47; H, 2.90. Found: C, 41.2; H, 2.98.

Al(koj)$_3$. IR data (KBr, cm^{-1}): 1613, 1578 (C═O); 1527 (C═C); 1307, 1249 (C–O). Elemental analysis: [calcd for $C_{18}H_{15}O_{10}Al$], calc.: C, 48.01; H, 3.36. Found: C, 48.09; H, 3.30.

Mn(koj)$_2$. IR data (KBr, cm^{-1}): 3449 (O–H); 1613, 1576 (C═O); 1528 (C═C); 1292, 1246 (C–O). Elemental analysis: [calcd for $C_{12}H_{10}O_8Mn$], calc.: C, 42.75; H, 2.99. Found: C, 42.48; H, 3.05.

Fe(koj)$_3$. IR data (KBr, cm^{-1}): 3331 (O–H); 1610, 1561 (C═O); 1513 (C═C); 1276, 1249 (C–O). Elemental analysis: [$C_{18}H_{15}O_{10}Fe \cdot 1/2H_2O$], calc.: C, 45.12; H, 3.16. Found: C, 45.19; H, 3.12.

General procedure for the cycloaddition reaction of epoxides with CO_2

A mixture of the epoxide (5 mmol), metal catalyst, and TBAI was placed into a glass tube, and then the tube was placed into a 25 ml stainless steel autoclave. The reactor was charged with CO_2 to the desired pressure. Then, the autoclave was placed into an oil-bath and heated. After the reaction, the reactor was cooled in an ice-water bath, and the CO_2 was carefully vented. Diethyl ether was added to extract the carbonate products and unreacted epoxide. The yield of cyclic carbonate was determined using NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard. The products were purified using column chromatography with ethyl acetate–petroleum ether as the eluent. The precipitated catalyst was washed with diethyl ether five times and dried using a pressure blowing concentrator ready to be used directly for the next reaction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

1 Mauna Loa Observatory (Hawaii), Scripps Institution of Oceanography at UC San Dieg, https://scripps.ucsd.edu/programs/keelingcurve/, Accessed 23 Dec 2017.

2 M. Y. He, Y. H. Sun and B. X. Han, *Angew. Chem., Int. Ed.*, 2013, **52**, 2.

3 (*a*) K. Sekine and T. Yamada, *Chem. Soc. Rev.*, 2016, **45**, 4524; (*b*) C. Chauvier and T. Cantat, *ACS Catal.*, 2017, **7**, 2107.

4 (*a*) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365; (*b*) I. Omae, *Coord. Chem. Rev.*, 2012, **256**, 1384; (*c*) Y. N. Li, R. Ma, L. N. He and Z. F. Diao, *Catal. Sci. Technol.*, 2014, **4**, 1498; (*d*) B. Yu and L. N. He, *ChemSusChem*, 2015, **8**, 52; (*e*) F. Juliá-Hernández, T. Moragas, J. Cornella and R. Martin, *Nature*, 2017, **545**, 84; (*f*) Y. Y. Gui, W. J. Zhou, J. H. Ye and D. G. Yu, *ChemSusChem*, 2017, **10**, 1337.

5 (*a*) M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2014, **114**, 1709; (*b*) M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH, 2010.

6 (*a*) M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing and C. Detrembleur, *Catal. Sci. Technol.*, 2017, **7**, 2651; (*b*) H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf and T. Werner, *Top. Curr. Chem.*, 2017, **375**, 50.

7 (*a*) B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, *Chem. Rev.*, 2010, **110**, 4554; (*b*) B. Yu, Z. F. Diao, C. X. Guo, C. L. Zhong, L. N. He, Y. N. Zhao, Q. W. Song, A. H. Liu and J. Q. Wang, *Green Chem.*, 2013, **15**, 2401.

