Ytterbium(III) Triflate Catalyzed Synthesis of Quinoline Derivatives from *N*-Arylaldimines and Vinyl Ethers

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[4 + 2] Cycloaddition reaction of *N*-arylaldimines with vinyl ethers is effectively catalyzed by ytterbium(III) triflate to give quinoline derivatives in good yields. Furthermore, the reaction with silyl enol ethers affords 4-siloxytetrahydroquinolines, whereas an imino aldol reaction takes place in the reaction with ketene silyl acetals.

Since quinoline derivatives are an important class of natural products, many synthetic methods for them have been developed.[1] Of the methods, [4 + 2] cycloaddition reaction of *N*-arylaldimines with nucleophilic olefins like vinyl ethers is one of the most convenient methods, which is usually catalyzed by Lewis acids.[2] $BF_3 \cdot OEt_2$ has been mainly used for this purpose since the pioneering work of Povarov[3] and transition metal catalysts such as $Co_2(CO)_8$ and $Ni(CO)_4$ have also been found to be effective.[4] However, the reaction using these catalysts resulted in low yields of the quinoline derivatives in some cases. For example, *N*-arylaldimines having aliphatic substituents, except for carbonyl groups,[5] on the iminium carbon were less reactive and *N*-aryl substituents with electron-withdrawing groups decreased the yields extremely.

On the other hand, lanthanide salts have been expected to serve as unique Lewis acids and have been applied to many synthetic reactions.[6] There are some examples of their use in the hetero Diels–Alder reactions of a carbonyl compound as a dienophile[7] and α,β-unsaturated aldehyde as a diene.[8] Lanthanide salts are also able to activate the carbon–nitrogen double[9] and triple bonds.[10] In addition, an ene reaction of vinyl ethers catalyzed by lanthanide salts has been reported recently.[11] Thus we applied lanthanide Lewis acids to the [4 + 2] cycloaddition reaction of *N*-arylaldimines in order to overcome the limitations described above and found that ytterbium(III) triflate [$Yb(OTf)_3$] was an effective catalyst for the synthesis of quinolines having various types of substituents.

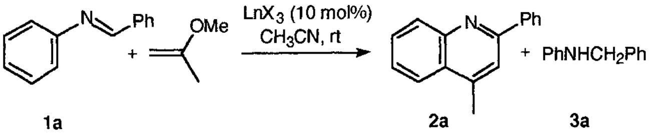
When benzylideneaniline (**1a**) and 2-methoxypropene were added successively to a solution of lanthanide salts in acetonitrile at room temperature (method A), 4-methyl-2-phenylquinoline (**2a**) and *N*-benzylaniline (**3a**) were formed in various yields (Table 1). $YbCl_3$, $Yb(fod)_3$, and $Yb(OAc)_3$ were ineffective. Of the lanthanide triflates studied, $Yb(OTf)_3$ showed the highest catalyst activity and **2a** was obtained in 74% yield along with a small amount of **3a** (2%). When the reaction using $Yb(OTf)_3$ was carried out at −35 °C, the yield of **2a** decreased to 59% and that of **3a** increased to 22%, probably due to the increase of hydrogen concentration in the solution which was generated on aromatization to the quinoline **2a**. Acetonitrile was the best solvent among those tested, such as dichloromethane (55% for **2a** and 10% for **3a**), toluene (49% and 11%), tetrahydrofuran (53% and 11%), and diethyl ether (37% and 8%).

N-Arylaldimines **1** having various substituents reacted with 2-methoxypropene in the presence of $Yb(OTf)_3$ catalyst to afford quinolines **2** in good yields (Table 2). However, addition order of the substrates and presence of molecular sieves have influence on the yields of the products **2** as shown in Table 2 [method B: first addition of the propene to $Yb(OTf)_3$, followed by **1**; method C: concurrent addition of the two; method D: use of molecular sieves (4 Å) in method A]. Although similar results were obtained by the three methods A, B, and C in the synthesis of **2a**, method D gave a superior yield of **2b** compared to other methods. The quinoline **2c** was obtained in the best yield by the method B. With respect to the byproducts, trace amounts of the corresponding amines **3** were detected by GC in all cases. In addition, the reaction of **1c** gave 4-anilino-4-(4-methoxyphenyl)butan-2-one **(4)** in 5% yield. 4-Methyl-2-(2-methylphenyl)-1,2-dihydroquinoline **(5)**, a precursor of **2d**, was isolated in 6% yield in the reaction of **1d**.

