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Catalytic activity of a zirconium(IV) Schiff base complex in facile and highly efficient synthesis of indole derivatives

Maasoumeh Jafarpour · Abdolreza Rezaeifard · Somayeh Gazkar · Maryam Danehchin

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Abstract Eight Schiff base compounds were prepared by condensation of 1-amino-2-propanol with different benzaldehydes in water. One of the Schiff bases, (z)-N-bezylidene-2-hydroxypropane-1-amine (HL^1), was used as a bidentate ligand for preparation of a zirconium complex ($Zr(L^1)_2Cl_2$). The complex has been used as a catalyst for efficient synthesis of wide variety of indole derivatives in EtOH under mild conditions. The turnover number and reusability of the catalyst indicate that it has high efficiency and is fairly stable under the reaction conditions.

Introduction

The chemistry of transition metal complexes with Schiff base ligands has been widely investigated in organometallic chemistry and catalysis. Despite the extensive investigations on complexes of salen-type ligands with middle and late d-block transition metals as catalysts for diverse organic reactions, very few reports have appeared describing the synthesis [1, 2], crystal structures [3, 4] or catalytic properties of group IV metal complexes with such ligands [5, 6].

Zirconium(IV), with a high charge-to-size ratio (Z^2/r is 22.22 e^2m^{-10}) [7], has a strong coordinating ability with oxygen- and nitrogen-containing ligands, and zirconium salen complexes have proved to be efficient catalysts both in homogeneous and in heterogeneous reactions. The activities of these complexes vary markedly with the type of ligands and coordination sites [8–17].

Indole derivatives have attracted much interest due to their manifold applications in materials science, agrochemicals and pharmaceuticals. In particular, compounds containing the bis (indolyl) motif, such as secondary metabolites and marine sponge alkaloids, are of great interest. Indoles can readily undergo electrophilic substitution reactions with the oxygen atom of carbonyl compounds in the presence of a suitable catalyst to form bis- and tris (1H-indol-3-yl) methanes. Different compounds are known to catalyze this reaction [18].

In continuation of our ongoing research on the development of new eco-friendly organic synthesis, particularly by mediation of zirconium salts [19–27], herein, we report the facile preparation of some new Schiff bases and the catalytic performance of a zirconium(IV) complex of one of these Schiff base ligands for the mild and facile synthesis of indole derivatives in ethanol (Schemes 1, 2).