8 (*a*) J. Steinbauer, A. Spannenberg and T. Werner, *Green Chem.*, 2017, **19**, 3769; (*b*) S. Yue, P. P. Wang, X. J. Hao and S. L. Zang, *J. CO2 Util.*, 2017, **21**, 238; (*c*) Q. N. Zhao, Q. W. Song, P. Liu, Q. X. Zhang, J. H. Gao and K. Zhang, *Chin. J. Chem.*, 2018, **36**, 187; (*d*) S. Kaneko and S. Shirakawa, *ACS Sustainable Chem. Eng.*, 2017, **5**, 2836; (*e*) C. Maeda, J. Shimonishi, R. Miyazaki, J. Hasegawa and T. Ema, *Chem.–Eur. J.*, 2016, **22**, 6556; (*f*) S. He, F. Wang, W. L. Tong, S. M. Yiu and M. C. W. Chan, *Chem. Commun.*, 2016, **52**, 1017; (*g*) H. Zhou, G. X. Wang, W. Z. Zhang and X. B. Lu, *ACS Catal.*, 2015, **5**, 6773; (*h*) M. North, S. C. Z. Quek, N. E. Pridmore, A. C. Whitwood and X. Wu, *ACS Catal.*, 2015, **5**, 3398; (*i*) S. Sopena, G. Fiorani, C. Martin and A. W. Kleij, *ChemSusChem*, 2015, **8**, 3248; (*j*)

R. Ma, L. N. He, X. F. Liu, X. Liu and M. Y. Wang, *J. CO2 Util.*, 2017, **19**, 28.

9 (*a*) C. Maeda, T. Taniguchi, K. Ogawa and T. Ema, *Angew. Chem., Int. Ed.*, 2015, **54**, 134; (*b*) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adan, E. Martin and A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**, 1228.

10 (*a*) Y. Yang, Y. Hayashi, Y. Fujii, T. Nagano, Y. Kita, T. Ohshima, J. Okuda and K. Mashima, *Catal. Sci. Technol.*, 2012, **2**, 509; (*b*) M. V. Escárcega-Bobadilla, M. M. Belmonte, E. Martin, E. C. Escudero-Adán and A. W. Kleij, *Chem.–Eur. J.*, 2013, **19**, 2641.

11 R. Ma, L. N. He and Y. B. Zhou, *Green Chem.*, 2016, **18**, 226.

12 (*a*) S. Emami, S. J. Hosseinimehr, S. M. Taghdisia and S. Akhlaghpoorb, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 45; (*b*) H. S. Rho, S. M. Ahn, D. S. Yoo, M. K. Kim, D. H. Cho and J. Y. Cho, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 6569; (*c*) V. M. Nurchi, G. Crisponi, J. I. Lachowicz, S. Murgia, T. Pivetta, M. Remelli, A. Rescigno, J. Niclós-Gutíerrez, J. M. González-Pérez, A. Domínguez-Martín, A. Castiñeiras and Z. Szewczuk, *J. Inorg. Biochem.*, 2010, **104**, 560.

13 (*a*) M. C. Barret, M. F. Mahon, K. C. Molloy, J. W. Steed and P. Wright, *Inorg. Chem.*, 2001, **40**, 4384; (*b*) A. F. Sowinski and K. P. Dockery, *US Pat.*, U.S.20120105553, 2012; (*c*) O. Vajragupta, P. Boonchoong, Y. Sumanont, H. Watanabe, Y. Wongkrajang and N. Kammasu, *Bioorg. Med. Chem.*, 2003, **11**, 2329.

14 (*a*) J. Martínez, J. A. Castro-Osma, A. Earlam, C. Alonso-Moreno, A. Otero, A. Lara-Sánchez, M. North and A. Rodríguez-Diéguez, *Chem.–Eur. J.*, 2015, **21**, 9850; (*b*) J. Meléndez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323; (*c*) C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo and A. W. Kleij, *Chem.–Eur. J.*, 2014, **20**, 2264; (*d*) M. E. Wilhelm, M. H. Anthofer, M. Cokoja, I. I. E. Markovits, W. A. Herrmann and F. E. Kühn, *ChemSusChem*, 2014, **7**, 1357; (*e*) S. Gennen, M. Alves, R. Méreau, T. Tassaing, B. Gilbert, C. Detrembleur, C. Jerome and B. Grignard, *ChemSusChem*, 2015, **8**, 1845.