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Rational Design of Lewis-Acid Catalysts for Direct Alcohol Amination, Part 2 – Titanium Triflimide as New Active Catalyst

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Abstract: The reactivity of a new titanium triflimide salt (see Part 1) was investigated for the direct amination of alcohols. The combination of this new Lewis acid with pyridine-based ligands allowed a significant increase of its activity. The scope of the reaction was increased compared to other Lewis-acid-based protocols. Finally, some mechanistic insights based on EPR spectroscopy and DFT calculations are provided.

Introduction

Amines are important building blocks in the chemical industry, serving as intermediates in the manufacture of agrochemicals, surfactants, polymers, pharmaceuticals, solvents and dyes.^[1] Among the existing technologies for amine synthesis, direct alcohol amination stands out as an atom-efficient and environmentally benign route, since water is generated as sole by-product.^[2] Three main catalytic systems have been developed for direct alcohol amination: (i) the borrowing hydrogen method using either Ru or Ir complexes,^[3] or non-noble metal complexes based on Mn^[4] or Fe,^[5] (ii) Tsuji-Trost type reactions for allylic alcohols using Pd^[6] or Ni^[6a,7] complexes, and (iii) Lewis-acid (LA) catalysts based on a variety of salts and ligands.^[2a,2d] In the latter case, metal triflate [M(OTf)_n] and triflimide [M(NTf₂)_n] salts, based on Ca,^[8] Al,^[9] In,^[10] Yb,^[11] Bi,^[12] Ag,^[13] Hg,^[14] and HOTf,^[15] proved to be efficient. However, the reaction scope is limited to electron-poor amine derivatives, such as amides, sulfonamides, carbamates and activated alcohols.

In a previous study on Al(OTf)₃, we demonstrated the possibility of extending the amination reaction of benzyl alcohol to electron-rich *N*-derivatives using nonpolar solvents.^[16] Indeed, polar solvents promoted catalyst deactivation by the amine by favoring Al(OTf)₃ dissociation. However, even in low polar solvents, aluminum salts gave rather poor yields. For this reason, we investigated various descriptors of Lewis acids reactivity in part I paper, which appointed titanium triflimide (complex **4**) as a promising candidate to catalyze the direct amination of benzyl alcohol (BnOH, **1a**) with aniline (PhNH₂, **2a**) (Figure 1). Complex **4** was thus prepared by addition of excess trifluoromethane-sulfonimide (HNTf₂) on metal Ti in water under reflux during 48 h, followed by removal of water and excess

HNTf₂ under vacuum. The synthetic procedure and complete characterization of this compound are described in Part I of this paper, (alternative protocols and the associated characterization are reported in the SI of this paper). This catalyst proved to be a mixture of several Ti^{III} and Ti^{IV} triflimide species, based on elemental and TG analyses, and EPR studies. Ti^{III}_{0.2}Ti^{IV}_{0.8}(NTf₂)₂(O)_x(OH)_y(H₂O)_z·2.5H₂O was proposed as molecular formula for this salt. To our delight, under the initial conditions used for Al(OTf)₃, the desired product **3aa** was obtained with good yield and selectivity (Figure 1).

Figure 1. Direct amination of BnOH (**1a**) with aniline (**2a**) catalyzed by titanium triflimide (complex **4**) in toluene.

Here, we report on the catalytic activity of complex **4** and the optimization of the reaction conditions for more challenging amination reactions. Addition of a ligand allows significantly broadening the reactant scope for the LA-catalyzed amination of a library of alcohols with electron-rich amines.

Results and Discussion

Catalytic activity of complex **4**

To further increase the robustness of catalyst **4** in the direct amination process, we explored the effect of added ligands (Table 1). For this purpose, we started using the previous described conditions (see Part I) using 2 equiv of amine with respect to benzyl alcohol in the presence of 5 mol% of **4** in toluene at 180 °C under microwave irradiation for 2 h (Table 1, entry 1). Surprisingly, addition of 2,2'-bipyridine (bpy) or terpyridine as ligand resulted in a higher isolated yield of **3aa** (93% and 97%, respectively, Table 1). The optimal amount of ligand was 2 equiv against **4** while excess of ligand deactivated the catalyst. Different bipyridines were tested, giving either similar or poorer results (Table 1, entries 5-9). Neither addition of catalytic amounts of Brønsted acids such as triflic acid (HOTf) or

triflimidic acid (HNTf₂), nor addition of the sterically hindered tertiary diamine Proton Sponge® affected significantly the reaction, ruling out a “hidden proton” mechanism. Also noteworthy, the experiments carried out in mesitylene under thermal heating led to much lower performance even at longer reaction times. Increasing the catalyst loading from 5 mol% to 7.5 mol% allowed reducing the temperature and reaction time (Table 1, entries 10-11).

