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Graphic Abstract

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Sanhu Zhao,[*a,b] Meiyan He,[a] Zhaonan Guo,[a] Na Zhou,[a] Dou Wang,[a] Jinlong Li,[a] and Liwei Zhang[*b]

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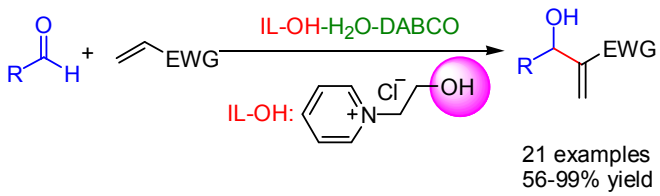

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PAPER

[HyEtPy]Cl-H_2O: An efficient and versatile solvent system for the DABCO-catalyzed Morita-Baylis-Hillman reaction †

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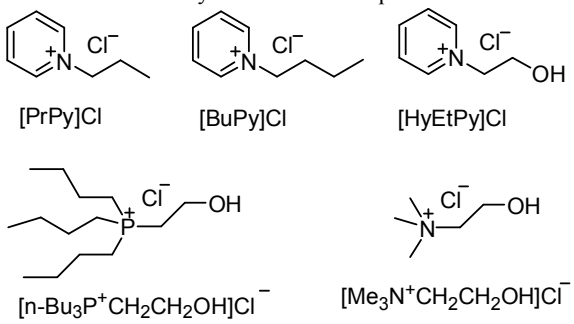
An efficient and versatile solvent–catalyst system, [HyEtPy]Cl-H_2O-DABCO, has been developed and used in the Morita–Baylis–Hillman reaction. Under the mild reaction conditions, Morita–Baylis–Hillman proceeds very quickly and efficiently. This protocol has notable advantages such as eco-friendly, ease of work-up and reuse of ionic liquid conveniently, which could help reduce disposal costs and contribute to the development of new solvent–catalyst system for use in green and continuous chemical processes.

Introduction

The Morita–Baylis–Hillman (M-B-H) reaction, typically catalized by tertiary amine bases such as DABCO,[1] DBU[2] and quinuclidines,[3] is one of the most versatile carbon-carbon bond-forming reactions in modern organic synthesis.[4] In the past decade, due to its atom economy, mild reaction conditions and generality of functional groups, the Morita–Baylis-Hillman reaction has attracted much attention.[5] However, even for the most favorable systems, this reaction often suffers from poor reaction rates and long reaction time. To circumvent this sluggish nature of the reaction, recent efforts in this area have been focused largely on developing efficient reaction systems, some homogeneous aqueous solvent system and binary aqueous solvent system have been reported and lead to higher reaction yields.[6] These studies shown that the use of protic solvents such as methanol and water can accelerate the amine-catalyzed Morita-Baylis-Hillman reaction,[7] as for the reason, it may be through either stabilization of the enolate or activation of the aldehyde by hydrogen bonding. Currently, ionic liquids (ILs) are receiving great attention for application as innovative solvents or additives in a variety of organic reactions.[8] In relation to the common molecular solvent, the main characteristic of ILs is completely composed of ions, which makes them ideal candidates to stabilize the zwitterionic intermediate generated from the Michael addition of a nucleophilic Lewis base to an activated alkene in the M-B-H reaction.[9] Based on this, we speculate that the use of ionic liquid containing hydroxyl group may exert excellent accelerating effect on the Morita-Baylis-Hillman reaction. This deduction was considered to be reasonable, because it was observed previously that a hydroxyl group or a active hydrogen in an amine type catalyst did exert accelerating effect on some coupling reactions.[10] To meet our research interesting, a serious of ionic salts containing hydroxyl group were synthesized or purchased and applied in the DABCO-catalyzed M-B-H reaction (Scheme 1). To our delight, a significant beneficial effect of the1-(2-hydroxy-ethyl)-pyridinium chloride ([HyEtPy]Cl) over its non-hydroxyl counterpart was indeed observed, short reaction time and good to excellent yields of object products were achieved. Herein, we would like to present the catalytic application of the novel hydroxyl pyridinium ionic liquid ([HyEtPy]Cl) in the M-B-H reaction. In comparison to other reported M-B-H reaction systems associated with the use of ionic liquid as solvent, the present solvent–catalyst system composed of [HyEtPy]Cl, H_2O and DABCO works very well at room temperature.



Scheme 1 Five ionic salts containing chloride ion.

