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Abstract: A novel and efficient catalytic system of the Morita–Baylis–Hillman (MBH) reaction between aromatic aldehyde and activated alkenes has been developed. The novel system of a combination of $Sc(OTf)_3$ and 3-hydroxyquinuclidine (3-HQD) showed a high catalytic activity for the MBH reaction.

Keywords: 3-Hydroxyquinuclidine, Morita–Baylis–Hillman reaction, $Sc(OTf)_3$

INTRODUCTION

The Morita–Baylis–Hillman (MBH) reaction,[1–6] an important reaction, has been added to the list of the useful carbon–carbon bond-forming reactions. Since the MBH reaction possesses the two most important requirements, atom economy and generation of functional groups, it qualifies to be in the list of efficient synthetic reactions.[7] However, the major drawback of the MBH reaction is its slow reaction rate (e.g., the reaction of tert-butyl acrylate with benzaldehyde using 10 mol% DABCO catalyst takes 28 days to complete).[8] So, it was very significant to develop a novel efficient synthesis for the reaction. A number of physical and chemical methods have been developed to accelerate the notoriously slow MBH reaction.[9] For example, the Aggarwal group has found that the use of $Sc(OTf)_3$ (5 mol%) in the MBH reaction with 1,4-dimethylaminopyridine

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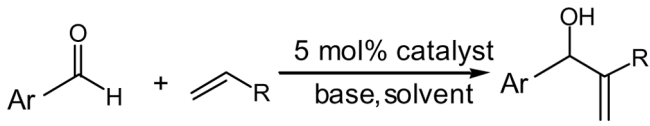
(DABCO) (100 mol%) as the catalyst resulted in an acceleration of the reaction [K_{rel} (DABCO) = 3.3], but the yield can increase up to only 11.6% after 24 h when the reaction was conducted using tert-butyl acrylate and benzaldehyde.[10] Then, after a few years, they found that 3-HQD with GnCl can also caused an increase in the rate of the reaction in water [K_{rel} (DABCO) = 9.5]. In contrast to not using Lewis acid, no additional rate acceleration was observed with $Sc(OTf)_3$ in water.[11] Herein, we report a novel and efficient condition for the MBH reaction using $Sc(OTf)_3$ and 3-HQD as cocatalysts and dimethylformamide (DMF) as the solvent.

RESULTS AND DISCUSSION

To establish the reaction conditions, we first examined the reaction of p-nitrobenzaldehyde and methyl acrylate in CH_3CN and investigated the effect of different amine catalysts on reaction rate as shown in Scheme 1, and the results are summarized in Table 1. We found that no reaction occurred when using pyridine as a Lewis base (Table 1, entry 3). As expected, no product was observed after stirring for 24 h at 20 °C when $Sc(OTf)_3$ alone was employed as the catalyst. DMAP has been compared with imidazole and found to be superior in the reaction between p-nitrobenzaldehyde and methyl acrylate in CH_3CN. We found that DMAP was indeed better than imidazole, but with reactions conducted neat, 3-HQD gave the highest yield and fastest rate. Therefore, we selected 3-HQD as the base in MBH reaction for further investigation.

It is well-known that the MBH reaction is affected by solvents. Auge has shown that the MBH reaction between acrylonitrile and various aldehydes can be accelerated in water.[12] However, they had chosen to study reactions involving acrylonitrile, as this is already a relatively fast-reacting substrate in the MBH reaction. Besides this, we also focused on slower reacting substrates: acrylates. We found that water did not work well in these reactions, but to our delight, the use of DMF as a solvent allowed for a dramatic increase in the yield of the MBH reaction (Table 2, entries 4–10). Also, we found that raising the temperature accelerated the reaction and led to increase in yield. The optimal reaction



Scheme 1. Morita–Baylis–Hillman reaction.

Table 1. Effect of base on the MBH reaction[a]

Entry	Lewis base	Time (h)	Yield (%)[b]
1	Imidazole	24	30
2	Et_3N	24	23
3	Pyridine	24	—
4	3-HQD	3	59
5	DMAP	24	44

[a]Reaction conditions: 3.0 mmol of methyl acrylate, 1.0 mmol of p-nitrobenzaldehyde, 100 mmol% of Lewis base using CH_3CN as solvent.
[b]Isolated yield based on p-nitrobenzaldehyde.

temperature for the reaction was 40 °C (Table 2, entries 11 and 12); higher reaction temperature did not significantly improve the result.