Table 1. Ligand effect on catalytic performance of **4**^{a)}

Entry	Ligand	yield of 3aa (%) ^{b)}
1	None	69
2	2,2'-bipyridine (1 equiv)	61
3	2,2'-bipyridine (2 equiv)	93
4	2,2'-bipyridine (3 equiv)	57
5	Phenanthroline	93
6	4,4'-dibromo-2,2'-bipyridine	78
7	6,6'-dibromo-2,2'-dipyridyl	79
8	4,4'-dimethyl-2,2'-dipyridyl	93
9	4,4'-di-tert-butyl-2,2'-dipyridyl	91
10	2,2'-bipyridine	96 ^{c)}
11	Terpyridine	97 ^{c)}

^{a)} Reaction conditions: **1a** (1 mmol) and **2a** (2 mmol, 2 equiv) were sequentially added at RT to a solution of **4** (0.075 mmol, 0.075 equiv) and the ligand (0.1 mmol, 0.1 equiv) in toluene (0.5 mL) in a MW vial equipped with a magnetic stirrer. The vial was then capped and heated under MW irradiation at 180 °C for 2 h. ^{b)} Measured by ¹H NMR using 2,4,6-trimethoxybenzene as an internal standard. ^{c)} Using 7.5 mol% of **4**, at 160 °C.

Table 2. Scope of the direct amination of alcohols using the **4**/ligand system^{a)}

Entry	alcohol (1)	amine (2)	product (3)	yield (%) ^{b)}
1	BnOH 1a	2a	3aa	96 (A) 76 ^{c)} (100) (B)
2	BnOH 1a	2b	3ab	96 (B)
3	BnOH 1a	2c	3ac	20 ^{c)} (100) (A)
4	BnOH 1a	2d	3ad	60 ^{c)} (100) (A)
5	BnOH 1a	2e	3ae	98 (B)
6	BnOH 1a	2f	3af	75 ^{d)} (B)
7	BnOH 1a	2g	3ag	86 ^{e)} (B)

8	BnOH 1a	2h	3ah	91 ^{f)} (B)
9	BnOH 1a	2i	3ai	96 ^{f)} (B)
10	BnOH 1a	2j	3aj	36 ^{g)} (B)

^{a)} Reaction conditions: **1** (1 mmol) and **2** (2 mmol, 2 equiv) were sequentially added at RT to a solution of **4** (0.075 mmol, 0.075 equiv) and bpy (A) or tpy (B) (0.15 mmol, 0.2 equiv) in toluene (0.5 mL) in a MW vial equipped with a magnetic stirrer. The vial was then capped and heated under MW irradiation at 160 °C for 1 h. ^{b)} Isolated yield; ¹H NMR yield using 2,4,6-trimethoxybenzene as an internal standard are indicated between parentheses. ^{c)} 4.5 mol%, 180 °C, 2 h; ^{d)} 140 °C, 8 h; ^{e)} 160 °C, 8 h; ^{f)} 180 °C, 12 h; ^{g)} 190 °C, 8 h.

Table 3. Scope of direct alcohol amination using the **4**/ligand system^{a)}

Entry	alcohol (1)	amine (2)	product (3)	yield (%) ^{b)}
1	1b	PhNH ₂ 2a	3ba	61
2	1c	PhNH ₂ 2a	3ca	93 ^{c)}
3	1d	PhNH ₂ 2a	3da	98 ^{d)}
4	1e	PhNH ₂ 2a	3ea	81 ^{e)} (N-/C- = 67:33)
5	1f	PhNH ₂ 2a	3fa	99 ^{f)} (N-/C- = 80:20)
6	1g	PhNH ₂ 2a	3ga	98 ^{f)} (N-/C- = 36:64)

^{a)} Same reaction conditions as in Table 2; ^{b)} Isolated yield. ^{c)} **4** (5 mol%), 180 °C, 2 h; ^{d)} 100 °C, 2 h; ^{e)} 80 °C, 16 h; ^{f)} 120 °C, 30 min.