Results and discussion

Recently, several ionic liquids were synthesized and applied in the M-B-H reaction, some even achieved excellent results.[11] However, preperation of these ionic liquids often involves a consecutive quaternization-metathetic procedures. Which make them expensive and lead the large scale industrial application in

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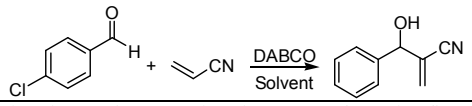
difficult. [12] Therefore, to explore the low cost, high reaction rate, simple synthesis of ionic liquids, and use them in organic synthesis is a very meaningful work. At present, halogenated ionic salts can be easily prepared with high yields and large scale by one step reaction of tertiary amine, tertiary phospnine or heterocyclic compounds containing nitrogen with halogenated hydrocarbon, but these ionic salts are mostly solid at room temperature, which hamper their use directly as solvents in organic reactions.[13]

Recently, as a kind of environmental friendly solvent, water has been often used to prompot organic reaction.[14] To our knowledge, it is generally easy to dissolve halogenated ionic salts in water to form homogeneous system. Comparing the pure ionic salts or water, the homogeneous system made up of water and ionic salts may be have more excellent properties, which put oppotunity for the application of solid state halogenated ionic salts in organic reactions. Based on this point, several ionic salts containing chloride were conveniently synthesized by one step reaction according to literature procedures (Scheme 1). [15] Then mixed these ionic salts with water, the water-ionic liquid composite system was formed and used in the M-B-H reaction of 4-chloro-benzaldehyde with acrylonitrile. Experimental results are summarized in Table 1. As therein revealed, In the presence of water-ionic liquid composite system, the reactions (Table 1, entries 1-5) proceeded quite smoothly and showed a significant acceleration effect with DABCO as base. For example, the reaction in common molecular solvents, such as acetonitrile and tetrahydrofuran (THF), gave 30 and 39% yields of the desired Baylis–Hillman product after 48 h (Table 1, entries 6, 7). While the same reaction in water, only trace amount of product was found after 24 h (Table 1, entry 8). It was also show that the aromatic pyridinium ionic salts [HyEtPy]Cl, [PrPy]Cl and [BuPy]Cl had a better effect than quaternary ammonium (Choine chloride) and quaternary phosphonium ([n-$Bu_3P^+CH_2CH_2OH]Cl^-$) ionic liquid (Table 1, entries 1-5). About the reason, is it trace amount of pyridine in the pyridinium ionic salts? In an earlier literature,[7a] Rezgui report that the DMPA (pyridine derivative) can catalyzed the M-B-H reaction. To find out the truth, we carefully examed the NMR spectra(see Supplementary Material) of the ionic salt [HyEtPy]Cl, the signal of the residual pyridine was not found. And at the same time, to further confirm the enhancement is not from the residual pyridine, the ionic salt [HyEtPy]Cl was further purified by recrystallization and applied in the M-B-H reaction, when using the purified ionic salt [HyEtPy]Cl and H_2O as reaction medium, comparing with the former reaction, the same reaction result was obtained (Table 1, entry 9). When one drop pyridine was added the parallel reaction (Table 1, entry 10), no better result was achieved. So the reason is indeed result from the ionic liquid itself not from the residual pyridine. Among all three pyridinium ionic salts examined, the hydroxyl ionic salt [HyEtPy]Cl provided slightly better results in terms of reaction yield and reaction time (Table 1, entry 1). Considering the similarity of the structures of three pyridinium ionic salts, it was envisioned that the hydroxyl group in the ionic liquid [HyEtPy]Cl must be responsible for its higher activity, the [HyEtPy]Cl itself may serve as a protic additive to promote the M-B-H reaction in a manner similar to the protic additives in conventional cases.

Further optimization of reaction conditions revealed that the amount of H_2O also affect the reaction, when the quality of the water percentage reaches 25% (Table 1, entry 12) the optimal reaction results (yield 99%, 2.6 h) is got, with the increase of water, the reaction time significantly longer (Table 1, entries 1, 11). After careful observation to the reaction phenomena, we noticed that the reaction system become cloudy and has obvious insoluble raw material when the water content was increased over 25% or decreased under 25%, this suggests that the much or less than the amount of water can reduce the dissolve of raw material, which will affect the reaction rate and product yield. Further increasing the amount of DABCO, resulted in a decrease in reaction time. When the 15 mmol of DABCO was added, the shortest reaction time 33min was obtained. The analysis of the results of Table 1 showed that the [HyEtPy]Cl-H_2O composite system (m_{H_2O} : $m_{ionic\ salt}$ = 1:3) is most suitable for the M–B–H reaction, in the presence of DABCO, the best yield and shortest reaction time was obtained (Table 1, entry 14).