Thus alkyl substituents and 2-furyl group can be introduced at the 2-position of the quinoline ring in fairly good yields as shown in the reactions of **1g–h** and **1f**. Furthermore, quinolines having electron-withdrawing or -donating substituents at the 2- and 6-positions, such as **2b–e** and **2i–j** were prepared conveniently.

Next the reaction of *N*-arylaldimine **1j** with various vinyl ethers instead of 2-methoxypropene was investigated (Scheme). The reaction with ethyl vinyl ether gave the expected product **6** in 95% yield. In the reaction with

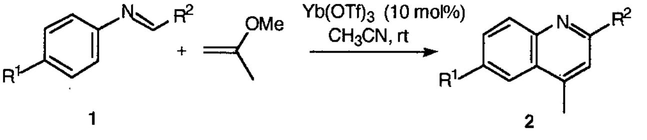
Table 1. Effect of the Lanthanide Catalysts on the Reaction of Benzylideneaniline (**1a**) with 2-Methoxypropene[a]



LnX$_3$	Time (h)	Yield (%) 2a	Yield (%) 3a
none	15	0	0
$YbCl_3$	2	26	6
$Yb(fod)_3$	3.5	8	trace
$Yb(OAc)_3$	3.5	1	trace
$Yb(OTf)_3$	3.5	74	2
$Sm(OTf)_3$	5	63	4
$La(OTf)_3$	4	56	7
$Y(OTf)_3$	3.5	72	7
$Sc(OTf)_3$	2	57	14

[a] Method A.

Table 2. Synthesis of 4-Methylquinoline Derivatives **2**



Product	R^1	R^2	Method	Time (h)	Yield (%)
2a	H	Ph	A	3.5	74
2a	H	Ph	B	0.5	65
2a	H	Ph	C	0.5	76
2b	H	2-$MeOC_6H_4$	A	4	44[a]
2b	H	2-$MeOC_6H_4$	C	2.5	42[a]
2b	H	2-$MeOC_6H_4$	D	4.5	69[a]
2c	H	4-$MeOC_6H_4$	A	1.5	57
2c	H	4-$MeOC_6H_4$	B	0.5	76
2c	H	4-$MeOC_6H_4$	D	1	11
2d	H	2-MeC_6H_4	D	0.5	89
2e	H	4-ClC_6H_4	B	0.5	80
2f	H	2-furyl	C	1	64
2g	H	$CHMe_2$	B	1.5	47
2h	H	cyclohexyl	B	1	51
2i	Cl	Ph	B	3	77
2j	OMe	Ph	C	1	88

[a] 5 Mol% of $Yb(OTf)_3$ was used.