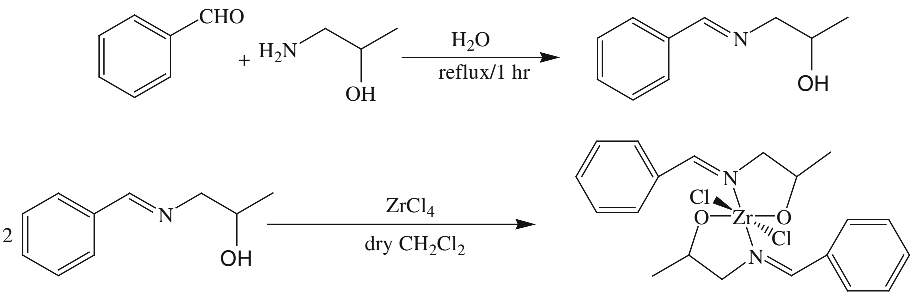
Experimental

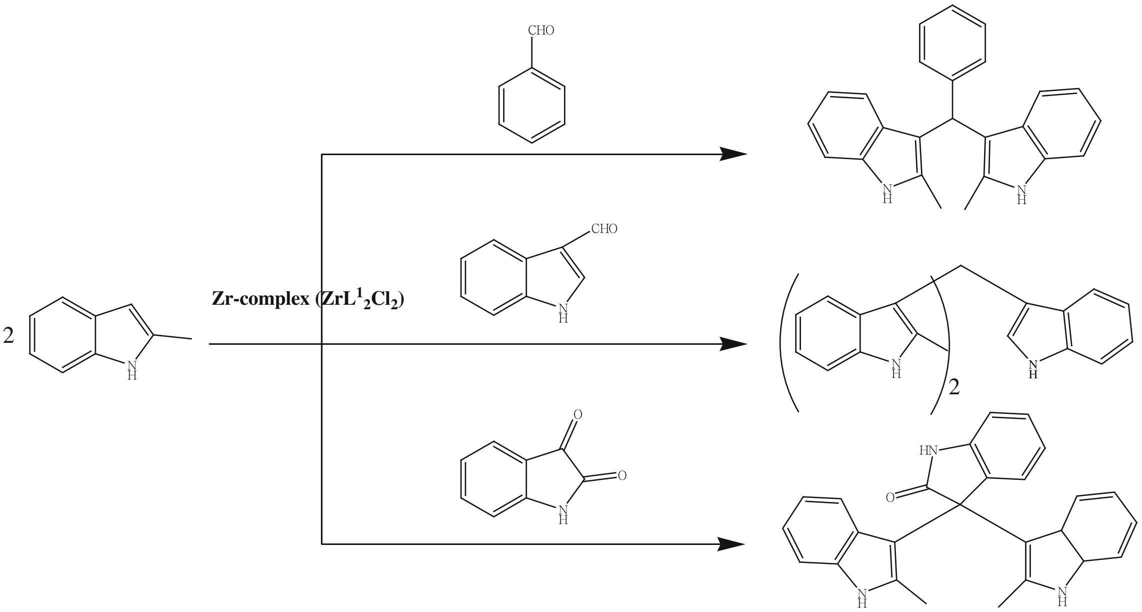
Carbonyl compounds, indoles, $ZrCl_4$ and amino alcohol were purchased from Merck or Fluka. The progress of each reaction was monitored by TLC using silica gel SIL G/UV 254 plates and also by GC-FID on a Shimadzu GC-16A instrument using a 25-m CBP1-S25 (0.32 mm ID, 0.5 µm coating) capillary column. NMR spectra were recorded on Bruker Avance DPX 250 MHz and 400 MHz spectrometers. Mass spectra were recorded on a Shimadzu GC–MS-QP 5050A instrument.

M. Jafarpour (✉) · A. Rezaeifard (✉) · S. Gazkar · M. Danehchin
Catalysis Research Laboratory, Department of Chemistry, Faculty of Science, University of Birjand, Birjand 97179-414, Iran
e-mail: mjafarpour@birjand.ac.ir

A. Rezaeifard
e-mail: rrezaeifard@gmail.com; rrezaeifard@birjand.ac.ir

Scheme 1 Synthesis of Zr-complex ($ZrL^1_2Cl_2$)





Scheme 2 Synthesis of indole derivatives in the presence Zr-complex ($ZrL^1_2Cl_2$) (2 mol%) in ethanol at room temperature

*General procedure for the preparation of the Schiff base ligands (**HL$^{1–8}$**)*

The appropriate aldehyde (1 mmol) was added to a solution of 1-amino-2-propanol (0.17 mL, 1.5 mmol) in distilled water (0.2 mL). The mixture was refluxed for 1 h. The precipitate which formed upon cooling was filtered off and washed with cold water. The Schiff bases were purified by recrystallization from n-hexane (Table 1). [Note: some of Schiff base ligands precipitated after hours or days (HL^2, HL^3, HL^6, HL^7)].

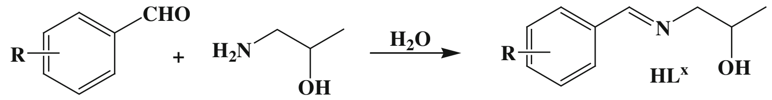
HL^1; M.P: 73–75 °C; IR (KBr,): (C=N) 1,638 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δppm = 1.33 (d, 3H, $J = 6.25$ Hz), 2.69 (s, 1H, OH), 3.43–3.51(m, 1H), 3.66–3.72 (m, 1H), 4.04–4.11 (m, 1H), 7.40–7.74 (m, 5H, *Ar*), 8.3 (s, 1H, CH=N); ^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm) = 20.6, 67.47, 68.59, 128.18, 128.62, 130.88, 135.85, 162.77; Anal. Calcd for ($C_{10}H_{13}NO$): C, 73.6; H, 8.0; N, 8.6. Found: C, 73.6; H, 8.1; N, 8.6; MS (*m*/*e*) = 163 $[M]^+$.