Table 1 The combined effects of ionic liquids, water and DABCO on the Morita–Baylis–Hillman Reaction [a]



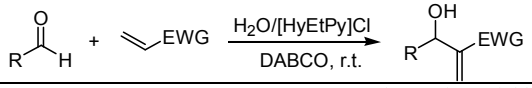
Entry	Ionic salts or other organic solvents	V_{H_2O}/mL	Time/h	Yield (%)
1	[HyEtPy]Cl	3	3.8	99
2	[PrPy]Cl	3	9	95
3	[BuPy]Cl	3	10	93
4	[n-$Bu_3P^+CH_2CH_2OH]Cl^-$	3	12	94
5	[$Me_3N^+CH_2CH_2OH]Cl^-$	3	24	72
6	CH_3CN	0	48	30
7	THF	0	48	39
8	—	3	24	ND[b]
9	Further purified [HyEtPy]Cl	3	3.8	99
10[c]	Further purified [HyEtPy]Cl+pyridin	3	3.8	99
11	[HyEtPy]Cl	9	7.5	99
12	[HyEtPy]Cl	1	2.6	99
13[d]	[HyEtPy]Cl	1	52min	99
14[e]	[HyEtPy]Cl	1	33min	99

[a] General reaction conditions: 4-chlorobenzaldehyde (10 mmol), DABCO (5 mmol), ionic salt (3.0 g), acrylonitrile (12 mmol), no further increase in yield after the reported time.
[b] Only trace amount of product was detected and its yield not determined.
[c] 3g purified [HyEtPy]Cl + one drop of pyridine.
[c] DABCO was 10 mmol. [d] DABCO was 15 mmol.

With the optimized reaction conditions in hand, the scope of the M–B–H reaction was investigated by employing a variety of aldehydes to react with acrylonitrile or acrylates. As shown in Table 2, both aliphatic and aromatic aldehydes can undergo very efficient Baylis–Hillman reactions giving the corresponding Baylis–Hillman adducts in good to excellent yields. Comparing the aromatic aldehydes bearing electron-donating groups (CH_3O, CH_3), the electron deficient aromatic aldehydes provided a better yields and shorter reaction time. It is worth mentioning that the electron-rich 2-methoxybenzaldehyde, which is usually quite an inert substrate, could provide an excellent yield of 92% after 70min (entry 9) under the present conditions. To our delight, heteroaryl aldehydes, also underwent M–B–H reaction to give the

corresponding adduct with a fairly good yield (Table 2, entries 13, 14). Another important observation that needs special mention is that the reaction of benzene-1,4-dicarbaldehyde with acrylonitrile, in our previous work,[16] we only get the Baylis–Hillman adduct of one aldehyde group, however, under the present conditions, the product of two aldehyde group was obtained with high yield and short reaction time (entry 10). When the hydrophobic butyl acrylate was selected as activated alkene (entry 21), the good reaction yield 86% was also obtained after 3h. Thus the [HyEtPy]Cl-H_2O composite system is indeed a very effective solvent media for all substrates tested. The identities of the products were confirmed by their melting points and ^1H and ^{13}C NMR data, which were found to be consistent with reported values.

Table 2 Morita–Baylis–Hillman reactions between aldehydes and acrylonitrile or acrylates catalyzed by DABCO in H_2O-[HyEtPy]Cl composite system [a]



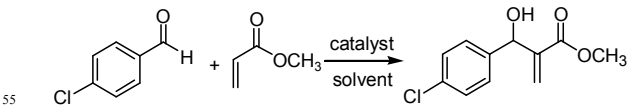
Entry	R	EWG	Time (min)	Yield (%) [b]
1	C_6H_5	CN	38	95
2	4-ClC_6H_4	CN	33	99
3	4-FC_6H_4	CN	60	97
4	4-$NO_2C_6H_4$	CN	5	97
5	3-$NO_2C_6H_4$	CN	10	95
6	3,4-$Cl_2C_6H_3$	CN	25	99
7	2,4-$Cl_2C_6H_3$	CN	60	99
8	4-$CH_3OC_6H_4$	CN	4h	56
9	2-$CH_3OC_6H_4$	CN	70	92
10 [c]	4-$CHOC_6H_4$	CN	10	99
11	4-$CH_3C_6H_4$	CN	60	67
12	2-Naphthalyl	CN	2.2h	98
13	2-Pyridyl	CN	6	97
14	2-Furyl	CN	1d	68
15	CH_3	CN	1d	92
16	n-C_3H_7	CN	20h	91
17	C_6H_5	$COOCH_3$	5h	92
18	4-ClC_6H_4	$COOCH_3$	40	96
19	4-$NO_2C_6H_4$	$COOCH_3$	20	98
20	4-$CH_3C_6H_4$	$COOCH_3$	1d	65
21	4-$NO_2C_6H_4$	$COOCH_2CH_2CH_2CH_3$	3h	86

