Letter

# Fe(BF<sub>4</sub>)<sub>2</sub> catalyzed inter- and intramolecular carbonyl-ene reaction of trifluoropyruvate

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**Abstract** Inter- and intramolecular carbonyl-ene reactions have been developed using 5 mol% Fe(BF4)<sub>2</sub> as catalyst, affording homoallylic alcohols in 36 to 87% isolated yields. This catalyst, prepared from FeCl<sub>2</sub> and AgBF4, is the first Fe<sup>II</sup> Lewis acid reported for the carbonyl-ene reaction using ethyl trifluoropyruvate. The method was successfully applied to the reaction of various 1,1-disubstituted alkenes with ethyl trifluoropyruvate and to the cyclization of citronellal.

Key words ene reaction, Lewis acids, iron, trifluoropyruvate, cyclization.

The carbonyl-ene reaction is a very powerful C-C bond forming transformation.1a It readily converts available alkenes and carbonyl compounds into homoallylic alcohols via a synthetically economical route in an intra- or intermolecular fashion.1b, 1c The scope of the reaction has been studied extensively in terms of the aldehyde scope used in the carbonyl-ene reaction, and a variety of metal salts have been investigated as Lewis acid catalysts, such as AlMe<sub>2</sub>Cl,<sup>2</sup> TiCl<sub>4</sub>,<sup>3</sup> SnCl<sub>4</sub>,<sup>4</sup> Sc(OTf)<sub>3</sub>.<sup>5</sup> Chiral catalysts, such as BINOL-Ti,6 BINAP-Pd/Pt,7 BOX-Cu,8 DPPF-Ni,9 and Salen-Co,10 have been disclosed in enantioselective versions. To the best of our knowledge, there are only two precedents of iron salts used in the carbonyl-ene reaction, but they have been employed in intramolecular cases and in a stoichiometric fashion.<sup>11</sup> In the past decade, research was focused on using trifluoropyruvates as activated ketones, since ketones were usually more difficult to react as an enophile,<sup>12a</sup> allowing the formation of chiral alcohols possessing tetrasubstituted stereogenic centers containing a trifluoromethyl group, which are important building blocks for pharmaceuticals and agrochemicals.12b Metal Lewis acids, such as Ca,13 Pd,14 In,15 Ru16 complexes, and organocatalysts17 were proved to be efficient catalysts in the trifluoropyruvate-ene reaction. However, there is a need to develop a catalytic ironmediated carbonyl-ene reaction. Indeed, a carbonyl-ene reaction catalyzed by an environmentally benign iron salt would be highly valuable. From a green chemistry perspective, developing new synthetic methods using iron, which is inexpensive, ubiquitous, and relatively less toxic in comparison with other metals, represents a major advantage.18

Following our studies in iron catalysis, such as in iron-catalyzed enantioselective Mukaiyama aldol, *meso*-epoxide opening, and aromatic sulfoxide oxidation reactions,<sup>19</sup> this article describes the study of iron-catalyzed carbonyl-ene reaction of ethyl 3,3,3-trifluoropyruvate with various alkenes. The studies were

initiated by selecting the model reaction of  $\alpha$ -methyl styrene **1** and ethyl trifluoropyruvate **2**, using various iron salts (Table 1). Fe<sup>III</sup> catalysts only led to side reactions (Table 1, entries 1 and 2). Using Fe<sup>II</sup> salts, the obtained products were a mixture of the eneproduct and side products (Table 1, entries 3–7). Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O afforded homoallylic alcohol **3a** in a 75% yield, which encouraged us to further optimize the conditions (Table 1, entry 7). The yield decreased to 62% by using Fe(OTf)<sub>2</sub>, and a longer reaction time or an increased catalyst loading (10 mol%) had little effect on the reaction efficiency (Table 1, entry 8). Optimization of the ra-