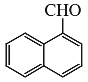
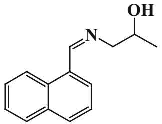
HL^2; M.P: 77–78 °C; IR (KBr,): (C=N) 1,639 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δppm = 1.28 (d, 3H, $J = 6.25$ Hz), 2.49 (s, 1H, OH), 3.50–3.58 (m, 1H), 3.72–3.77 (m, 1H), 4.08–4.20 (m, 1H), 7.87 (d, 2H, $J = 8.25$ Hz), 8.16(d, 2H, $J = 8.25$ Hz), 8.39 (s, 1H, CH=N); ^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm) = 20.74, 67.37, 68.66, 123.87, 128.84, 141.26, 149.09, 160.39 ppm; Anal. Calcd for ($C_{10}H_{12}N_2O_3$): C, 57.7; H, 5.8; N, 13.4. Found: C, 57.7; H, 5.8; N, 13.4; MS (*m*/*e*) = 208 $[M]^+$.

HL^3; M.P**:** 81–82 °C; IR (KBr,): (C=N) 1,644 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δppm = 1.29 (d, 3H, $J = 6.25$ Hz), 2.55 (s, 1H, OH), 3.50–3.58 (m, 1H), 3.71–3.77 (m, 1H), 4.07–4.17 (m, 1H), 7.51 (m, 1H), 8.03 (d, 1H, $J = 7.5$ Hz), 8.23 (d, 1H, $J = 8$ Hz), 8.38 (s, 1H), 8.55 (s, 1H, CH=N); ^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm) = 20.74, 67.37, 68.66, 123.77, 124.20, 128.84, 135.20, 141.16, 148.89, 160.40 ppm; Anal. Calcd for ($C_{10}H_{12}N_2O_3$): C, 57.7; H, 5.8; N, 13.4. Found: C, 57.7; H, 5.8; N, 13.4; MS (*m*/*e*) = 208 $[M]^+$.

HL^4; M.P**:** 61–62 °C; IR (KBr,): (C=N) 1,644 cm^{-1}; ^1H NMR($CDCl_3$, TMS, 250 MHz): δ 1.25 (d, 3H, $J = 6.25$ Hz), 2.51 (s, 1H, OH), 3.42–3.50 (m, 1H), 3.64–3.71 (m, 1H), 4.01–4.13 (m, 1H), 7.49 (m, 4H), 8.25 (s, 1H, CH=N) ppm; ^{13}C

Table 1 Synthesis of Schiff base ligands[a]



Entry	Aldehyde	Product[b]	Isolated yield (%)	m.p (°C)	IR (cm^{-1})
1	R=H	HL^1 (R=H)	75	73–76	1,638
2	R=*p*-NO_2	HL^2 (R=*p*-NO_2)	82	77–78	1,639
3	R=*m*-NO_2	HL^3 (R=*m*-NO_2)	90	81–82	1,644
4	R=*p*-Br	HL^4 (R=*p*-Br)	90	61–62	1,644
5	R=*p*-Cl	HL^5 (R=*p*-Cl)	85	56–57	1,644
6	R=*p*-Me	HL^6 (R=*p*-Me)	75	51–52	1,641
7	R=*p*-NMe_2	HL^7 (R=*p*-NMe_2)	74	101–103	1,630
8	 CHO	 OH N HL^8	90	50–56	1,637

[a] The reactions were run at reflux and the molar ratio of aldehyde/aminoalcohol was 1:1.5 in 0.2 mL H_2O

[b] All products were identified by their spectroscopic data

NMR ($CDCl_3$, 63 MHz) δ (ppm) = 20.64, 67.40, 68.53, 124.31,130.07, 131.12, 137.20, 161.35 ppm; Anal. Calcd for ($C_{10}H_{12}BrNO$): C, 49.6; H, 5.0; N, 5.8. Found: C, 49.6; H, 5.1; N, 5.8; MS (*m/e*) = 242 [M^+].