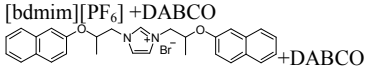
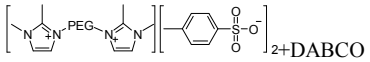
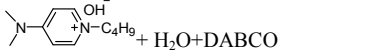
[a] All reactions were performed with aldehydes (10 mmol), activated alkenes (12 mmol) in the H_2O-[HyEtPy]Cl composite system (1 mL H_2O and 3 g [HyEtPy]Cl) in the presence of the catalyst DABCO (15 mmol) at room temperature. The reaction was monitored by TLC analysis;
[b] Refers to isolated yield;
[c] Acrylonitrile was 23 mmol.

In order to further evaluate the reactivity of the solvent–catalyst system [HyEtPy]Cl-H_2O-DABCO, we also compared it with some homogeneous or heterogeneous catalysts reported in the literature for the M-B-H reaction (Table 3, Entries1-14). As shown in Table 3, in terms of the reaction conditions, yields and costs, etc., the present solvent–catalyst system [HyEtPy]Cl-H_2O-DABCO has obvious advantages over reported solvent-catalyst systems.

To evaluate the possibility of recycling the composite system ([HyEtPy]Cl-H_2O) used for the M-B-H reaction, methy acrylate (12 mmol) and DABCO (15 mmol) were added to a solution of 4-chlorobenzaldehyde (10 mmol) in the composite system [HyEtPy]Cl-H_2O (1 mL H_2O and 3g -[HyEtPy]Cl). The reaction mixture was stirred at room temperature. The reaction progress was monitored by thin layer chromatography (TLC) until aldehyde was consumed. The reaction mixture was extracted with diethyl ether (2×20 ml). The combined diethyl ether mixture was washed with saturated brine (2×20 mL) and dried over anhydrous Na_2SO_4, then the solvent was removed on a rotary vacuum evaporator and the almost pure product was obtained. Then 4-chlorobenzaldehyde, acrylic acid methyl ester and DABCO were added to the recycled composite system [HyEtPy]Cl-H_2O to repeat the reaction. The recovered composite system was used at least six times almost without reduction of the reaction yields (Table 4, Entries 1-6).

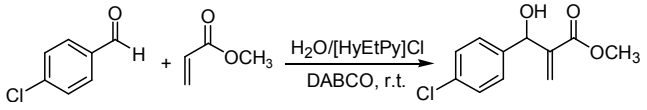
Table 3 Comparisons of the solvent-catalyst system ([HyEtPy]Cl-H_2O-DABCO) with various homogeneous or heterogeneous solvent-catalyt systems in the Morita–Baylis–Hillman reaction of 4-chlorobenzaldehyde with methy acrylate.



Entry	Solvent-catalyst system	Time	Yield (%)	Ref.
1	[bmim][PF_6]+DABCO	24h	66	18
2	[bdmim][PF_6] +DABCO	24h	99	18
3	 +DABCO	27h	58	19
4	 2+DABCO	8h	88	16
5	[EPy][BF_4] +DABCO	5h	72	9a
6	 + H_2O+DABCO	18h	83.2	20
7	CH_3OH+ quinuclidine	3h	88	6d
8	[n-Bu_3P^+Et]Br^- + H_2O+DABCO	1h	98	17
9	[HPDABCO][BF_4]+ DBU	3.5h	87	21
10	CH_3OH+3-hydroxyquinuclidine	24h	78	22
11	DMF+3-hydroxyquinuclidine+ $Sc(OTf)_3$	6h	79	23
12	dioxane+water +hexamethylenetetramine	48h	42	24
13	CH_3OH+H_2O+trimethylamine	8h	77	6c
14	[HyEtPy]Cl+H_2O+DABCO	40min	96	

ref.: references.