#### Table 1 Screening of iron salts in carbonyl-ene reaction

	+ F <sub>3</sub> C OEt	5 mol% FeX <sub>n</sub> CH <sub>2</sub> Cl <sub>2</sub> , rt, 48 h	HO CF3 OEt
1	2		3a
Entry	1/2	FeXn	Yield (%)ª
1	2:1	FeCl <sub>3</sub>	
2	2:1	Fe(OTf)₃	-
3	2:1	FeCl <sub>2</sub>	58
4	2:1	Fe(OAc)2	44
5	2:1	Fe(NTf) <sub>2</sub>	63
6	2:1	Fe(ClO <sub>4</sub> ) <sub>2</sub> .6H <sub>2</sub> O	53 b
7	2:1	Fe(BF <sub>4</sub> ) <sub>2</sub> .6H <sub>2</sub> O	75 b
8	2:1	Fe(OTf) <sub>2</sub>	62 (66) <sup>c</sup>
9	4:1	Fe(OTf) <sub>2</sub>	68
10	1:1.5	Fe(OTf) <sub>2</sub>	72
11	1:2	Fe(OTf) <sub>2</sub>	73
12	1:1.2	Fe(OTf)2	54
13	1:1.5	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	75 <sup>b</sup>
14	1:1.5	FeCl <sub>2</sub> + 2 AgBF <sub>4</sub>	83 b
15	1:1.5	FeCl <sub>2</sub> + 2 AgBF <sub>4</sub>	87 b,d

<sup>a</sup> Isolated yield.
 <sup>b</sup> With 4Å molecular sieves (for entries 7 and 13, the yields were the same without 4Å MS).

° 10 mol% iron salt, 60 h.

d Using filtration on cotton and celite.

a Using filtration on cotton and cellte.

-tio of α-methyl styrene to ethyl trifluoropyruvate was performed in both ways (Table 1, entries 9-12). Using excess of styrene (4 equivalents) did not lead to much increase of the yield (Table 1, entry 9). Using an excess of ethyl trifluoropyruvate afforded a better yield (Table 1, entries 10-11). However, using Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, and changing the ratio of 1/2 from 2:1 to 1:1.5 had no impact on the yield (Table 1, entries 7 and 13). When comparing Fe(OTf)<sub>2</sub> with Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, the latter exhibited a better catalytic activity (Table 1, entries 10 and 13). Anhydrous Fe(BF<sub>4</sub>)<sub>2</sub>, generated from the mixture of FeCl<sub>2</sub> and AgBF<sub>4</sub>, was also tested and showed better catalytic efficiency than Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Table 1, entry 14). In order to suppress any competing catalytic effect resulting from AgCl in the mixture of FeCl<sub>2</sub> and AgBF<sub>4</sub>, a control experiment with filtration of AgCl demonstrated that anhydrous Fe(BF<sub>4</sub>)<sub>2</sub> in the absence of silver salt was a more efficient catalyst than Fe(BF<sub>4</sub>)<sub>2</sub> in its presence, affording 87% yield of 3a (Table 1, entry 15). However, Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, being a commercial catalyst, was used for the screening of solvents (Table 2).



Entry	Solvent	Yield (%) <sup>a</sup>
1	MeCN	-
2	$Et_2O$	52
3	DCE	46
4	Toluene	71
5	$CH_2Cl_2$	75
6	THF	-
7	Me-THF	< 5 <sup>b</sup>
8	CPME	72
9	TBME	42
10	DMC	59
a Jacolated wield		

<sup>b</sup> Calculated by <sup>1</sup>H NMR.

In MeCN, the carbonyl-ene reaction did not proceed and the starting materials were recovered (Table 2, entry 1). Et<sub>2</sub>O and DCE gave moderate yields of **3a** (Table 2, entries 2 and 3). Toluene led to higher yield of **3a** (Table, entry 4). Both THF and Me-THF afforded only traces of the product and ethyl trifluoropyruvate was recovered (Table 2, entries 6–7). A few other green solvents were considered (Table 2, entries 8–10). Cyclopentyl methyl ether (CPME) afforded a slightly lower yield than with dichloromethane (Table 2, entry 8). *Tert*-butyl methyl ether (TBME) and dimethyl carbonate (DMC) led to moderate yields (Table 2, entries 9 and 10). Among the list of selected solvents, CH<sub>2</sub>Cl<sub>2</sub> provided the highest yield (Table 2, entry 5) and

it was consequently chosen for studying the scope of the reaction using various alkene substrates. However, cyclopentyl