HL⁵; M.P**:** 56–57 °C; IR (KBr,): (C=N) 1,644 cm^{-1}; ^1H NMR($CDCl_3$, TMS, 250 MHz): δ 1.25 (d, 3H, $J = 6.25$ Hz), 2.68 (s, 1H, OH), 3.41–3.50 (m, 1H), 3.64–3.70 (m, 1H), 4.01–4.13 (m, 1H), 7.34 (d, 2H, $J = 8.5$ Hz), 7.62 (d, 2H, $J = 8.25$ Hz), 8.23 (s, 1H, CH=N) ppm;^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm) = 20.64, 67.40, 68.53, 128.87, 129.35, 134.31, 136.80, 161.35 ppm; Anal. Calcd for ($C_{10}H_{12}ClNO$): C, 60.8; H, 6.1; N, 7.1. Found: C, 60.8; H, 6.1; N, 7.1; MS (*m/e*) = 197 [M^+].

HL⁶; M.P: 51–52 °C; IR (KBr,): (C=N) 1,641 cm^{-1}; ^1HNMR($CDCl_3$, TMS, 250 MHz): δ 1.24 (d, 3H, $J = 6.25$ Hz), 2.37 (s, 3H), 2.93 (s, 1H, OH), 3.40–3.48 (m, 1H), 3.63–3.68 (m, 1H), 4.04–4.08 (m, 1H), 7.18 (d, 2H, $J = 7.5$ Hz), 7.59 (d, 2H, $J = 7.5$ Hz), 8.24 (s, 1H, CH=N) ppm;^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm) = 20.61, 21.18, 67.45, 68.62, 128.17, 129.04, 133.29, 141.15, 162.67 ppm; Anal. Calcd for ($C_{11}H_{15}NO$): C, 74.5; H, 8.5; N, 7.9. Found: C, 74.5; H, 8.5; N, 7.9; MS (*m/e*) = 177 [M^+].

HL⁷; M.P: 101–103 °C; IR (KBr,): (C=N) 1,630 cm^{-1}; ^1HNMR($CDCl_3$, TMS, 250 MHz): δ 1.23 (d, 3H, $J = 6.25$ Hz), 2.85 (s, 1H, OH), 3.00 (s, 6H), 3.39–3.44 (m, 1H), 3.65–3.67 (m, 1H), 4.01–4.06 (m, 1H), 6.66 (d, 2H, $J = 8.75$ Hz), 7.58 (d, 2H, $J = 8.75$ Hz), 8.16 (s, 1H, CH=N) ppm;^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm) = 20.51, 40.18, 67.59, 68.47, 111.56, 123.98, 129.67, 152.20, 162.63 ppm; Anal. Calcd for ($C_{12}H_{18}N_2O$): C, 69.9; H, 8.8; N, 13.6. Found: C, 69.9; H, 8.8; N, 13.6; MS (*m/e*) = 206 [M^+].

HL⁸; M.P: 50–56 °C; IR (KBr,): (C=N) 1,637 cm^{-1}; ^1H NMR($CDCl_3$, TMS, 250 MHz): δ 1.34 (d, 3H, $J = 6.25$ Hz), 2.66 (s, 1H, OH), 3.53–3.65 (m, 1H), 3.79–3.85 (m, 1H), 4.17–4.18 (m, 1H), 7.49–7.61 (m, 3H, Ar), 7.80–8.00 (m, 3H, Ar), 8.85 (d, 1H, $J = 8$ Hz), 8.96(s, 1H, CH=N) ppm; ^{13}CNMR($CDCl_3$, TMS, 62.9 MHz): 20.71, 67.62, 69.58, 124.13, 125.21, 126.08, 127.21, 128.68, 128.89, 131.25, 133.83, 162.42 ppm; Anal. Calcd for ($C_{14}H_{15}NO$): C, 78.8; H, 7.1; N, 6.6. Found: C, 78.9; H, 7.1; N, 6.6; MS (*m/e*) = 213 [M^+].