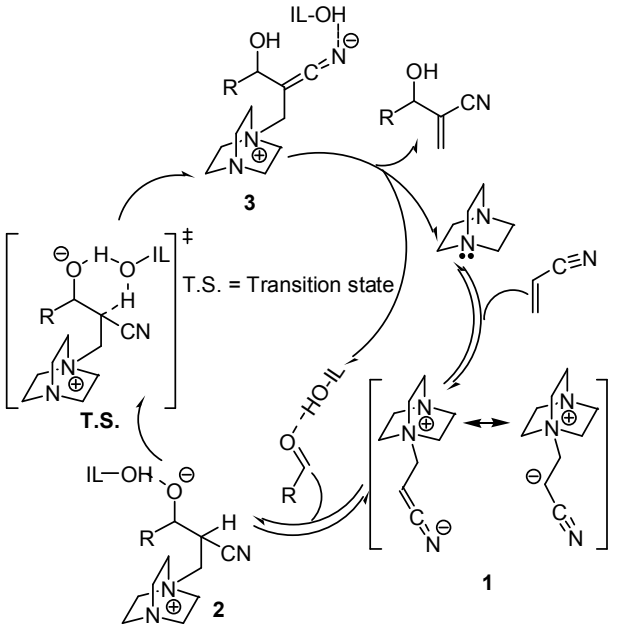
Table 4 Reuse of the solvent system [HyEtPy]Cl-H_2O.



Cycle	Time (min)	Yield (%)
1	40	97
2	40	94
3	40	96
4	40	97
5	40	95
6	40	93

[a] All reactions were performed with 4-chlorobenzaldehyde (10 mmol) and methy acrylate (12 mmol) in the H_2O-[HyEtPy]Cl composite system (1 mL H_2O and 3 g [HyEtPy]Cl) in the presence of the catalyst DABCO (15 mmol) at room temperature. The reaction was monitored by TLC analysis.

In the presence of solvent–catalyst system [HyEtPy]Cl-H_2O-DABCO, a plausible reaction pathway for the formation of the M-B-H adduct was suggested. As in depicted in Scheme 2, not only the [HyEtPy]Cl (IL-OH) can active the aldehyde and stable the intermediate, but also it can accelerate the M-B-H reaction by allowing the proton-transfer to occur via a concerted step, in which IL-OH act as a shuttle to transfer the proton from the α-position to the alkoxide of intermediate 2.



Scheme 2 Possible the cyclic pathway for the [HyEtPy]Cl-H_2O-DABCO prompoted M-B-H reaction.

Conclusion

In summary, a recyclable protic-ionic-liquid solvent system, [HyEtPy]Cl-H_2O, has been developed and used in the M-B-H reaction of aromatic aldehydes with activated alkenes. The composite system ([HyEtPy]Cl-H_2O) could be readily prepared by simply mixing the solid state [HyEtPy]Cl with water at a given ratio. Under room temperature, the M-B-H reaction promoted by the protic-ionic-liquid solvent–catalyst system proceeded very well, and the ([HyEtPy]Cl-H_2O solvent system could be recycled for at least 6 times showing no significant loss of activity. This protocol has notable advantages, such as being eco-friendly, low disposal costs, the ease of the work-up and reuse of the ionic liquid conveniently, which makes the present protocol practical for the preparation of multifunctional M-B-H products. As a result, it is expected that the present method will find its application in future organic synthesis, pharmaceutical use and in green and continuous chemical processes.

Experimental

General

^{1}H NMR (600, 400 or 300 MHz) and ^{13}C NMR (151 or 101 MHz) spectra were recorded on a Bruker Avance 600 (600 MHz), 400 (400 MHz) or DRX300 (300 MHz) spectrometer at ambient temperatures and using $CDCl_3$ or DMSO-d_6 as solvent. ^{1}H and ^{13}C NMR chemical shifts were reported in ppm relative to internal Me_4Si. The elemental analyses were performed on the Vario EL element analyzer. Melting points were measured on WRS-1B digital melting point meter and are uncorrected. The ionic salts 1-propylpyridinium chloride and choline chloride were obtained from commercial suppliers and used without further purification.

Preparation and characterization of the ionic salts

1-(2-Hydroxy-ethyl)-pyridinium chloride([HyEtPy]Cl).