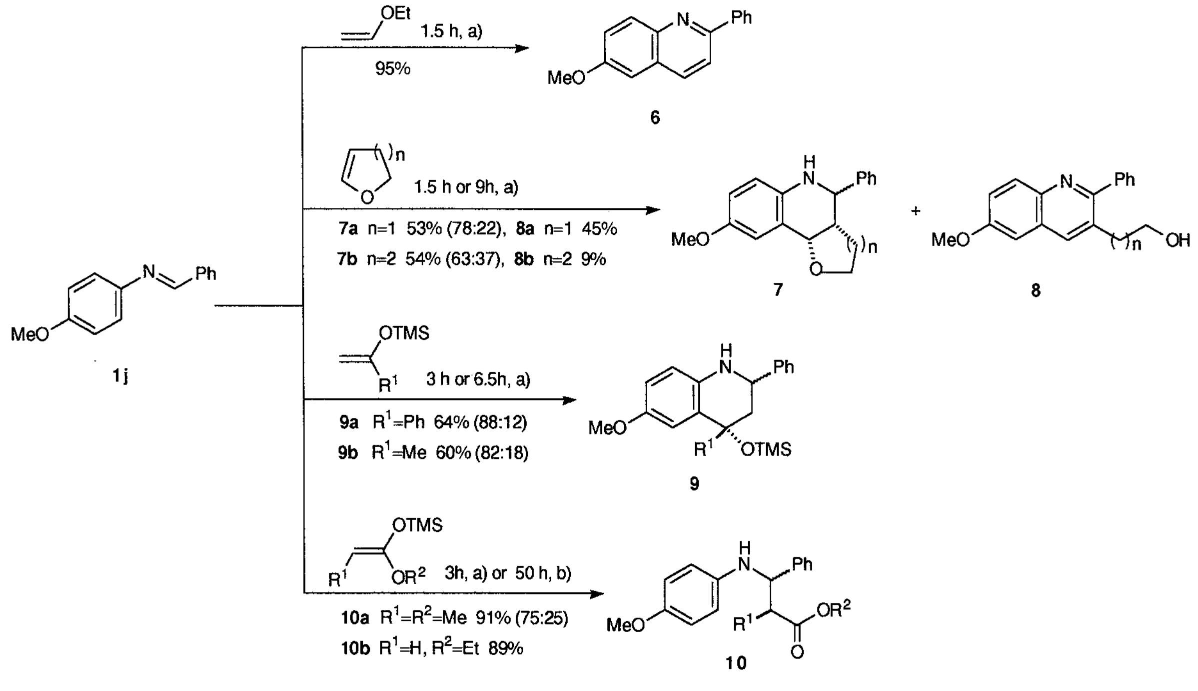
2,3-dihydrofuran, hexahydrofuro[3,2-*c*]quinoline **7a** and 3-(2-hydroxyethyl)quinoline **8a** were formed in 53 % and 45% yields, respectively. The product **7a** was obtained as a mixture of *cis* and *trans* isomers in a ratio of 78 : 22, determined by ^1H and ^{13}C NMR spectra and NOE measurement. Similarly, the reaction with 3,4-dihydro-2*H*-pyran afforded hexahydropyrano[3,2-*c*]quinoline **7b** in 54% yield, which was separated by column chromatography into *cis* and *trans* isomers (63 : 37), along with 3-(3-hydroxypropyl)quinoline **8b** (9%). Interestingly, when the trimethylsilyl enol ether of acetophenone was used as a dienophile, 4-trimethylsiloxytetrahydroquinoline **9a** was obtained in 64% yield as a mixture of two stereoisomers (88 : 12),[12] in spite of the labile substituent. The reaction with trimethylsilyl enol ether of acetone gave also the corresponding quinoline **9b** in 60% yield (82 : 18).[12] In contrast, *N*-arylaldimine **1j** reacted with ketene trimethylsilyl acetals of methyl propionate and ethyl acetate to give imino aldol products **10a** and **10b** in 91 % and 89 % yields, respectively, but no cyclization product was formed.

In summary, the results demonstrated here reveal the wide utility of $Yb(OTf)_3$ in the [4 + 2] cycloaddition reaction of azadienes.

^1H NMR and ^{13}C NMR spectra were recorded on JEOL JNM-EX270 and Bruker AMX-400 spectrometers ($CDCl_3$/TMS). IR spectra were measured on a Perkin-Elmer 1600 FTIR (Nujol or neat). Mass spectra were obtained on a Shimadzu GCMS QP-1000 apparatus (70 eV). HRMS were taken on a Hitachi G-3000 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Elemental analyses were performed with a Yanagimoto CHN recorder. MeCN was distilled from CaH_2 under N_2. *N*-Arylaldimines were prepared from the corresponding aniline derivatives and aldehydes. Trimethylsilyl enol ethers and ketene trimethylsilyl acetals were prepared according to the literature method.[13] Lanthanide(III) triflates were prepared by the reported procedure[10] and dried by heating at 200 °C under reduced pressure prior to use.