Preparation of $ZrL^1_2Cl_2$

$ZrCl_4$ (0.233 g, 1 mmol) was added to a solution of (z)-N-bezylidene-2-hydroxypropane-1-amine (HL^1) (2 mmol, 0.326 g) in dry CH_2Cl_2 (10 mL). The mixture was stirred under N_2 for 2 h at room temperature. The precipitate was filtered off and washed with cold, dry CH_2Cl_2 then with dry n-hexane. The solid was dried under reduced pressure to give the complex as a deep yellow powder in 80% yield. M.P.: 143 °C; IR (KBr,): (C=N) 1,665 cm^{-1}; ^1H NMR (400 MHz, d_6-DMSO) δppm = 1.17 (d, 6H, $J = 6.4$ Hz), 3.58–3.88 (m, 4H, CH_2), 4.26 (m, 2H), 7.49–7.62 (m, 10H, Ar), 9.05(s, 2H, CH=N). ^{13}CNMR(100.64 MHz, d_6-DMSO)**:** 21.31, 63.46, 64.16, 128.21, 129.03, 130.06, 137.07, 171.72; Anal. Calcd for ($C_{20}H_{24}N_2O_2ZrCl_2$): C, 49.4; H, 5.0; N, 5.8. Found: C, 49.4; H, 5.0; N, 5.7. MS (*m*/*e*) = 484 [M^+].

General procedure for the condensation of indoles with carbonyl compounds catalyzed by the complex

The appropriate indole (10.5 mmol) was added to a solution of the carbonyl compound (5 mmol) and $ZrL^1_2Cl_2$ complex (0.1 mmol, 0.048 g) in ethanol (2.5 mL). The mixture was stirred at room temperature for an appropriate time, as monitored by TLC (Table 2). After completion of the reaction, the product was extracted by plate chromatography eluted with n-hexane/EtOAc (3/1). Structural assignments of the products are based on their ^1H NMR, ^{13}C NMR and MS spectra and elemental analysis.

Results and discussion

The Schiff base ligands (Table 1) were prepared by the condensation of 1-amino-2-propanol with a number of aldehydes with different electronic and steric substituents and purified by recrystallization from n-hexane.

One of the Schiff bases, namely (z)-N-bezylidene-2-hydroxypropane-1-amine (HL^1), was chosen for reaction with $ZrCl_4$.

Analytical and spectroscopic data for the complex are given in the experimental section. Spectroscopic data and elemental analyses are consistent with a monomeric complex with a ligand/Zr ratio of 2:1. When the synthesis reaction was performed using three equivalents of HL^1, the same product was formed, as observed with two equivalents of L^1. The infrared spectrum of $ZrL^1_2Cl_2$ shows that the imine band of HL^1, observed at 1,638 cm^{-1} for the free ligand, shifts to higher wavenumbers after coordination of the azomethine nitrogen to the Zr center, appearing at 1,665 cm^{-1}. In the ^{1}HNMR, a singlet at 8.3 ppm that is assigned to the azomethine proton of $HL^1$is shifted downfield to 9.05 ppm, resulting from the coordination of the azomethine nitrogen. The absence of a broad singlet at 2.75 ppm in the spectrum of the complex compared with the free Schiff base HL^1 indicates coordination of the hydroxyl group after deprotonation.

Catalytic activity of the complex

Our preliminary experiments were addressed to the condensation of benzaldehyde with indole as a model reaction, to determine the best conditions with respect to temperature and reaction time. The use of 1 mmol of benzaldehyde and 2.1 mmol of indole in ethanol in the presence of a catalytic amount of the complex (2 mol%) gave the desired bisindolylmethane in 95% yield within 5 min at room temperature.

Based on the optimized reaction conditions, the present protocol was applied to a variety of carbonyl compounds and indoles. As shown in Table 2, aromatic aldehydes having both electron-donating and electron-withdrawing groups afforded bis(indolyl)methanes in excellent yields. Rapid condensation of various carbonyl compounds with 2-methyl indole under the same reaction conditions was observed (Table 2, entries 11–16). Moreover, when 3-formylindole was employed as a carbonyl compound, the corresponding trisindolylmethane was obtained in excellent yield (Table 2, entry 9, 15).

When we applied similar reaction conditions for the condensation of isatin and indoles, the desired 3,3′-diindolyloxindole derivatives were secured in 85–90% yields (Table 2, entries 10, 16).

However, the reaction of indole with acetophenone in the presence of 2 mol% of catalyst was not successful, and after a prolonged reaction time, most of the starting materials were observed intact (Table 2, entry 18).

The high yields of condensation products (80–97%) obtained by this catalytic system in short reaction times (<30 min) indicates the high efficiency of this Zr(IV) Schiff base complex catalyst. This was further supported by the high turnover numbers obtained for the catalyst in the condensation of benzaldehyde with indole (3,300/24 h) using a 10,000:21,000:2 molar ratio of benzaldehyde/indole/catalyst.