The ionic salt [HyEtPy]Cl was prepared according to a literature procedure[15] with the following modifications: Transfer excess 2-chloroethanol (51 mL, 0.76 mol) and pyridine (53 mL, 0.63 mol) to a 250 mL round bottom flask which is fitted with reflux condenser and nitrogen protecting facilities, and the reaction mixture was gently stirred at 70 ^{o}C for 24 h in the dark, the crude product [HyEtPy]Cl was formed. Then the crude product was purified by the recrystallization with the solvent of 5 mL acetonitrile and 25 mL ethyl acetate, and the residual solvent was removed in vacuum to give the product [HyEtPy]Cl (95 g, 94%) as a white crystal. m.p. 124 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.85 (dd, J = 10.1, 5.2 Hz, 2H, CH_2O), 4.73 (t, J = 6.0 Hz, 2H, N-CH_2), 5.61 (d, J = 6.0 Hz, 1H, OH), 8.18 (t, J = 6.0 Hz, 2H, CH=), 8.63 (t, J = 7.8 Hz, 1H, CH=), 9.12 (d, J = 6 Hz, 2H, CH=N$^+$); ^{13}C NMR (151 MHz, DMSO-d_6) δ 148.86, 148.61, 131.01, 66.28, 63.28. Anal. calcd for $C_7H_{10}ClNO$: C 52.67, H 6.31; found C 52.70, H 6.48.

1-Butylpyridinium chloride ([BuPy]Cl).

The same procedure was followed as that described above for [HyEtPy]Cl, except for the use of 1-chlorobutane (99 mL, 0.95 mol) instead of 2-chloroethanol. The product ([PrPy]Cl (99 g, 92%) was obtained as a white crystal solid. m.p. 87 °C (lit.,[15e] 86 °C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.89 (s, 3H, CH_3), 1.28 (s, 2H, CH_2), 1.89 (s, 2H, CH_2), 4.72 (t, J = 10.0 Hz, 2H, N-CH_2), 8.20 (s, 2H, CH=), 8.66 (s, 1H, , CH=), 9.35 (s, 2H, CH=N$^+$); ^{13}C NMR (125 MHz, DMSO-d_6) δ 145.66, 144.77, 128.04, 60.19, 32.60, 18.95, 13.45.

1-Tributyl-(2-hydroxy-ethyl)-phosphonium chloride ([n-$Bu_3P^+CH_2CH_2OH$]Cl$^-$).

The ionic salt [n-$Bu_3P^+CH_2CH_2OH$]Cl$^-$ was prepared according to a literature procedure[25] with the following modifications: Transfer excess 2-chloroethanol (16.1 mL, 0.24 mol) and tributyl phosphine (50 mL, 0.20 mol) to a 250 mL round bottom flask which is fitted with reflux condenser and nitrogen protecting facilities, and the reaction mixture was gently stirred at 90 ^{o}C for 48 h. After the reaction was complete, the mixture was vacuum stripped to remove excess 2-chloroethanol, and a colorless viscous liquid (51.4 g, 90%) was obtained. ^{1}H NMR (DMSO-d_6, 600 MHz) δ 0.92 (t, J = 7.3 Hz, 9H), 1.39-1.42 (m, 6H), 1.46-1.51 (m, 6H), 2.23 (t, J = 12 Hz, 6H), 2.43 (t, J = 6.0 Hz, 2H), 3.60 (t, J = 6.0 Hz, 2H), 3.78 (s, 1H); ^{13}C NMR (DMSO-d_6, 151 MHz) δ 65.01, 57.53, 49.65, 26.80, 21.71, 16.76. Anal. calcd for $C_{14}H_{32}ClOP$: C 59.45, H 11.40; found C 59.49, H 11.58.

General procedure for M-B-H reaction

To a stirred mixture of 10 mmol aldehyde and 12 mmol activated alkene in 4.0 g [HyEtPy]Cl-H_2O (1 ml H_2O and 3g [HyEtPy]Cl)

at room temperature was added 15 mmol DABCO. The reaction was stopped by dilution with diethyl ether and washed with saturated brine, followed by water. After drying over anhydrous Na_2SO_4, the solvents were removed under reduced pressure to give the crude product, which was further purified by a short column chromatography (silica gel, 200–300 mesh; ethyl acetate/petroleum ether, 1:5–1:3). The products were confirmed by NMR spectroscopy and the spectral datas of all products are listed as follows.

2-(Hydroxy-phenyl-methyl)-acrylonitrile (Table 2, entry 1). [24]

Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.84 (s, 1H), 5.97 (s, 1H), 6.03 (s, 1H), 6.13 (t, J = 6.0 Hz, 1H), 7.44 (s, 5H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 135.66, 130.76, 129.56, 129.20, 128.96, 127.66, 124.56, 78.14.

2-[(4-chloro-phenyl)-hydroxy-methyl]-acrylonitrile (Table 2, entry 2).