Scope of the Reaction

The scope of the reaction was then assessed using the most efficient catalytic system based on **4** and either bpy (A) or terpyridine (B) as ligand (Table 2). Electron-rich anilines proved to be less reactive than electron-poor anilines, most likely due to catalyst deactivation (Figure S1).^[16] Primary anilines **2b-2f** bearing electron-donating (entries 2-4) and electron-withdrawing groups (Table 2, entries 5-6) reacted to give selectively the secondary amines **3ab-3af** with excellent yield. 6-Amino-2-bromopyridine **2g** could be benzylated, but longer reaction times were required to allow isolation of product **3ag** in good yield (Table 2, entry 7). Owing to their bulkier nature, secondary benzylamines such as tetra-hydroisoquinoline **2h** and dibenzylamine **2i** were more reluctant to undergo benzylation with **1a**, demanding higher catalyst/ ligand loading and longer reaction time (Table 2, entries 8-9). Finally, the reaction of dodecylamine **2j** with **1a** only afforded moderate yield due to a significant drop of the selectivity (entry 10).

Subsequently, we assessed the reactivity of a library of alcohols (Table 3). Benzyl alcohols bearing electron-donating groups either at the *p*- (**1b**) or *m*-position (**1c**) reacted smoothly with aniline (**2a**), affording the secondary amines **3ba** and **3ca**, respectively, in good yield (Table 3, entries 1-2). Interestingly, biomass-derived furfuryl alcohol (**1d**) proved to be an excellent substrate for the reaction, and the desired furfuryl aniline (**3da**) was obtained at 98% yield at mild reaction conditions (Table 3, entry 3). The reactivity of allyl alcohols towards amination was then evaluated (Table 3, entries 4-6). Even at low temperature, the thermodynamically favored C-alkylated product was formed together with the *N*-alkylated kinetic product, which could arise from a LA-catalyzed aza-Claisen rearrangement of the latter.^[15] The reaction of nerol (**1e**) with aniline (**2a**) at 80 °C delivered a ca. 2:1 mixture of *N*- and C-alkylated isomers in good overall yield (Table 3, entry 4). The isolation of the latter product revealed partial isomerization of the original (*Z*) double bond. Likewise, the reaction of **1f** and **1g** with **2a** led to a mixture of isomers (Table 3, entries 5-6).

Reaction mechanism

In all cases, the mixture of **4** with a ligand turned out to be efficient to catalyze the amination of activated alcohols. To rationalize this catalytic system, a mechanistic study was carried out. First, a possible redox mechanism (i.e. non-Lewis acid, type "borrowing hydrogen"^[3]) was ruled out. The crude reaction mixtures were carefully examined: plausible imine intermediates were not detected, thus providing evidence for a S_N -type rather than a "borrowing hydrogen" mechanism. An additional crossover experiment using an equimolar mixture of *m*-methylbenzyl alcohol (**1h**) and deuterated BnOH (**1a'**) led to neither deuterated product **3h'a** nor the loss of deuterium in **3a'a** as attested by ¹H NMR and HRMS (Figure 2). To go further into our mechanistic investigation and discriminate between S_N1 - and S_N2 -type mechanisms, (*R*)-1-phenylethanol (**1i**) was reacted with **2a** and racemic **3ia** was isolated, which advocates for a carbocationic intermediate (Figure 2).

Figure 2. Reaction of deuterated (**1a'**) and chiral alcohols (**1m**) with aniline (**2a**) catalyzed by titanium triflimide (complex **4**) in toluene.

Subsequently, we attempted to answer two main questions by combining experiments with DFT calculations relying on our previous study on $Al(OTf)_3$ ^[13]: i) as we start with a mixture of Ti(III) and Ti(IV) triflimide (see Part I for characterization of **4**), what is the oxidation state of the catalyst during the reaction? and ii) what is the role played by the ligands, i.e. triflimides, bpy and the reactants (alcohols and amines)?