The catalyst proved to be reusable for at least three times in multiple sequential condensations by the addition of new samples of benzaldehyde and indole to the reaction mixture.

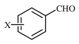
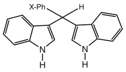
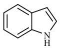
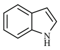
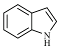
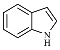
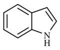
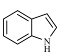
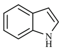
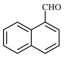
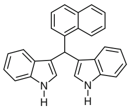
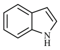
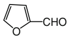
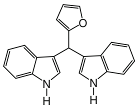
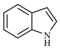
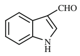
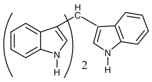
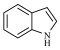
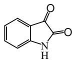
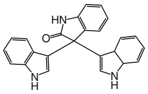
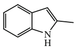
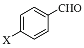
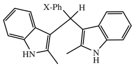
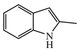
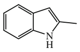
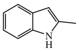
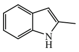
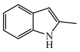
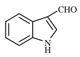
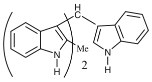
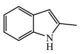
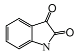
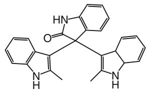
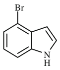
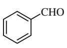
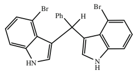
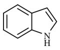
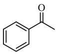
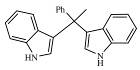
The reactions are also scalable; thus, the condensation of benzaldehyde and indole as substrates in a semi-scale-up procedure (20 times) gave the desired product in 95% yield.

In order to show the merit of $ZrL^1_2Cl_2$ in comparison with the other catalysts used for similar reactions, we have compared the results obtained using condensation of benzaldehyde and indole with some of those reported in the literature in Table 3.

Conclusion

In conclusion, the catalytic activity of $ZrL^1_2Cl_2$ in the synthesis of wide variety of indole derivatives under mild conditions has been established. The employment of ethanol as an environmentally benign solvent in this high yielding method, along with high turnover numbers and reusability of the catalyst providing ready scalability, makes it appropriate for practical applications.

Table 2 Condensation of indoles with carbonyl compounds catalyzed by Zr-complex ($ZrL^1_2Cl_2$)[a]

Entry	Indole	Carbonyl Compounds	Product[b]	Time (min)	Isolated Yield%
					
1		X=H	X=H	5	95
2		X=4-Me	X=4-Me	10	97
3		X=4-OMe	X=4-OMe	15	96
4		X=4-OH	X=4-OH	5	97
5		X=4-Br	X=4-Br	30	95
6		X=4-NO_2	X=4-NO_2	20	90
7				25	85
8				20	95
9				20	78
10[c]				20	97
					
11		X=H	X=H	<1	95
12		X=4-OMe	X=4-OMe	<1	96
13		X=4-NO_2	X=4-NO_2	<1	95
14		X=4-Br	X=4-Br	<1	97
15				4	96
16[c]				10	97
17				25	95
18				120	20

[a] The reactions were run at 25–27 °C, and the molar ratio of carbonyl compound/indole/catalyst was 100:210:2 in 0.5 mL ethanol

[b] All products were identified by their spectroscopic data and their comparison with known samples [20, 26, 28]

[c] The reactions were run at 25–27°C and the molar ratio of carbonyl compound/indole/catalyst was 100:210:2 in 1 mL ethanol

Table 3 Catalytic activity of Zr-complex ($ZrL^1_2Cl_2$) in comparison with other catalysts used for condensation of benzaldehyde and indole

Entry	Catalyst	Catalyst (mol %)	Time (h)	Yield (%)	Ref.
1	Zr-complex ($ZrL^1_2Cl_2$)/ethanol	2	5 min	95	–[a]
2	$ZrCl_4/CH_3CN$	5	31 min	91	[29]
3	$ZrOCl_2.8H_2O/CH_3CN$	10	35 min	89	[30]
4	$Dy(OTf)_3/EtOH.H_2O$	10	12	95	[31]
5	HMTAB[b]/H_2O	0.1 g	2.5	86	[32]
6	$FeCl_3.6H_2O$/[omim]PF_6	5	1.5	98	[33]
7	$Al(HSO_4)_3$	100	2.5	92	[34]

[a] This work

[b] Hexamethylenetetraamine-Bromine

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