White crystal solid; m.p. 75 °C (lit.,[17] 74.8-75.3 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.12 (s, 1H) , 5.25 (s, 1H), 6.02 (s, 1H), 6.08 (s, 1H), 7.31 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 137.68, 134.72, 130.40, 129.07, 127.92, 125.93, 116.77, 73.40.

2-[(4-fluoro-phenyl)-hydroxy-methyl]-acrylonitrile (Table 2, entry 3). [4d]

Yellow oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.35 (s, 1H), 6.12 (s, 1H), 6.21 (s, 1H), 6.36 (s, 1H), 7.22 (t, J = 8.9 Hz, 2H), 7.44 (t, J = 8.9 Hz, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 165.93, 140.82, 133.85, 131.68, 130.41, 120.68, 118.56, 75.24.

2-[Hydroxy-(4-nitro-phenyl)-methyl]-acrylonitrile (Table 2, entry 4).

Yellow solid; m.p. 74 °C (lit.,[6c] 72-75 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.42 (s, 1H), 5.45 (s, 1H), 6.09 (s, 1H), 6.19 (s, 1H), 7.60 (d, J = 8.5 Hz, 2H), 8.22 (d, J = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.07, 146.46, 131.30, 127.51, 125.37, 123.72, 116.39, 73.17.

2-[Hydroxy-(3-nitro-phenyl)-methyl]-acrylonitrile (Table 2, entry 5).

Pale white solid; m.p. 65 °C (lit.,[17] 64-66 °C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.55 (s, 1H), 6.21 (s, 1H), 6.32 (s, 1H), 6.66 (s, 1H), 7.72 (t, J = 7.9 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 8.20 (d, J = 11.6 Hz, 1H), 8.26 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.12, 146.76, 136.07, 135.17, 133.29, 129.83, 126.35, 124.18, 120.38, 75.24.

2-[(3,4-Dichloro-phenyl)-hydroxy-methyl]-acrylonitrile (Table 2, entry 6).[4d]

Yellow oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.39 (s, 1H), 6.17 (s, 1H), 6.26 (s, 1H), 6.53 (s, 1H), 7.38 (d, J = 6.0 Hz, 1H), 7.63 (s, 1H), 7.68 (s, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 145.60, 134.92, 134.50, 134.18, 133.85, 131.45, 129.89, 129.54, 120.42, 74.75.

2-[(2,4-Dichloro-phenyl)-hydroxy-methyl]-acrylonitrile (Table 2, entry 7).

White solid; m.p. 73°C (lit.,[24] 74 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.07 (s, 1H), 5.67 (s, 1H), 6.05 (s, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.39 (s, 1H), 7.55 (d, J = 8.01, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.57, 137.73, 135.60, 134.09, 131.97, 131.36, 130.38, 126.7, 72.55.

2-[Hydroxy-(4-methoxy-phenyl)-methyl]-acrylonitrile (Table 2, entry 8). [24]

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25 (s, 1H), 3.82 (s, 3H), 5.24 (s, 1H), 6.12 (d, J = 1.3 Hz, 1H), 6.24 (d, J = 1.8 Hz,1H), 6.84 (d, J = 7.2 Hz, 2H), 7.32 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.30, 134.72, 129.16, 128.65, 121.48, 117.57, 114.86, 74.89, 56.42.

2-[Hydroxy-(2-methoxy-phenyl)-methyl]-acrylonitrile (Table 2, entry 9). [11a]

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (s, 1H), 3.83 (s, 3H), 5.51 (s, 1H), 5.96 (s, 1H), 5.99 (s, 1H), 6.91 (d, J = 8.2 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 7.34 (dd, J = 18.2, 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.45, 129.89, 127.65, 127.32, 125.90, 121.09, 117.33, 110.96, 70.00, 55.44.

2-{[4-(2-cyano-1-hydroxy-allyl)-phenyl]-hydroxy-methyl}-acrylonitrile (Table 2, entry 10).

White crystal solid; m.p. 134 °C (lit.,[17] 134.8-135.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 2H), 5.37 (s, 2H), 6.08 (s, 2H), 6.17 (s, 2H), 7.48 (s, 4H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 141.17, 130.96, 127.46, 126.76, 117.87, 72.86.

2-[Hydroxy-(4-methyl-phenyl)-methyl]-acrylonitrile (Table 2, entry 11). [7c]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.12 (s, 1H), 5.25 (s, 1H), 6.02 (s, 1H), 6.12 (s, 1H), 7.18-7.23 (m, 4H).