Quinoline Derivatives 2, 6 and 8; General Procedures:

Method A: A solution of *N*-arylaldimine **1** (0.4 mmol) in MeCN (1 mL) was addd to a solution of $Yb(OTf)_3$ (25 mg, 0.04 mmol) in MeCN (1 mL) and the mixture was stirred at r.t. for 10 min. Then



Scheme a) $Yb(OTf)_3$ (10 mol%), CH_3CN, rt, method C b) $Yb(OTf)_3$ (10 mmol%), CH_2Cl_2, rt, method C

2-methoxypropene (1.0 mmol) was added to the mixture and stirring was continued at r.t. The mixture was quenched with 2 M HCl (1 mL) and extracted with $CHCl_3$ (3 x 5 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on silica gel using hexane/EtOAc as eluent to give analytically pure quinoline derivative.

Table 3. Spectroscopic Data of the Selected Products **2** and **4–10** Prepared[a,b]

Product[c]	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR($CDCl_3$/TMS) δ	IR (Nujol or neat)[d] ν (cm^{-1})	MS (70 eV) m/z
2d	2.41 (3 H, s, CH_3), 2.76 (3 H, s, CH_3), 7.26–7.48 (5 H, m), 7.58 (1 H, t, J = 7.6), 7.73 (1 H, t, J = 7.6), 8.03 (1 H, d, J = 8.4), 8.16 (1 H, d, J = 8.4)	18.9 (CH_3), 20.3 (CH_3), 123.1, 123.6, 125.9, 126.1, 126.8 (C), 128.4, 129.3, 129.6, 130.2, 130.8, 136.0 (C), 140.9 (C), 144.2 (C), 147.7 (C), 160.1 (C)	3050, 2920, 1600, 1545	233 (M$^+$), 218, 105, 98
2i	2.69 (3 H, s, CH_3), 7.41–8.14 (9 H, m)	18.9 (CH_3), 120.3, 122.7 (C), 127.4, 127.9 (C), 128.8, 129.4, 130.1, 131.7, 131.8, 139.3 (C), 143.9 (C), 146.5 (C), 157.2 (C)	2920, 2850, 1600, 1460, 1372	253 (M$^+$), 238, 218, 204, 141
4	2.09 (3 H, s, CH_3), 2.90 (2 H, d, J = 6.5, CH_2) 3.77 (3 H, s, OCH_3), 4.40 (1 H, br s, NH), 4.80 (1 H, t, J = 6.5 NCH), 6.29–7.28 (9 H, m)	30.8 (CH_3), 51.3 (CH_2), 53.8 (CH), 55.2 (OCH_3), 113.7, 114.2, 117.8, 127.4, 129.1, 134.4 (C), 146.8 (C), 158.8 (C), 207.4 (CO)	3400, 2980, 2940, 1700, 1600, 1500	212 (M$^+ - CH_2COCH_3$), 168, 105