**Scheme 1** Reaction scope of the Fe(BF<sub>4</sub>)<sub>2</sub> catalyzed trifluoropyruvate carbonyl-ene reaction

methyl ether, which is a green solvent, gave a very promising yield in the model reaction. In order to demonstrate the reaction scope, various substituted  $\alpha$ -methyl styrenes were selected (Scheme 1), using the best conditions selected in Table 1 (5 mol% FeCl<sub>2</sub>, 10 mol% AgBF<sub>4</sub>, entry 15). Using substrates possessing an electron donating group, such as a methyl group in the para position, the yield was good (3b). With a more electron-donating group such as *p*-MeO, side reaction of the alkene occurred as a competing reaction and the yield of the carbonyl decreased to 60% (Scheme 1, 3c). Steric hindrance was another factor influencing the reaction. Methoxy group in ortho position led to further decrease of the yield (3d). Moreover, electronwithdrawing groups (Br, F) on the aryl ring of the styrene derivatives led to moderate yields (3e-f). Using less nucleophilic 2-isopropenylnaphthalene, the yield dropped to a lower stage (3g). A moderate yield was obtained by using 2-(prop-1-en-2yl)thiophene as nucleophile (3h). More nucleophilic 1,1methylene-cyclopentane and -cyclohexane disubstituted afforded the products in moderate to good yields (3i-j). Only traces of product were obtained by using 2-(1-methylethenyl)pyridine as an heteroatom aromatic alkene, probably because the pyridine deactivated the catalyst. 20 Less nucleophilic non-cyclic aliphatic alkenes, such as mono-substituted alkene, i.e. 1-hexene, led only to traces of the expected product. Indeed, 1-hexene has often been used in the literature with a large excess of the enophile.12a Overall, the developed catalytic system was efficient with 1,1-disubstituted aromatic and aliphatic alkenes.

Intramolecular carbonyl-ene reaction is a useful method for making C–C bonds in organic synthesis.<sup>1,21</sup> The cyclization of (*R*)-(+)-citronellal affording (–)-isopulegol **5** is a known reaction. The latter is a desirable precursor to a widely employed chemical (–)-menthol.<sup>22</sup> A few catalysts have been used for this process, *i.e.* Sc(OTf)<sub>3</sub>,<sup>23a</sup> SnCl<sub>4</sub>,<sup>24b</sup> BiCl<sub>3</sub>,<sup>24c</sup> and Bi(OTf)<sub>3</sub>·xH<sub>2</sub>O.<sup>24d</sup> FeCl<sub>3</sub> (10 mol%) was used in the literature but a low yield (20%) with a

76:24 ratio of isopulegol **5** to other diastereomers was achieved.<sup>24</sup> Hence, it was still very valuable to test  $Fe(BF_4)_2$  in the cyclization of citronellal, since iron salts were less explored compared to other metal salts. In this catalytic system of  $Fe(BF_4)_2$ , by using (*S*)-(–)-citronellal **4**, a total 70% yield was obtained in a 70:30 *trans/cis* ratio of (+)-isopulegol to (–)-*neo*-isopulegol in the crude product while the isolated yields were: (+)-isopulegol **5**, 45%, (–)-*neo*-isopulegol **6**, 25%, and no (–)-*iso*-isopulegol or (–)-*neo*-isopulegol was identified (Scheme 2).<sup>25</sup>



Through the evaluation of a variety of iron salts, we have found that the Fe<sup>II</sup> salts were more appropriate to catalyze the studied reaction. Indeed, FeIII salts, such as FeCl3 and Fe(OTf)3, failed to catalyze the carbonyl-ene reaction of  $\alpha$ -methyl styrene and trifluoropyruvate (Table 1, entries 1 and 2). Secondly, it was reported that a marked effect of the counterion existed on the conversion of Lewis acid-catalyzed reaction between methylene cyclohexane and ethyl trifluoropyruvate.<sup>26</sup> Anhydrous Fe(BF<sub>4</sub>)<sub>2</sub>, generated from FeCl2 and AgBF4, led to higher yields than  $Fe(BF_4)_2 \cdot 6H_2O$ . Furthermore, a bidentate coordination can be postulated such that in the Cu<sup>II</sup> catalyzed carbonyl-ene reaction of ethyl glyoxylate disclosed by Evans.12a Fell coordinating with two carbonyl oxygens in one molecule of trifluoropyruvate was drawn in a bidentate manner in the proposed mechanism (Scheme 3). The Lewis acid-promoted ene reaction is usually discussed in terms of the continuum from concerted to cationic mechanism.1b.27 However, a stepwise radical pathway could also



