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Asymmetric Michael addition reactions of 2-silyloxyfurans catalyzed by binaphthyldiimine–Ni(II) complexes†

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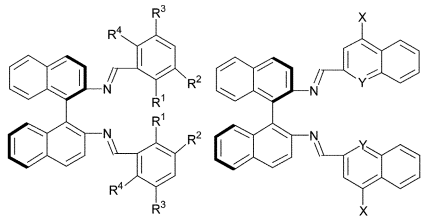
***N*,*N*′-Bis(2-quinolylmethylene)-1,1′-binaphthyl-2,2′-diamine–Ni(II) complex and analogous complexes were found to be efficient chiral Lewis acid catalysts for the asymmetric Michael addition reactions between 2-silyloxyfurans and 3-alkenoyl-2-oxazolidinones, for which asymmetric inductions of up to 97% ee were obtained.**

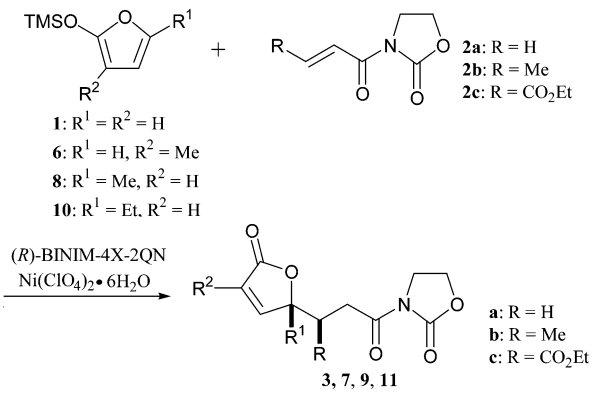
Chiral γ-butenolides and their derivatives are common structural subunits in natural products and biologically active compounds.[1] Accordingly, the development of an efficient procedure for the asymmetric synthesis of these compounds is an important objective in organic syntheses. Recently, MacMillan has reported that an organic catalyst, such as chiral imidazolidinone, was effective in affording chiral γ-butenolides in the asymmetric Michael addition reactions between 2-silyloxyfurans and α,β-unsaturated aldehydes with high *syn*- and enantioselectivties; the reaction was subsequently applied towards the synthesis of spiculisporic acid.[2] Chiral Lewis acids can also be expected to act as effective catalysts for the synthesis of optically active γ-butenolides *via* nucleophilic addition reactions of 2-silyloxyfurans. In fact, several Mukaiyama aldol reactions of 2-silyloxyfurans with carbonyl compounds promoted by Lewis acids have been reported.[3] However, only a few examples of Michael addition reactions of 2-silyloxyfurans catalyzed by chiral Lewis acids are known.[4] These examples typically employed 3-crotonoyl-2-oxazolidinone as the Michael acceptor, and their applications to other 2-silyloxyfuran derivatives and 3-alkenoyl-2-oxazolidinones were not studied in detail. Herein, we report on the use of Ni(II)-complexes of chiral *N*,*N*′-bis(2-quinolylmethylene)-1,1′-binaphthyl-2,2′-diamine (BINIM-2QN) derivatives as efficient chiral Lewis acid catalysts for the Michael addition reactions of 2-silyloxyfuran and its derivatives with various 3-alkenoyl-2-oxazolidinones.[5]

Initially, several chiral binaphthyldiimines (BINIMs), in combination with $Ni(ClO_4)_2·6H_2O$, were tested as chiral catalysts for the reaction between 2-(trimethylsilyloxy)furan (**1**) and 3-acryloly-2-oxazolidinone (**2a**) (Scheme 1). Following the preparation of the Ni(II) complexes (10 mol%) by stirring chiral BINIMs (BINIM-DC, BINIM-OH, BINIM-DCOH, BININ-2NAP, or BINIM-2QN; see Fig. 1) and $Ni(ClO_4)_2·6H_2O$ in CH_2Cl_2 for 6 h in the presence of 4Å molecular sieves (MS 4A), the reaction was carried out at −25 °C in the presence of hexafluoro-2-propanol[6] (HFIP, 1 equiv.) for 1–7 h to afford Michael adduct **3a** in 75% to quantitative yields (Table 1, Entries 1–5). Among the BINIMs tested, the result for (*R*)-BINIM-2QN was promising in terms of enantioselectivity (82% ee, Entry 5). Substitution with a methyl or phenyl group at the 4-position on the quinoline rings of BINIM-2QN resulted in slight increases in the enantioselectivities (Entries 10 and 17). The investigation of the solvents (Entries 6, 7, and 11) revealed that



(*R*)-BINIM-DC: R^1= R^4=Cl, R^2=R^3=H
(*R*)-BINIM-OH: R^1=OH, R^2=R^3=R^4=H
(*R*)-BINIM-DCOH: R^1=OH, R^4=H, R^2=R^3=Cl
(*R*)-BINIM-2NAP: Y=CH, X=H
(*R*)-BINIM-2QN: Y=N, X=H
(*R*)-BINIM-4Me-2QN: Y=N, X=Me
(*R*)-BINIM-4Ph-2QN: Y=N, X=Ph

Fig. 1 Structures of (*R*)-BINIMs.