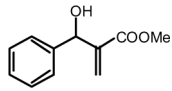
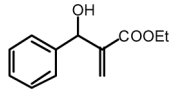
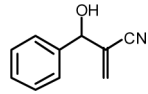
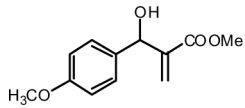
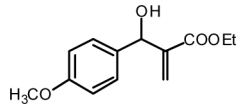
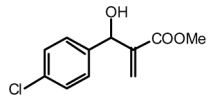
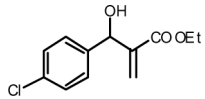
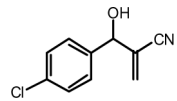
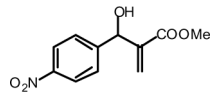
Based on these results, the reaction was best conducted in DMF at 40 °C with 5 mol% of catalyst in a 1:4 molar ratio of $Sc(OTf)_3$ to 3-HQD. Naturally, with optimized conditions in hand, we examined a set of aromatic aldehydes coupled with activated alkenes (methyl acrylate, ethyl acrylate, and acrylonitrile). The experimental results are listed in Table 3.

Table 2. MBH reactions of p-nitrobenzaldehyde (1.0 equiv.) with methyl acrylate (3.0 equiv.) in the presence of $Sc(OTf)_3$ and 3-HQD

Entry	$Sc(OTf)_3$ (mol %)	3-HQD (mol %)	Solvent	Temperature (°C)	Time (h)	Yield (%)[a]
1	0	50	CH_3CN	20	3	59
2	5	10	CH_3CN	20	3	52
3	5	20	CH_3CN	20	1	78
4	5	50	CH_3CN	20	1	79
5	5	20	CH_2Cl_2	20	1	66
6	5	20	Toluene	20	1	71
7	5	20	H_2O	20	1	<10
8	5	20	DMF	20	50 min	84
9	5	20	THF/H_2O (1:1)	20	1	66
10	5	20	DMF/H_2O (1:1)	20	1	62
11	5	20	DMF	0	3	44
12	5	20	DMF	40	50 min	88

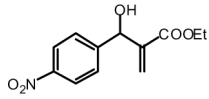
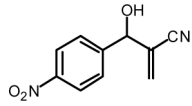
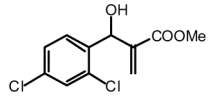
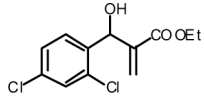
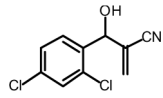
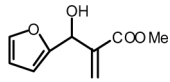
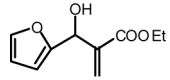
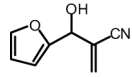
[a]Isolated yield based on p-nitrobenzaldehyde.

Table 3. $Sc(OTf)_3$/3-HQD cocatalyzed the MBH reaction[a]

Entry	Products	Time (h)	Yield (%)[b]
1		8	73
2		9	70
3		9	73
4		36	30
5		36	23
6		6	79
7		8	74
8		4	82
9		50 min	92

(*Continued*)

Table 3. Continued

Entry	Products	Time (h)	Yield (%)[b]
10		1	88
11		10 min	98
12		3	88
13		4	88
14		1.5	90
15		1	88
16		1	88
17		40 min	92

[a]Reaction conditions: 3.0 mmol of α,β-unsaturated ester, 1.0 mmol of aromatic aldehydes, 5 mmol% of $Sc(OTf)_3$, and 20 mmol% of Lewis base using DMF as solvent.

[b]Isolated yield based on aromatic aldehyde.

As shown in Table 3, all aromatic aldehydes were converted to their corresponding MBH products in moderate to high yields in reaction times as short as 10 min. It is worth mentioning that the system was tested synthetically on various substrates and found to give good rate accelerations with aromatic aldehydes with acceptor groups and lower rate accelerations with aromatic aldehydes with donor groups. Notable examples from Table 3 include a fast reaction with 2-furaldehyde and acrylonitrile (entry 17) and a very rapid reaction with p-nitrobenzaldehyde (entry 11). Acrylamide is not a suitable substrate with 3-HQD; no reaction was observed with it.