Scheme 3 Postulated mechanism for the Fe(BF<sub>4</sub>)<sub>2</sub> catalyzed carbonyl-ene reaction between ethyl trifluoropyruvate and  $\alpha$ -methylstyrene

be envisioned.<sup>28</sup> A control experiment using TEMPO as a radical scavenger (methylstyrene **1**, 1.5 equiv. trifluoromethyl pyruvate 2, 5 mol% FeCl<sub>2</sub>, 10 mol% AgBF<sub>4</sub>, 5 mol% TEMPO) led to a major decrease of the yield of **3a** (43% instead of 83%). The observation that the reaction still occurs in the presence of TEMPO does not indicate unambiguously that a radical process is not involved in the process, at least to some extent.

To sum up, we reported the first iron catalytic system for both inter- and intramolecular carbonyl-ene reactions. Using low catalytic loading of Fe(BF<sub>4</sub>)<sub>2</sub>, the reaction proceeds smoothly to afford ene products in 36 to 87% isolated yields.<sup>29</sup> The method was applied to 1,1-disubstituted alkenes with trifluoropyruvate and cyclization of citronellal. The carbon–carbon bond forming process was affected by the electronic and steric properties of the substituents on the arene ring in the intermolecular carbonyl-ene reaction. Good yield and selectivity of isopulegol were obtained in the intramolecular carbonyl-ene reaction. Further development of iron catalysis in carbonyl-ene reaction will be reported in due course.

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#### Supporting Information

YES

### **Primary Data**

NO

## **References and Notes**

- For review of carbonyl-ene reaction, see: (a) Clark, M. L.; France, M. B. *Tetrahedron* 2008, 64, 9003. (b) Mikami, K.; Shimizu, M. *Chem. Rev.* 1992, 92, 1021. (c) Mikami, K.; Aikawa, K. In *Catalytic Asymmetric Synthesis*, Ojima. I., Ed.; Thieme: Hoboken, 2010, 683.
- (2) Johnston, M. I.; Kwass, J. A.; Beal, R. B.; Snider, B. B. J. Org. Chem. 1987, 52, 5419.
- (3) Andersen, N. H.; Hadley, S. W.; Kelly, J. D.; Bacon, E. R. J. Org. Chem. 1985, 50, 4144.
- (4) Andersen, N. H.; Uh, H. S.; Wuts, P. G. M.; Smith, S. E. J. Chem. Soc., Chem. Commun. 1972, 956.
- (5) Sultana, S. Bondalapati, S.; Indukuri, K.; Gogoi, P.; Saha, P.; Saikia, A. K. Tetrahedron Lett. 2013, 54, 1576.
- (6) Terada, M.; Motoyama, Y.; Mikami, K. *Tetrahedron Lett.* **1994**, *35*, 6693.
- (7) (a) Hao, J.; Hatano, M.; Mikami, K. Org. Lett. 2000, 2, 4059. (b) Tudor, M. D.; Becker, J. J.; White, P. S.; Gagné, M. R. Organometallics 2000, 19, 4367.
- (8) Evans, D. A.; Burgey, C. S.; Paras, N. A. J. Am. Chem. Soc. 1998, 120, 5824.
- (9) Mikami, K.; Aikawa, K. Org. Lett. 2002, 4, 99.
- (10) Kezuka, S.; Kogami, Y.; Ikeno, T.; Yamada, T. Bull. Chem. Soc. Jpn. 2003, 76, 49.
- (11) (a) Laschat, S.; Grehl, M. Chem. Ber. 1994, 127, 2023. (b) Laschat, S.; Fox, T. Synthesis 1997, 45.
- (12) (a) Evans, D. A.; Tregay, S. W.; Burgey, C. S.; Paras, N. A.; Vojkovsky,
   T. J. Am. Chem. Soc. 2000, 122, 7936. (b) Mikami, K.; Terada, M. In

Comprehensive Asymmetric Catalysis; Jacobsen, E. N.; Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. III, Chapter 32. (c) Snider,B. B. InComprehensive Organic Synthesis; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991.