In order to clarify the first point, we tried other sources of titanium: Ti(III) and Ti(IV), with or without triflimide counter-anion. Ti(IV) halides ($TiCl_4$ and $TiBr_4$) were found inactive for the

reaction of BnOH with aniline. On the contrary, Ti(III) halides catalyzed the reaction: $TiBr_3$ generated *in-situ* from $TiBr_4/Zn$ and $TiCl_3(THF)_3$ gave product **3aa** with 20% and 15% yield, respectively, at 160 °C after 1 h and, with $TiCl_3(THF)_3/bpy$ provided 39% of isolated product. The higher activity of Ti(III) could be attributed to lower hydrolysis/oxolation than Ti(IV). This would point out Ti(III) as active catalyst. However, triflimide anions also display an important role and Ti(IV)/triflimides are good pre-catalysts. Indeed, a mixture of $TiCl_4$ and $LiNTf_2$ (or $AgNTf_2$), as well as $Cp_2Ti(NTf_2)_2$, were catalytically active. Moreover, the reaction worked similarly both under Ar and under air. Thus, to get more insight on the oxidation state of Ti under reaction conditions we turned to EPR spectroscopy, which is a sensitive technique for the analysis of paramagnetic Ti(III) species ($S=1/2$). Complex **4** was not soluble in toluene and the EPR spectrum was similar to that measured on the solid salt. According to DFT calculations, the experimental *g*-tensor was compatible with $Ti(NTf_2)_3$ (**5**, Table 4). Adding BnOH (20 equiv) solubilized **4**, generating two EPR active species. The *g*-tensor of the main species, accounting for 80% of the EPR intensity, was distinctive of a Jahn-Teller distorted octahedral complex ($g = [1.992\ 1.901\ 1.901]$, 80%) (Figure S2). The remaining 20% of the intensity encompassed a more symmetrical signal at $g = [1.963\ 1.950\ 1.935]$. The first signal could be attributed to $Ti(NTf_2)_3(BnOH)_3$ (**6-7**) as inferred from DFT calculations (Table 1, Figures S3-S4). However, a Ti(III) complex featuring an alkoxy ligand, i.e. $Ti(NTf_2)_2(BnO)(BnOH)_2$ (**9**) or $Ti(NTf_2)_2(BnO)$ (**10**), was predicted to show a very fine EPR signal (Figure S3), which is in agreement with reported experimental and simulated data for the $TiCl_3/MeOH$ system.^[17] Relying on DFT calculations, we propose a *fac*- $Ti(NTf_2)_3(BnOH)_3$ (**7**) complex as the main species together with partial formation of $Ti(NTf_2)_2(BnO)(BnOH)_2$ (**10**).

Table 4. DFT-predicted *g*-tensor of some Ti(III)-complexes resulting from the coordination of BnOH, aniline and bpy^{a)}

Species	<i>g</i>		
$Ti(NTf_2)_3$ (5) ^{b)}	1.920	1.944	1.976
<i>mer</i> - $Ti(NTf_2)_3(BnOH)_3$ (6)	1.924	1.945	1.995
<i>fac</i> - $Ti(NTf_2)_3(BnOH)_3$ (7)	1.942	1.951	1.997
<i>fac</i> - $Ti(NTf_2)_3(H_2O)_3$ (8)	1.923	1.942	2.000
$Ti(NTf_2)_2(BnO)(BnOH)_2$ (9)	1.961	1.973	1.979
$Ti(NTf_2)_2(BnO)$ (10)	1.958	1.975	1.985
<i>mer</i> - $Ti(NTf_2)_3(PhNH_2)_3$ (11)	1.933	1.953	1.981
<i>fac</i> - $Ti(NTf_2)_3(PhNH_2)_3$ (12)	1.932	1.947	1.984
$[Ti(NTf_2)_2(PhNH_2)_2]^+$ (13)	1.921	1.946	1.988
$[Ti(NTf_2)_2(PhNH_2)_4]^+$ (14)	1.954	1.956	1.974
$[Ti(PhNH_2)_4]^{3+}$ (15)	1.929	1.978	1.997
$[Ti(PhNH_2)_6]^{3+}$ (16)	1.930	1.962	1.989
$[Ti(bpy)_2]^{3+}$ (17)	1.874	1.980	1.998
$[Ti(bpy)_3]^{3+}$ (18)	1.878	1.936	1.997
$[Ti(bpy)_2(BnOH)_2]^{3+}$ (19)	1.972	1.974	1.998
$[Ti(bpy)_2(BnO)(BnOH)]^{2+}$ (20)	1.973	1.982	1.991

^{a)} See SI for a comparison of DFT-calculated and EPR spectra.^{b)} Since complex **4** consisted of a Ti(III) and Ti(IV) mixture, we chose to model Ti(III) by $Ti(NTf_2)_3$ (noted as **5**).