Scheme 1 Michael addition reactions of 2-trimethylsilylfurans with 3-alkenoyl-2-oxazolidinones catalyzed by chiral BINIM-Ni(II) complexes.

Table 1 Michael addition reactions of silyloxyfuran **1** with oxazolidinone **2a** catalyzed by chiral BINIM-Ni(II) complexes[a]

Entry	BINIM	Additive[b]	Solvent	MS[c]	Time (h)	Temp. (°C)	Yield (%)	ee[d] (%)
1	DC	HFIP	CH_2Cl_2	4A	1	−25	75	2
2	OH[e]	HFIP	CH_2Cl_2	4A	7	−25	quant	34
3	DCOH	HFIP	CH_2Cl_2	4A	3	−25	90	−10
4	2NAP	HFIP	CH_2Cl_2	4A	1	−25	quant	32
5	2QN	HFIP	CH_2Cl_2	4A	1	−25	94	82
6	2QN	HFIP	$CHCl_3$	4A	1	−25	92	84
7	2QN	HFIP	Toluene	4A	48	−25	66	55
8	2QN	PFP	CH_2Cl_2	4A	1	−25	84	85
9	2QN	PFP	$CHCl_3$	4A	2	−25	90	89
10	4Me-2QN	HFIP	CH_2Cl_2	4A	1	−25	98	84
11	4Me-2QN	HFIP	$CHCl_3$	4A	1	−25	82	86
12	4Me-2QN	none	CH_2Cl_2	4A	2	−25	13[f]	22
13	4Me-2QN	*i*-PrOH	CH_2Cl_2	4A	2	−25	15[g]	69
14	4Me-2QN	PhOH	CH_2Cl_2	4A	1	−25	96	85
15	4Me-2QN	PFP	CH_2Cl_2	4A	1	−25	87	83
16	4Me-2QN	PFP	$CHCl_3$	4A	1	−25	90	91
17[h]	4Ph-2QN	HFIP	CH_2Cl_2	4A	1	−25	99	84
18[h]	4Ph-2QN	PFP	$CHCl_3$	4A	1	−25	93	91
19	4Ph-2QN	PFP	$CHCl_3$	none	96	−25	11	41
20[h]	4Ph-2QN	PFP	$CHCl_3$	3A	1	−25	89	91
21[h]	4Ph-2QN	PFP	$CHCl_3$	5A	1	−25	87	91

[a] All reactions were carried out in the presence of chiral BINIM-Ni(II) complexes (10 mol%). [b] One equiv. of the additive was used. [c] Thirty mg of molecular sieves per 0.25 mmol of **2a** were used. [d] Determined by HPLC. [e] (*S*)-BINIM was used. [f] Double Michael addition product **4** was obtained in 49% yield. [g] Double Michael addition product **4** was obtained in 75% yield. [h] The complexes were prepared for 2 h.

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b4/b402826k/

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Table 2 Asymmetric Michael addition reactions of silyloxyfurans **1**, **6**, **8**, and **10** with oxazolidinones **2a**, **2b**, and **2c**.[a]

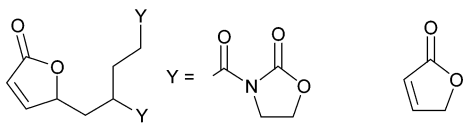
Entry	**1**, **6**, **8**, **10**	**2**	BINIM-4X-2QN	Additive[b] /Solvent	Time (h)	Temp (°C)	Yield (%)	*anti*/*syn*	ee[c] (%)
1	**1**	**2b**	4H	PFP/$CHCl_3$	168	−25	78	98 : 2	70
2	**1**	**2b**	4H	HFIP/$CHCl_3$	96	−25	93	98 : 2	85
3	**1**	**2b**	4H[d]	HFIP/$CHCl_3$	42	−25	quant	98 : 2	88
4	**1**	**2b**	4Me[d]	HFIP/CH_2Cl_2	20	−25	95	95 : 5	86
5	**1**	**2b**	4Ph[d]	HFIP/$CHCl_3$	72	−25	89	99 : 1	89
6	**1**	**2c**	4H	HFIP/CH_2Cl_2	3	−40	98	> 99 : 1	91
7	**1**	**2c**	4H	PFP/$CHCl_3$	15	−40	97	> 99 : 1	93
8	**1**	**2c**	4H[e]	PFP/$CHCl_3$	36	−40	93	> 99 : 1	91
9	**1**	**2c**	4H[f]	PFP/$CHCl_3$	168	−40	80	> 99 : 1	89
10	**1**	**2c**	4Me	PFP/$CHCl_3$	15	−40	93	> 99 : 1	88
11	**6**	**2a**	4H	PFP/$CHCl_3$	18	−25	84	—	97
12	**6**	**2a**	4Ph	PFP/$CHCl_3$	87	−25	75	—	94
13	**6**	**2b**	4H	HFIP/$CHCl_3$	87	−25	82	99 : 1	93
14	**6**	**2c**	4H	HFIP/$CHCl_3$	2	−25	95	> 99 : 1	97
15	**6**	**2c**	4H	HFIP/$CHCl_3$	2	−40	97	> 99 : 1	96
16	**8**	**2a**	4H	PFP/$CHCl_3$	6	−25	quant	—	88
17	**8**	**2c**	4H	HFIP/$CHCl_3$	55	−40	95	91 : 9	78
18	**10**	**2a**	4H	PFP/$CHCl_3$	21	−25	89	—	86