- (13) Rueping, M.;Bootwicha, T.; Kambutong, S.; Sugiono, E. *Chem. Asian. J.* **2012**, *7*, 1195.
- (14) (a) Mikami, K; Aikawa, K.; Kainuma, S.; Kawakami, Y.; Saito, T.; Sayo, N.; Kumobayashi, H. *Tetrahedron: Asymmetry* **2004**, *15*, 3885.
  (b) Zhao, J. F.; Tan, B. H.; Zhu, M. K.; Tjan, T. B. W.; Tec Peng, L. *Adv. Synth. Catal.* **2010**, *352*, 2085.
- (15) Luo, H.K.; Woo, Y-L.; Schumann, H.; Jacob, C.; Yang, H-Y.; Tan, Y-T. *Adv. Synth. Catal.* **2010**, *352*, 1356.
- (16) Wang, T.; Hao, X-Q.; Huang, J. J.; Niu, J-J.; Gong, J-F.; Song, M. P. J. Org. Chem. 2013, 78, 8712.
- (17) (a) Clarke, M. L.; Jones, C. E. S.; France, M. B. Beilstein J. Org. Chem. 2007, 3, 24. (b) Rueping, M.; Theissmann, T.; Kuenkel, A.; Koenigs, R. M. Angew. Chem. Int. Ed. 2008, 47, 6798. (c) Lv, J.; Zhang, Q.; Zhong, S.; Luo, S. Z. J. Am. Chem. Soc. 2015, 137, 15576.
- (18) Bauer, I.; Knölker, H-J. Chem. Rev. 2015, 115, 3170.
- (19) (a) Plancq, B.; Ollevier, T. *Chem. Commun.* 2012, *48*, 3806. (b) Lafantaisie, M.; Plancq, B.; Mirabaud, A.; Ollevier, T. *ChemCatChem* 2014, *6*, 2244. (c) Jalba, A.; Régnier, N.; Ollevier, T. *Eur. J. Org. Chem.* 2017, 1628.
- (20) Interestingly, the reaction of 2-methyl quinoline and ethyl trifluoropyruvate was reported to occur thermally using Fe(OAc)<sub>2</sub>, the trifluoropyruvate being activated by an Fe<sup>II</sup>-enamide acetate species: Pi, D.; Jiang, K.; Zhou, H.; Sui, Y.; Uozumi, Y.; Zou, K. *RSC Adv.* **2014**, *4*, 57875.
- (21) (a) Zhao, Y.-J.; Li, B.; Tan, S.; Shen, Z.-L.; Loh, T.-P. *J. Am. Chem. Soc.* **2010**, *132*, 10242. (b) Tymann, D.; Klüppel, A.; Hiller, W.; Hiersemann, M. *Org. Lett.* **2014**, *16*, 4062. (c) Okamoto, R.; Takeda, K.; Tokuyama, H.; Ihara, M.; Toyota, M. *J. Org. Chem.* **2013**, *78*, 93.
- (22) (a) Misono, M.; Nojiri, N. Appl. Catal. 1990, 64, 1. (b) Akutagawa, S. In Chirality in Industry; Collins, A. N.; Sheldrack, G. N.; Crosby, J., Eds.; John Wiley, 1992, 313.
- (23) (a) Aggarwal, B. K.; Vennal, G. P.; Davey, P. N.; NewMan, C. *Tetrahedron Lett.* **1998**, *39*, 1997. (b) Nakatani, Y.; Kawashima, K. *Synthesis* **1978**, 147. (c) Peidro, L.; Le Roux, C.; Laporterie, A.; Dubac, J. *J. Organomet. Chem.* **1996**, *521*, 397. (d) Anderson, E. D.; Ernat, J. J. Nguyen, M. P.; Palma, A. C.; Mohan, R. S. *Tetrahedron Lett.* **2005**, *46*, 7747.
- (24) Nakatani, Y.; Kawashima, K. Synthesis 1978, 147.
- (25) (a) Isolated yields were given for **5** and **6**, <sup>1</sup>H NMR spectra in agreement with: (b) Kropp. P. J.; Breton, G. W.; Graig. S. L. Crawford,