Upon addition of aniline to **4**, a dark blue precipitate appeared that quickly discolored, most likely due to oxidation by

oxygen traces, yielding a yellowish solid. The EPR spectrum of the blue precipitate was characterized by a sharp resonance $g = [1.966\ 1.940\ 1.903]$ (Figure S5), while the mixture became EPR silent when turning yellowish, revealing the absence of residual Ti(III) after addition of aniline. The formation of a solid is consistent with the formation of an ionic salt through triflimide displacement by aniline. This result was confirmed by addition of aniline to $\text{TiCl}_3(\text{THF})_3$, showing a very similar spectrum, which confirms that both chloride and triflimide anions are displaced by aniline. Addition of BnOH to the mixture of **4** and aniline did not modify the EPR spectrum (Figure S6-S8), which confirms the poisoning role of aniline.^[16] The species are prone to be oxidized, probably due to the electron-donation ability of aniline. Based on this observation, i.e. Ti(III)/aniline is easily oxidized, it seems very unlikely that Ti(III) species would be still present under reaction conditions. Therefore, a possible role of Ti(III) in this case would be to protect Ti triflimide from hydrolysis preventing the formation of TiO_2 (see the discussion on Part I of the paper).

Finally, we tried to get some clues on the role of the polypyridine ligands. To mimic the experimental conditions, increasing amounts of bpy were added to a solution of **4** solubilized by 20 equiv of BnOH . The resulting blue precipitate exhibited a sharp signal at $g = [1.978\ 1.966\ 1.952]$ (Figures S9), which cannot be attributed to $\text{Ti}(\text{bpy})_3^{3+}$ (**18**) (see the spectra of TiCl_3 in the presence of excess bpy, Figure S9, and detailed discussion in the SI). By comparison with DFT calculations, the experimental g -tensor should be compatible with $[\text{Ti}(\text{bpy})_2(\text{BnOH})_2]^{3+}$ (**19**) or $[\text{Ti}(\text{bpy})_2(\text{BnO})(\text{BnOH})]^{2+}$ (**20**) complexes (see more details in Figure S10-S15).

We propose that complexes (**19-20**) (Table 1) or most likely Ti(IV) analogues of these complexes are catalytically active for amination. Bipyridine could thus possibly help to: i) improve the catalyst solubility, ii) avoid catalyst deactivation by aniline (and or hydrolysis), and iii) form a more active cationic species (**19-20**).

Conclusion

In summary, titanium triflimide, first designed by computational studies, proved to be a very interesting catalytic system if combined with bipyridine ligand for the direct amination of alcohols with amines in toluene. This rational design along with optimization of the reaction conditions allowed to widely extend the scope of the reaction including electron-rich amines and primary aliphatic amines. Finally, EPR spectroscopy and DFT calculations shed light into the reaction mechanism.

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Keywords: Amination • Alcohol • Lewis Acidity • DFT • Titanium Triflimide