CONCLUSIONS

In conclusion, we have developed a new condition that accelerates the MBH reaction. The novel catalytic system of a combination of $Sc(OTf)_3$ and 3-HQD showed high catalytic activity for the MBH reaction.

EXPERIMENTAL

All chemicals and resin were obtained from commercial suppliers and were used without further purification. Infrared (IR) spectra were recorded on a Perkin-Elmer 983 Fourier transform infrared (FT-IR) spectrometer, and ^1H NMR spectra were made on a Bruker Avance DMX 300 instrument. Mass spectral (MS) analyses were performed on an HP-5973 spectrometer.

General Procedure for the Synthesis of 1–17

Aromatic aldehyde (1 mmol) was mixed with activated alkenes (3 mmol) in a 25-mL flask. $Sc(OTf)_3$ (5 mol%), 3-HQD (20 mol%), and DMF (4 mL) were added to the mixture. The vessel was immersed in a preheated oil bath and stirred vigorously until thin-layer chromatography (TLC) and/or gas chromatography (GC) of the crude reaction mixture indicated that the aromatic aldehyde had been completely consumed. The reaction mixture was allowed to cool to room temperature, Et_2O was added to the reaction mixture, and the organic phase was separated. The filtrate was concentrated, and the resulting residue was purified by flash chromatography (hexane–ethyl acatate) to provide the desired product.

Data

Methyl 2-[1-Hydroxy-1-(4-nitrophenyl)Methyl]Acrylate (Table 3, Entry 1)

A yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.46 (brs, 1H), 3.67 (s, 3H), 5.57 (d, H, $J = 6.52$ Hz), 5.84 (s, 1H), 6.33 (s, 1H), 7.50 (d, 2H, $J = 8.52$ Hz), 8.12 (d, 2H, $J = 8.51$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 51.86, 72.1, 123.25, 126.86, 127.02, 140.63, 147.04, 148.34, 166.02; IR ($CHCl_3$) 3490, 1715 cm^{-1}.

Ethyl 2-[1-Hydroxy-1-(4-nitrophenyl)Methyl]Acrylate (Table 3, Entry 2)

A yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (t, 3H, $J = 7.14$ Hz), 3.46 (brs, 1H), 4.24 (q, 2H, $J = 7.14$ Hz), 5.67 (d, H, $J = 6.15$ Hz), 5.91 (s, 1H), 6.45 (s, 1H), 7.63 (d, 2H, $J = 8.64$ Hz), 8.25 (d, 2H, $J = 8.64$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.63, 60.60, 65.36, 72.02, 123.17, 126.49, 140.94, 146.93, 148.59, 165.54; IR ($CHCl_3$) 3485, 1720 cm^{-1}.

2-[1-Hydroxy-1-(4-nitrophenyl)Methyl]Acrylonitrile (Table 3, Entry3)

A yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.98 (brs, 1H), 5.38 (d, 1H, $J = 6.3$ Hz), 6.04 (s, 1H), 6.13 (s, 1H), 7.54 (d, 2H, $J = 8.40$ Hz), 8.19 (d, 2H, $J = 8.40$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 72.85, 116.02, 123.70, 125.05, 127.04, 130.78, 145.82, 147.60; IR ($CHCl_3$) 3480, 1720 cm^{-1}.

Methyl 2-[1-Hydroxy-1-(2,4-dichlorophenyl)Methyl]Acrylate (Table 3, Entry 4)

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ3.52 (brs, 1H), 3.76 (s, 1H), 5.58 (d, 1H, $J = 6.87$ Hz), 5.89 (s, 1H), 6.33 (s, 1H), 7.26 (d, 1H, $J = 8.07$ Hz), 7.36 (s, 1H), 7.48 (d, 1H, $J = 8.31$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 51.86, 68.54, 126.78, 128.82, 133.07, 136.63, 139.88, 144.66, 166.50; IR ($CHCl_3$) 3490, 1715 cm^{-1}.