S. D.; Durland, W. F., Jr.; Jones, J. E., III; Raleigh, J. S. *J. Org. Chem.* **1995**, *60*, 4146. (c) Imachi, S.; Owada, K.; Onaka, M. *J. Mol. Catal. A: Chem.* **2007**, *272*, 174. (d) Jacolb, R. G.; Perin, G.; Loi, L. N.; Pinno, C. S.: Lenardão, F. I. *Tetrahedron Lett.* **2003**, *44*, 3605.

- (26) Doherty, S; Knight, Julian G.; Smyth, C. H.; Harrington, R. W.; Clegg, W. J. Org. Chem. 2006, 71, 9751.
- (27) Morao, I.; McNamara, J. P.; Hillier, I. H. J. Am. Chem. Soc. 2003, 125, 628.
- (28) (a) Thaler, W. A.; Franzus, B. J. Org. Chem. 1964, 29, 2226. (b) Huisgen, R.; Pohl, H. Chem. Ber. 1960, 93, 527. (c) Walling, C.; Thaler, W. J. Am. Chem. Soc. 1961, 83, 3877.
- (29) General procedure for the carbonyl-ene reaction of alkenes with ethyl 3,3,3-trifluoropyruvate: FeCl2 (1.7 mg, 0.0125 mmol) and AgBF<sub>4</sub> (5 mg, 0.025 mmol) were added into a flame-dried test tube. The test tube was put under high vacuum (pumped with argon three times). Afterwards, distilled THF (1 mL) was added and the resulting solution was stirred for 0.3 h. Then, using a pre-dried pipet plugged with cotton and celite to filter the precipitated AgCl under argon atmosphere. To the resulting solution was added 50 mg of 4Å MS and the solution was then evaporated under reduced pressure. The test tube was then put under high-vacuum (1 Torr) for 0.3 h. Under argon atmosphere fresh-distilled CH2Cl2 (0.5 mL) was then added into the tube and stirred the solution for 0.1 h. Then,  $\alpha$ -methyl styrene (30 mg, 0.25 mmol) and ethyl 3,3,3trifluoropyruvate (64 mg, 0.375 mmol) were added via a syringe into the solution. The tube was put under argon protection and the solution was stirred for 48 h. Then, the crude reaction mixture was directly purified by silica flash chromatography (eluent: hexane/ethyl acetate). 63 mg of carbonyl-ene product 3a was obtained (yield = 87%).

Ethyl 2-hydroxy-4-phenyl-2-(trifluoromethyl)pent-4-enoate (3a):<sup>30</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35–7.26 (m, 5H), 5.39 (d, *J* = 1.3 Hz, 1H), 5.28 (d, *J* = 1.3 Hz, 1H), 4.03 (dq, *J* = 10.6, 7.2 Hz, 1H), 3.76 (d, *J* = 0.9 Hz, 1H), 3.64 (dq, *J* = 10.6, 7.2 Hz, 1H), 3.28 (d, *J* = 14.0 Hz, 1H), 3.04 (d, *J* = 14.0, 1.0 Hz, 1H), 1.11 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 141.0, 128.1, 127.9, 126.8, 123.4 (q, *J* = 286.2 Hz), 119.4, 77.09 (q, *J* = 28.9 Hz), 63.5, 37.0, 13.5. IR (NaCl): 3491, 2985, 1741, 1629, 1446, 1370, 1312, 1227, 1184, 1136, 1050, 911, 778, 701 cm<sup>-1</sup>.

(30) Luo, H.-K.; Woo, Y.-L.; Schumann, H.; Jacob, C.; Meurs, M. V.; Yang, H.-Y.; Tan. Y.-T. Adv. Synth. Catal. 2010, 352, 1356.