Notes

- [1] H. A. Wittcoff, B. G. Reuben, J. S. Plotkin, *Industrial Organic Chemicals*, 2nd ed., Wiley, NY, **2004**.
- [2] a) E. Emer, R. Sinisi, M. G. Capdevila, D. Petruzzello, F. De Vincentiis P. G. Cozzi, *Eur. J. Org. Chem.* **2011**, 2011, 647-666; b) M. Pera-Titus, F. Shi, *ChemSusChem*. **2014**, 7, 720-722; c) S. Bähn, S. Imm, L. Neubert, M. Zhang, H. Neumann, M. Beller, *ChemCatChem*. **2011**, 3, 1853-1864; d) A. Baeza, C. Nájera, *Synthesis*, 2014, **46**, 25-34.
- [3] (a) T. D. Nixon, M. K. Whittlesey, J. M. J. Williams, *Dalton Trans.* **2009**, 753-762; (b) G. Guillena, D. J. Ramón, M. Yus, *Chem. Rev.* **2010**, 110, 1611-1641; (c) J. L. Klinkenberg, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2011**, 50, 86-95; (d) C. Gunanathan, D. Milstein, *Science* **2013**, 341, 1229712; (e) Q. Yang, Q. Wang, Z. Yu, *Chem. Soc. Rev.* **2015**, 44, 2305-2329.
- [4] J. Neumann, S. Elangovan, A. Spannenberg, K. Junge, M. Beller, *Chem. Eur. J.* **2017**, 23, 5410-5413.
- [5] B. Emayavaramban, M. Roy, B. Sundararaju, *Chem. Eur. J.* **2016**, 22, 3952-3955.
- [6] (a) H. Bricout, J.-F. Carpentier, A. Mortreux, *J. Mol. Cat. A: Chem* **1998**, 136, 243-251; (b) Y. Gumrukcu, B. de Bruin, J. N. H. Reek, *Catalysts* **2015**, 5, 349-365; (c) S. Sawadjoon, P. J. R. Sjöberg, A. Orthaber, O. Matsson, J. S. M. Samec, *Chem. Eur. J.* **2014**, 20, 1520-1524; (d) J. Muzart, *Eur. J. Org. Chem.* **2007**, 2007, 3077-3089.
- [7] (a) H. Bricout, J.-F. Carpentier, A. Mortreux, *Tetrahedron* **1998**, 54, 1073-1084; (b) Y. Kita, H. Sakaguchi, Y. Hoshimoto, D. Nakauchi, Y. Nakahara, J.-F. Carpentier, S. Ogoshi, K. Mashima, *Chem. Eur. J.* **2015**, 21, 14571-14578.
- [8] S. Haubenreisser, M. Niggemann, *Adv. Synth. Catal.* **2011**, 353, 469-474.
- [9] a) M. Gohain, C. Marais, B. C. B. Bezuidenhoudt, *Tetrahedron Lett.* **2012**, 53, 1048-1050; b) T. Ohshima, J. Ipposhi, Y. Nakahara, R. Shibuya, K. Mashima, *Adv. Synth. Catal.* **2012**, 354, 2447-2452.
- [10] J.-M. Yang, R. Jiang, L. Wu, X.-P. Xu, S.-Y. Wang, S.-J. Ji, *Tetrahedron* **2013**, 69, 7988-7994.
- [11] a) W. Huang, Q.-S. Shen, J.-L. Wang, X.-G. Zhou, *Chin. J. Chem.* **2008**, 26, 729-735; b) W. Rao, X. Zhang, E. M. L. Sze, P. W. H. Chan, *J. Org. Chem.* **2009**, 74, 1740-1743.
- [12] a) R. Jiang, C.-X. Yuan, X.-P. Xu, S.-J. Ji, *Appl. Organomet. Chem.* **2012**, 26, 62-66; b) H. Qin, N. Yamagiwa, S. Matsunaga, M. Shibasaki, *Angew. Chem. Int. Ed.* **2007**, 46, 409-413.
- [13] a) X. Giner, P. Trillo, C. Nájera, *J. Organomet. Chem.* **2011**, 696, 357-361; b) B. Sreedhar, P. Surendra Reddy, M. Amarnath Reddy, B. Neelima, R. Arundhati, *Tetrahedron Lett.* **2007**, 48, 8174-8177.
- [14] H. Yamamoto, E. Ho, I. Sasaki, M. Mitsutake, Y. Takagi, H. Imagawa, M. Nishizawa, *Eur. J. Org. Chem.* **2011**, 2011, 2417-2420.
- [15] P. Trillo, A. Baeza, C. Nájera, *Eur. J. Org. Chem.* **2012**, 2012, 2929-2934.
- [16] P.-A. Payard, Q. Gu, W. Guo, Q. Wang, M. Corbet, C. Michel, P. Sautet, L. Grimaud, R. Wischert, M. Pera-Titus, *Chem. Eur. J.* **2018**, 24, 14146-14153.
- [17] a) A. Dzudza, T. J. Marks, *Chem. Eur. J.* **2010**, 16, 3403-3422; b) T. T. Dang, F. Boeck, L. Hintermann, *J. Org. Chem.* **2011**, 76, 9353-9361; c) R. K. Schmidt, K. Muther, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.* **2012**, 134, 4421-4428.