Ethyl 2-[1-Hydroxy-1-(2,4-dichlorophenyl)Methyl]Acrylate (Table 3, Entry 5)

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.30 (t, 3H, $J = 6.40$ Hz), 3.58 (brs, 1H), 4.19 (q, 2H, $J = 6.40$ Hz), 5.19 (d, 1H, $J = 5.80$ Hz), 5.51 (s, 1H), 6.11 (s, 1H), 7.07 (d, 1H, $J = 8.31$ Hz), 7.11 (s, 1H), 7.21 (d, 1H,

$J = 8.31$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.67, 60.85, 65.13, 68.36, 126.94, 128.79, 133.67, 140.27, 142.85, 165.30; IR ($CHCl_3$) 3485, 1720 cm^{-1}.

2-[1-Hydroxy-1-(2,4-dichlorophenyl)Methyl]Acrylonitrile
(Table 3, Entry 6)

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.12 (brs, 1H), 5.70 (s, 1H), 6.07 (s, 1H), 6.08 (s, 1H), 7.35 (d, 1H, $J = 7.74$ Hz), 7.41 (s, 1H), 7.57 (d, 1H, $J = 7.74$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 69.75, 117.32, 123.64, 127.59, 128.58, 131.29, 134.62, 139.81; IR ($CHCl_3$) 3480, 1720 cm^{-1}.

Methyl 2-[1-Hydroxy-1-(4-chlorophenyl)Methyl]Acrylate
(Table 3, Entry 7)

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.11 (brs, 1H), 3.74 (s, 1H), 5.52 (d, 1H, $J = 5.58$ Hz), 5.83 (s, 1H), 6.34 (s, 1H), 7.28 (d, 2H, $J = 8.41$ Hz), 7.33 (d, 2H, $J = 8.37$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 51.74, 72.38, 120.64, 127.61, 129.71, 132.12, 138.41, 144.65, 165.11; IR ($CHCl_3$) 3490, 1715 cm^{-1}.

Ethyl 2-[1-Hydroxy-1-(4-chlorophenyl)Methyl]Acrylate (Table 3, Entry 8)

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ1.27 (t, 3H, $J = 7.07$ Hz), 3.34 (brs, 1H), 4.16 (q, 2H, $J = 6.96$ Hz), 5.51 (d, 1H, $J = 5.37$ Hz), 5.83 (s, 1H), 6.34 (s, 1H), 7.31 (d, 2H, $J = 8.47$ Hz), 7.38 (d, 2H, $J = 8.47$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): 1720 cm^{-1}.

2-[1-Hydroxy-1-(4-chlorophenyl)Methyl]Acrylonitrile (Table 3, Entry 9)

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.57 (brs, 1H), 5.20 (d, 1H, $J = 6.74$ Hz), 5.99 (s, 1H), 6.05 (s, 1H), 7.27 (d, 2H, $J = 8.41$ Hz), 7.34 (d, 2H, $J = 8.37$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 72.96, 116.48, 125.50, 127.59, 128.69, 130.26, 134.27, 137.33; IR ($CHCl_3$) 3480, 1720 cm^{-1}.

Methyl 2-[1-Hydroxy-1-(phenyl) Methyl] Acrylate (Table 3, Entry 10)

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.19 (brs, 1H), 3.71 (s, 3H), 5.54 (d, 1H, $J = 6.18$ Hz), 5.83 (s, 1H), 6.32 (s, 1H), 7.27–7.33 (m,

5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 51.63, 72.79, 125.76, 126.27, 127.49, 128.08, 140.93, 141.60, 166.42; IR ($CHCl_3$) 3490, 1715 cm^{-1}.

Ethyl 2-[1-Hydroxy-1-(phenyl)Methyl]Acrylate (Table 3, Entry 11)

A colorless oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.96 (brs, 1H), 5.30 (d, 1H, $J = 5.10$ Hz), 6.09 (s, 1H), 6.14 (s, 1H), 6.35 (d, 1H, $J = 4.98$ Hz), 6.37 (d, 1H, $J = 4.72$ Hz), 7.39 (d, 1H, $J = 4.50$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 74.31, 108.34, 110.47, 117.25, 123.61, 131.36, 143.20, 154.61; IR ($CHCl_3$) 3485, 1720 cm^{-1}.