5	2.00 (3 H, s, CH_3), 2.39 (3 H, s, CH_3), 3.93 (1 H, br s, NH), 5.39 (1 H, d, J = 3.3, NC$\underline{H}$CH=), 5.65 (1 H, d, J = 3.3, NCHC$\underline{H}$=), 6.40 (1 H, d, J = 7.8), 6.62–7.22 (6 H, m), 7.57 (1 H, d, J = 8.1)	18.7 (CH_3), 19.1 (CH_3), 54.0 (CH), 112.2 (C), 112.7, 117.2, 121.6, 123.8, 126.6, 127.3, 127.7, 128.8, 129.3 (C), 130.7, 134.1 (C), 143.3 (C), 144.0 (C)	3400, 3040, 2900, 1596, 1540, 1480	235 (M$^+$), 220, 189, 115
6[e]	3.99 (3 H, s, OCH_3), 7.28–9.40 (10 H, m)	56.2 (OCH_3), 105.6, 121.3, 124.0, 127.4, 128.7 (C), 129.4, 129.6, 129.7, 132.8, 135.1, (C), 144.0 (C), 151.8 (C), 159.9 (C)	2920, 1610, 1465, 1380	235 (M$^+$), 220, 193, 140, 129
7a[f]	(*cis*): 1.51 (1 H, m, C$\underline{H}$H), 2.01 (1 H, m, CH$\underline{H}$), 2.77 (1 H, m, CH), 3.67–4.15 (3 H, m, NH and OCH_2), 3.774 (3 H, s, OCH_3), 4.62 (1 H, d, J = 2.8, OCH), 5.25 (1 H, d, J = 7.8, NCH), 6.54 (1 H, d, J = 8.7), 6.72 (1 H, dd, J = 8.7, 2.8), 6.92 (1 H, d, J = 2.8), 7.30–7.47 (5 H, m); (*trans*): 1.70 (1 H, m, C$\underline{H}$H), 2.01 (1 H, m, CH$\underline{H}$), 2.48 (1 H, m, CH), 3.67–4.15 (4 H, m, NH, OCH_2, and NCH), 3.768 (3 H, s, OCH_3), 4.60 (1 H, d, J = 5.3, OCH), 6.58 (1 H, d, J = 8.7), 6.76 (1 H, dd, J = 8.7, 2.8), 6.98 (1 H, d, J = 2.8), 7.30–7.47 (5 H, m)	(cis) 28.9 (CH_2), 43.7 (CH), 55.8 (OCH_3), 58.5 (CH), 65.4 (CH_2), 76.4 (CH), 114.6, 116.0, 116.6, 121.0 (C), 126.5, 128.3, 128.6, 139.6 (C), 141.8 (C), 152.6 (C); (*trans*): 24.5 (CH_2), 45.9 (CH), 55.7 (OCH_3), 57.9 (CH), 66.9 (CH_2), 76.3 (CH), 113.7, 115.8, 116.2, 123.5 (C), 127.6, 128.1, 128.6, 139.1 (C), 142.4 (C), 153.2 (C)	3360, 2930, 1500, 1365, 1250	281 (M$^+$), 250, 237, 205, 177, 161
7b[g] (*cis*)	1.31–1.55 (4 H, m, 2 CH_2), 2.17 (1 H, m, CH), 3.43 (1 H, dt, J = 2.9, 11.5, OC$\underline{H}$H), 3.59 (1 H, m, OCH$\underline{H}$), 3.66 (1 H, br s, NH), 3.78 (3 H, s, OCH_3), 4.62 (1 H, br s, OCH), 5.31 (1 H, d, J = 5.5, NCH), 6.57 (1 H, d, J = 8.6), 6.72 (1 H, dd, J = 8.6, 2.7), 7.03 (1 H, d, J = 2.4), 7.25–7.43 (5 H, m)	17.9 (CH_2), 25.4 (CH_2), 39.1 (CH), 55.9 (OCH_3), 59.6 (CH), 60.9 (CH_2), 73.0 (CH), 111.9, 115.1, 115.7, 121.2 (C), 126.8, 127.4, 128.3, 139.2 (C), 141.4 (C), 152.9 (C)	3275, 2980, 1445, 1350	295 (M$^+$), 280. 264, 237, 225