2-(hydroxy-naphthalen-1-yl-methyl)-acrylonitrile (Table 2, entry 12). [11a]

Yellow oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.04 (s, 1H), 6.20 (s, 1H), 6.36 (s, 1H), 6.46 (s, 1H), 7.56 (dd, J = 19.5, 6.7 Hz, 3H), 7.72 (d, J = 7.1 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 9.2 Hz, 1H), 8.19 (d, J = 9.2 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 139.55, 136.79, 134.58, 133.39, 132.07, 131.96, 129.91, 129.56, 129.09, 128.74, 128.08, 127.01, 120.87, 73.31.

2-(Hydroxy-pyridin-2-yl-methyl)-acrylonitrile (Table 2, entry 13).[7c]

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (s, 1H), 6.08 (s, 1H), 6.25 (s, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 6.0 Hz, 1H), 8.60 (d, J = 5.6 Hz, 1H).

2-(Furan-2-yl-hydroxy-methyl)-acrylonitrile (Table 2, entry 14). [7c]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (br s, 1H), 5.39 (s, 1H), 6.08 (s, 1H), 6.18 (d, J =4.0 Hz, 1H), 6.29 (d, J = 4.0 Hz, 1H), 6.44 (d, J = 3.9 Hz, 1H), 7.36 (d, J = 4.0 Hz, 1H).

3-Hydroxy-2-methylene-butyronitrile(Table 2, entry 15). [9a]

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.32 (s, 1H), 3.71 (s, 3H), 5.50 (s, 1H), 5.85(s, 1H), 6.33 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.7, 119.7, 117.3, 68.1, 19.6.

3-Hydroxy-2-methylene-hexanenitrile (Table 2, entry 16). [9a]

Yellow oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 0.88 (d, J = 6.0 Hz, 3H), 1.27-1.37 (m, 2H), 1.46-1.50 (m, 2H), 4.10 (q, J = 6.0 Hz, 1H), 5.50 (s, 1H), 6.03 (d, J = 6.0 Hz, 2H); ^{13}C NMR (151 MHz,

DMSO-d_6) δ 133.62, 130.80, 121.05, 73.86, 40.82, 21.30, 17.03.

2-(Hydroxy-phenyl-methyl)-acrylic acid methyl ester(Table 2, entry 17). [6c]

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.10 (s, 1H), 3.67 (s, 3H), 5.45 (s, 1H), 5.86 (s, 1H), 6.28 (s, 1H), 7.32-7.42 (m, 5H).

2-[(4-Chloro-phenyl)-hydroxy-methyl]-acrylic acid methyl ester(Table 2, entry 18).

White solid; m.p. 44 °C (lit.,[6c] 43-44 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.32 (s, 1H), 3.72 (s, 3H), 5.50 (s, 1H), 5.85 (s, 1H), 6.33 (s, 1H), 7.30 (s, 4H).

2-[Hydroxy-(4-nitro-phenyl)-methyl]-acrylic acid methyl ester(Table 2, entry 19).

Yellow solid; m.p. 72 °C (lit.,[6c] 71-73 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.23 (s, 1H), 3.42 (s, 3H), 5.45 (s, 1H), 5.69 (s, 1H), 6.19 (s, 1H), 7.37 (d, J = 6.2 Hz, 2H), 7.98 (d, J = 6.2 Hz, 2H).

2-(Hydroxy-p-tolyl-methyl)-acrylic acid methyl ester(Table 2, entry 20).

White solid; m.p. 39 °C (lit.,[6c] 39-42 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.12 (s, 1H), 3.70 (s, 3H), 5.52 (s, 1H), 5.83 (s, 1H), 6.29 (s, 1H), 7.15-7.23 (m, 4H).

2-[(4-nitro-phenyl)-hydroxy-methyl]-acrylic acid butyl ester (Table 2, entry 21). [6c]

Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.6 Hz, 3H), 1.39-1.30 (m, 2H), 1.67-1.56 (m, 2H), 3.42 (br s, 1H), 4.14 (t, J = 6.4 Hz, 2H), 5.63 (s, 1H), 5.87 (s, 1H), 6.41 (s, 1H), 7.60 (d, J = 8.8 Hz, 2H), 8.22 (d, J = 8.4 Hz, 2H).

Reusability and recovery of the composite system [HyEtPy]Cl-H_2O

After the first run of the reaction was completed, the product was extracted by diethyl ether into the organic layer, and the remained composite system [HyEtPy]Cl-H_2O was directly reused for the next cycle of the reaction.

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