2-[1-Hydroxy-1-(phenyl)Methyl]Acrylonitrile (Table 3, Entry 12)

A colorless oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.62 (brs, 1H), 5.52 (d, 1H, $J = 5.36$ Hz), 6.01 (s, 1H), 6.09 (s, 1H), 7.36–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 73.85, 116.59, 125.86, 126.20, 128.62, 128.65, 129.51, 138.83; IR ($CHCl_3$) 3480, 1720 cm^{-1}.

Methyl 2-[1-Hydroxy-1-(furyl)Methyl]Acrylate (Table 3, Entry 13)

A colorless oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 3.31 (brs, 1H), 3.73 (s, 3H), 5.56 (d, 1H, $J = 4.92$ Hz), 5.93 (s, 1H), 6.22 (s, 1H), 6.30 (d, 1H, $J = 5.12$ Hz), 6.36 (d, 1H, $J = 4.99$ Hz), 7.34 (d, 1H, $J = 5.31$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 52.31, 74.10, 108.29, 110.69, 122.74, 140.31, 154.28; IR ($CHCl_3$) 3490, 1715 cm^{-1}.

Ethyl 2-[1-Hydroxy-1-(furyl)Methyl]Acrylate (Table 3, Entry 14)

A colorless oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.23 (t, 3H, $J = 7.17$ Hz), 3.70 (brs, 1H), 4.16 (q, 2H, $J = 7.18$ Hz), 5.55 (d, 1H, $J = 6.01$ Hz), 5.93 (d, 1H, $J = 2.67$ Hz), 6.18 (d, 1H, $J = 3.21$ Hz), 6.26 (d, 1H, $J = 2.83$ Hz), 6.33 (d, 1H, $J = 2.71$ Hz), 7.31 (d, 1H, $J = 2.05$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ13.62, 60.60, 66.29, 106.74, 109.98, 125.90, 139.50, 141.86, 153.98, 165.65; IR ($CHCl_3$) 3485, 1720 cm^{-1}.

2-[1-Hydroxy-1-(furyl)Methyl]Acrylonitrile (Table 3, Entry 15)

A colorless oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.96 (brs, 1H), 5.30 (d, 1H, $J = 5.10$ Hz), 6.09 (s, 1H), 6.14 (s, 1H), 6.35 (d, 1H, $J = 4.98$ Hz),

6.37 (d, 1H, $J = 4.72$ Hz), 7.39 (d, 1H, $J = 4.50$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 74.31, 108.34, 110.47, 117.25, 123.61, 131.36, 143.20, 154.61; IR ($CHCl_3$) 3480, 1720 cm^{-1}.

Methyl 2-[1-Hydroxy-1-(4-methoxyphenyl)Methyl]Acrylate
(Table 3, Entry 16)

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.91 (brs, 1H), 3.76 (s, 3H), 3.84 (s, 3H), 5.57 (d, 1H, $J = 4.79$ Hz), 5.88 (s, 1H), 6.36 (s, 1H), 6.90 (d, 2H, $J = 8.64$ Hz), 7.32 (d, 2H, $J = 8.58$ Hz); ^{13}C NMR ($CDCl_3$, 300 MHz): δ 52.30, 55.91, 74.21, 114.35, 122.96, 128.32, 133.62, 140.67, 159.30, 167.38; IR ($CHCl_3$) 3490, 1715 cm^{-1}.

Ethyl 2-[1-Hydroxy-1-(4-methoxyphenyl)Methyl]Acrylate
(Table 3, Entry 17)

A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.23 (t, 3H, $J = 7.14$ Hz), 3.24 (brs, 1H), 3.85 (s, 3H), 4.14 (q, 2H, $J = 6.93$ Hz), 5.50 (d, 1H, $J = 6.20$ Hz), 5.85 (s, 1H), 6.31 (s, 1H), 6.86 (d, 2H, $J = 8.61$ Hz), 7.27 (d, 2H, $J = 8.58$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.7, 54.89, 60.53, 72.36, 113.41, 124.99, 127.57, 133.21, 142.06, 158.81, 166.02; IR ($CHCl_3$) 3485, 1720 cm^{-1}.

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