(*trans*)	1.26–1.84 (4H, m, 2CH_2), 2.09 (1 H, m, CH), 3.72 (1 H, dt, J = 2.5, 11.5, OC$\underline{H}$H), 3.76 (3 H, s, OMe), 3.88 (1 H, br, s, NH), 4.09 (1 H, m, OCH$\underline{H}$), 4.38 (1 H, d, J = 2.8, OCH), 4.66 (1 H, d, J = 10.7, NCH), 6.50 (1 H, d, J = 8.7), 6.74 (1 H, dd, J = 8.7, 2.9), 6.82 (1 H, d, J = 2.8), 7.31–7.43 (5 H, m)	22.1 (CH_2), 24.2 (CH_2), 39.0 (CH), 55.2 (CH), 55.9 (OCH_3), 68.6 (CH_2), 74.6 (CH), 114.8, 115.5, 116.9, 121.3 (C), 127.8, 128.6, 139.1 (C), 142.4 (C), 152.0 (C)	3450, 2900, 1480, 1350	295 (M$^+$), 280, 264, 237, 225
8a	1.79 (1 H, br s, OH), 3.02 (2 H, t, J = 6.7, CH_2), 3.70 (2 H, J = 6.7, OCH_2), 3.94 (3 H, s, OCH_3), 7.07–8.02 (9 H, m)	36.0 (CH_2), 55.6 (OCH_3), 62.5 (OCH_2), 104.4, 122.0, 128.1, 128.4, 128.7, 128.9, 130.1 (C), 130.7 (C), 135.8, 140.7 (C), 142.8 (C), 157.9 (C), 158.2 (C)	3425, 2900, 1610, 1473	279 (M$^+$), 264, 248, 218, 201
8b	1.68 (1 H, br s, OH), 1.76 (2 H, tt, J = 7.8, 6.3, CH_2), 2.86 (2 H, t, J = 7.8, CH_2), 3.53 (2 H, t, J = 6.3, OCH_2), 3.95 (3 H, s, OCH_3), 7.06–8.03 (9 H, m)	29.1 (CH_2), 33.4 (CH_2), 55.6 (OCH_3), 61.9 (CH_2), 104.4, 121.8, 128.0, 128.4, 128.6, 128.8, 130.7, 133.2 (C), 134.9 (C), 141.0 (C), 143.5 (C), 157.9 (2 C)	3400, 2937, 1623, 1486, 1380	293 (M$^+$), 278, 262, 249, 234
9a[f,h]	(major): −0.03 [9 H, s, $Si(CH_3)_3$], 2.09 (2 H, d, J = 7.4, CH_2), 3.59 (3 H, s, OCH_3), 4.10 (1 H, t, J = 7.4, NCH), 4.70 (1 H, br s, NH), 6.40–7.48 (13 H, m); (minor): 0.09 [s, $Si(CH_3)_3$], 3.63 (s, OCH_3)	(major): 1.8 [$Si(CH_3)_3$], 50.6 (CH_2), 53.5 (NCH), 55.9 (OCH_3), 76.7 (C), 115.6, 116.2, 116.4, 126.49, 126.54, 126.8, 127.5 (C), 127.6, 127.7, 128.5, 140.4 (C), 143.8 (C), 147.7 (C), 151.1 (C); (minor): 1.3 [$Si(CH_3)_3$], 57.6 (OCH_3)	3390, 3010, 2945, 2840, 1490, 1460, 1040	313 (M$^+$ −TMSOH), 298, 268, 219, 191, 149