[a] All reactions were carried out in the presence of chiral BINIM-Ni(II) complexes (10 mol%). [b] One equiv of the additive was used. [c] Determined by HPLC. [d] Twenty mol% of the catalyst was used. [e] Five mol% of the catalyst was used. [f] One mol% of the catalyst was used.

$CHCl_3$ afforded slightly better results in terms of enantioselectivity, regardless of whether BINIM-2QN or BINIM-4Me-2QN were used as ligands. Furthermore, in several cases (Entries 9, 12–16, and 18), the inclusion of pentafluorophenol (PFP) as an additive in combination with $CHCl_3$ was found to improve enantioselectivities of up to 91% ee. It is interesting to note that tandem Michael addition product **4** was produced when the reaction was carried out in the absence of additives or in the presence of *i*-PrOH (Entries 12 and 13). These results suggested that an appropriate protonating agent such as HFIP or PFP is needed for the completion of the reaction after the Michael addition. And the addition reaction is probably in equilibrium with the reverse reaction before protonation or tandem addition, in which a protonating agent influences the enantioselectivity. The type of MS in the reaction did not show any significant effects on the yield and enantioselectivity (Entries 18, 20, and 21); the absence of MS, however, resulted in unsatisfactory yields and also in the hydrolysis of silyloxyfuran **1** to 2(5*H*)-furanone (**5**) (Entry 19). The high enantioselectivity in the Ni(II)-BINIM-catalyzed reaction with 3-acryloly-2-oxazolidinone (**2a**) is noteworthy in comparison to the moderate enantioselectivity using Cu(II)-bis(oxazoline) complex.[4b]

The optimized catalytic conditions were applied to the reactions between various 2-silyloxyfurans and 3-alkenoyl-2-oxazolidinones (Table 2). The BINIM-Ni(II)-catalyzed reaction of **1** with 3-crotonoyl-2-oxazolidinone (**2b**) at −25 °C resulted in high *anti*-selectivity; although the results were independent of the additives and ligands (Entries 1–5), the use of HFIP as an additive in combination with $CHCl_3$ showed better results in terms of enantioselectivity (Entries 2–5). In contrast, the use of PFP as an additive required a longer reaction time to complete the reaction with unsatisfactory results in terms of enantioselectivity (Entry 1). Reactions of **1** with oxazolidinone **2c** under similar conditions in the presence of the catalyst (10 mol%) proceeded at a lower temperature (−40 °C) to give the corresponding Michael adducts with high *anti*-selectivity (> 99 : 1) and enantioselectivities (88–93% ee) (Entries 6, 7, and 10). In this case, the use of PFP in combination with $CHCl_3$ afforded improved results in terms of enantioselectivity. It is interesting to note that catalyst loading could be decreased to 1 mol% without significant loss of diastereo- and enantioselectivities (Entries 8 and 9).

The reactions of 3-methyl-2-(trimethylsilyloxy)furan (**6**) with oxazolidinones **2a–2c** at −25 °C or −40 °C in the presence of the chiral Ni(II) complexes (10 mol%) were carried out to afford the corresponding products in high yields with extremely high enantioselectivities (93–97% ee) (Entries 11–15). Furthermore, high *anti*-selectivities for the reactions of **2b** and **2c** were observed. The chiral Ni(II) catalysts were also applied to the Michael addition reactions of 5-substituted-2-silyloxyfurans **8** and **10** with 3-alkenoyl-2-oxazolidinones. Good enantioselectivities were obtained with oxazolidinene **2a**, whereas a slightly decreased enantioselectivity was observed with oxazolidinoe **2c**.



4 **5**

In summary, chiral Ni(II) complexes, which are readily prepared from chiral BINIM-2QN or its derivatives and $Ni(ClO_4)_2 \cdot 6H_2O$, were found to be efficient Lewis acids catalyst in the synthesis of chiral γ-butenolides *via* Michael addition reactions of 2-silyloxyfurans with 3-alkenoyl-2-oxazolidinones resulting in high *anti*- and enantioselectivities.

Notes and references

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