Table 3. (continued)

Product[c]	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR($CDCl_3$/TMS) δ	IR (Nujol or neat)[d] ν (cm^{-1})	MS (70 eV) m/z
9b[f,h]	(major): 0.08 [9 H, s, $Si(CH_3)_3$], 1.66 (3 H, s, CH_3), 2.08 (1 H, dd, J = 12.2, 2.9, $C\underline{H}H$), 2.29 (1 H, t, J = 12.2, $CH\underline{H}$), 3.77 (3 H, s, OCH_3), 3.80 (1 H, br s, NH), 4.46 (1 H, dd, J = 12.2, 2.9, NCH), 6.44 (1 H, d, J = 8.6), 6.66 (1 H, dd, J = 8.6, 2.6), 7.01 (1 H, d, J = 2.6), 7.27–7.49 (5 H, m); (minor): 1.63 (s, CH_3), 6.51 (d, J = 8.6), 6.74 (dd, J = 8.6, 2.6)	(major): 2.4 [$Si(CH_3)_3$], 34.1 (CH_3), 47.1 (CH_2), 55.8 (CH), 56.3 (OCH_3), 73.1 (C), 111.9, 114.3, 115.0, 126.7, 127.8, 128.7, 130.3 (C), 137.2 (C), 143.9 (C), 152.2 (C)	3365, 2940, 1490, 1460, 1050	341 (M^+), 326, 252, 237, 223, 208
10a[f]	(major): 1.13 (3 H, d, J = 7.5, CH_3), 2.83 (1 H, quin, J = 7.5, $C\underline{H}CH_3$), 3.64 (3 H, s, OCH_3), 3.67 (3 H, s, OCH_3), 4.36 (1 H, br s, NH), 4.42 (1 H, d, J = 7.5, NCH), 6.46–6.51 (2 H, m), 6.64–6.68 (2 H, m), 7.20–7.32 (5 H, m); (minor): 1.15 (3 H, d, J = 7.8, CH_3), 2.94 (1 H, m, $C\underline{H}CH_3$), 3.61 (3 H, s, CH_3), 3.68 (3 H, s, OCH_3), 4.36 (1 H, br s, NH), 4.65 (1 H, d, J = 5.1, NCH), 6.46–6.51 (2 H, m), 6.64–6.68 (2 H, m), 7.20–7.32 (5 H, m)	(major): 15.3 (CH_3), 46.8 (CH), 51.8 (OCH_3), 55.7 (OCH_3), 61.7 (CH), 114.7, 115.0, 126.87, 127.4, 128.6, 141.0 (C), 141.3 (C), 151.9 (C), 175.6 (CO); (minor): 11.8 (CH_3), 46.1 (CH), 51.9 (OCH_3), 55.7 (OCH_3), 60.4 (CH), 114.7, 115.0, 126.90, 127.3, 128.5, 141.0 (C), 141.3 (C), 151.9 (C), 175.6 (CO)	3400, 2940, 1720, 1512, 1450	299 (M^+), 212, 169, 135
10b	1.18 (3 H, t, J = 7.1, CH_3), 2.77 (2 H, d, J = 6.6, CH_2), 3.68 (3 H, s, OCH_3), 4.09 (2 H, q, J = 7.1, OCH_2), 4.30 (1 H, br s, NH), 4.75 (1 H, t, J = 6.6, NCH), 6.50–7.38 (9 H, m)	14.1 (CH_3), 31.6 (CH_2), 42.9 (CH), 55.6 (OCH_3), 60.7 (CH_2), 114.7, 115.1, 126.3, 127.3, 128.7, 141.0 (C), 142.4 (C), 152.3 (C), 171.2 (CO)	3400, 1738, 1510	299 (M^+), 254, 212

[a] Satisfactory microanalyses obtained for **2i**, **4**, **7b**, **8b**, **9a**, **10a** and **10b**: C ± 0.24, H ± 0.22, N ± 0.39.

[b] Deviation in HRMS spectra for **2d**, **5**, **7a**, **8a** and **9b**: 0.9–5.0 ppm.

[c] Mp(°C): **2i**, 92–93; *cis*-**7b**, 144–146; **10a**, 95–97. Other products are viscous oils.

[d] Nujol for crystals and neat for oil.

[e] Ref. 4.

[f] Obtained as a mixture.

[g] Separated by column chromatography.

[h] Clearly distinguishable peaks are documented for the minor isomer.

Method B: 2-Methoxypropene (1.0 mmol) was added to a solution of $Yb(OTf)_3$ (25 mg, 0.04 mmol) in MeCN (1 mL) and the mixture was stirred at r.t. for 10 min. Then a solution of *N*-arylaldimine **1** (0.4 mmol) in MeCN (1 mL) was added to the mixture. The mixture was stirred at r.t. and worked up in a similar manner as described in Method A.

Method C: A mixture of *N*-arylaldimine **1** (0.4 mmol) and a solution of the appropriate vinyl ether (1.0 mmol) in MeCN (1 mL) was added to a solution of $Yb(OTf)_3$ in MeCN (1 mL), and the mixture was stirred at r.t. The reaction mixture was worked up in a similar manner as described in Method A.

Method D: A solution of *N*-arylaldimine **1** (0.4 mmol) in MeCN (1 mL) was added to a slurry of molecular sieves (4 Å, 50 mg) in MeCN (1 mL) containing $Yb(OTf)_3$ (25 mg, 0.04 mmol). After stirring for 10 min at r.t., 2-methoxypropene (1.0 mmol) was added to the mixture. The resulting mixture was stirred at r.t. and worked up in a similar manner as described in Method A. Spectroscopic data of the new products are summarized in Table 3, except for **6** which is known.[4]

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