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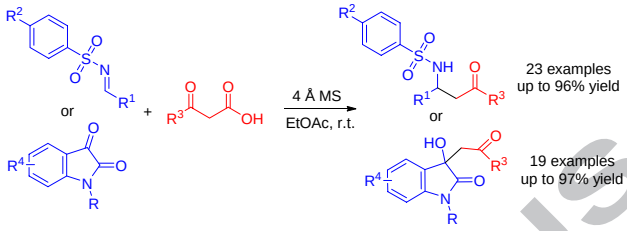

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Molecular sieve mediated decarboxylative Mannich and aldol reactions of -ketoacids

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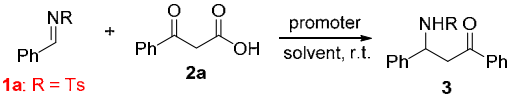
ABSTRACT

A molecular sieve mediated decarboxylative Mannich reaction of -ketoacids with sulfonyl imines is reported; this protocol leads to an efficient preparation of synthetically useful -amino ketones. An analogous molecular sieve promoted decarboxylative aldol reaction between -ketoacids and isatins is also described, which affords bioactive 3-substituted-3-hydroxy-oxindoles in excellent yields.

The catalytic Mannich reaction of carbonyl compounds with imines represents a powerful approach for the synthesis of -amino ketones, which are not only important due to their biological activities, but are also extremely useful as versatile building blocks for the construction of 1,3-amino alcohols, 1,3-amino acids and related bioactive molecules.[1] Therefore, not surprisingly, intense efforts have been devoted to these types of reactions.[2]

Aryl methyl ketones are interesting donors in the Mannich reaction. However, due to their intrinsically low reactivity, pre-activation is often required. For instance, the Lewis acid promoted Mukaiyama–Mannich reaction between silyl enol ethers and sulfonyl aldimines represents one of the most common approaches.[3] In recent years, biomimetic approaches using malonic acid half thioesters (MAHTs), as ester enolate equivalents in the decarboxylative reactions, have drawn much attention.[4] In the decarboxylative processes of MAHTs, a wide range of electrophiles, including aldehydes, ketones, imines, activated alkenes and azodicarboxylates have been employed as reaction partners under either metal[5] or organic[6] catalysis. From a more practical viewpoint, the employment of -ketoacids as ketone surrogates is highly desirable, and such decarboxylative processes have been realized under the catalysis of a suitable Brønsted base or metal.[7] With ever-growing concerns of performing organic reactions in a green and sustainable manner, we became interested in developing an efficient synthetic protocol involving decarboxylation of -ketoacids. Herein, we report a molecular sieve-mediated decarboxylative Mannich reaction of -ketoacids with *N*-sulfonyl imines. Moreover, the same decarboxylative process can be extended to the aldol reaction of -ketoacids with isatins.

Table 1. Decarboxylative Mannich reaction of -ketoacid **2a** with imines **1**[a]



1a: R = Ts
1b: R = Cbz
1c: R = CO_2Et

2a **3**

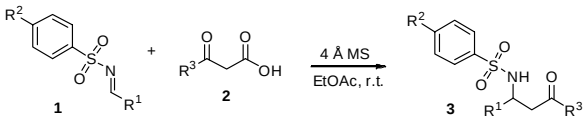
Entry	Imine	Promoter	Loading (mg/mmol)	Solvent	Time (h)	Conv. (%)[b]
1	**1a**	none	-	THF	24	<20
2	**1a**	4 Å MS	300	THF	1	>99
3	**1a**	4 Å MS	300	CH_3CN	3	>99
4	**1a**	4 Å MS	300	EtOAc	0.5	>99
5	**1a**	4 Å MS	300	acetone	1	>99
6	**1a**	4 Å MS	300	$CHCl_3$	24	80
7	**1a**	4 Å MS	300	CH_2Cl_2	24	85
8	**1a**	4 Å MS	300	toluene	24	<50
9	**1a**	4 Å MS	300	Et_2O	24	90
10	**1a**	4 Å MS	100	EtOAc	2	>99
11	**1a**	4 Å MS	50	EtOAc	4	>99
12	**1b**	4 Å MS	50	EtOAc	24	58
13	**1c**	4 Å MS	50	EtOAc	24	mixture

[a] Reactions were performed with **1** (0.1 mmol), **2a** (0.12 mmol) and the promoter in the solvent specified (1.0 mL).

[b] Determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. MS: molecular sieves.

We initiated our investigation by performing a model reaction between tosylimine **1a** and -ketoacid **2a**, and the results are summarized in Table 1. The background reaction was found to be very weak, and less than 20% conversion was observed after 24 hours at room temperature (Table 1, entry 1). We were delighted to discover that the reaction could be promoted effectively by molecular sieves. In the presence of 4 Å molecular sieves, full conversion of the Mannich product was observed in just 1 hour (entry 2). Further solvent screening revealed that ethyl acetate gave the best result (entry 4). To make the method greener and more synthetically useful, the loading of molecular sieves was reduced to 50 mg/mmol, with reference to the imine substrate, and full conversion was reached within 4 hours (entry 11). Notably, the sulfonyl protecting group was found to be crucial, and sluggish reactions were observed when *N*-Cbz imine **1b** or *N*-CO_2Et imine **1c** were employed under otherwise identical reaction conditions (entries 12 and 13).

Table 2. Scope of the molecular sieve-mediated Mannich reaction[a]



Entry	R^1	R^2	R^3	Product	Time (h)	Yield (%)[b]
1	C_6H_5	Me	C_6H_5	**3a**	4	91
2	C_6H_5	OMe	C_6H_5	**3b**	4	96
3	C_6H_5	NO_2	C_6H_5	**3c**	4	86
4	4-Br-C_6H_4	Me	C_6H_5	**3d**	4	94
5	4-F-C_6H_4	Me	C_6H_5	**3e**	4	88
6	4-MeO-C_6H_4	OMe	C_6H_5	**3f**	4	91
7	3-Br-C_6H_4	Me	C_6H_5	**3g**	4	90
8	3-Cl-C_6H_4	Me	C_6H_5	**3h**	5	88
9	3-NO_2-C_6H_4	OMe	C_6H_5	**3i**	3	92
10	2-Me-C_6H_4	OMe	C_6H_5	**3j**	12	75
11	2-Br-C_6H_4	OMe	C_6H_5	**3k**	6	89
12	2,4-Cl_2-C_6H_3	OMe	C_6H_5	**3l**	4	93
13	3-furyl	Me	C_6H_5	**3m**	24	84
14	2-naphthyl	OMe	C_6H_5	**3n**	6	92
15	hexyl	Me	C_6H_5	**3o**	12	89
16	cyclohexyl	Me	C_6H_5	**3p**	12	82
17	C_6H_5	Me	4-Me-C_6H_4	**3q**	4	84
18	C_6H_5	Me	4-F-C_6H_4	**3r**	24	81
19	C_6H_5	OMe	3-Cl-C_6H_4	**3s**	48	66
20	C_6H_5	Me	2-MeO-C_6H_4	**3t**	4	91
21	C_6H_5	Me	Me	**3u**	24	82
22	C_6H_5	Me	Pr	**3v**	24	86
23	C_6H_5	Me	*t*-Bu	**3w**	24	77
24[c]	C_6H_5	Me	C_6H_5	**3a**	4	86
25[d]	C_6H_5	Me	C_6H_5	**3a**	4	86-92

[a] Reactions were performed with **1** (0.1 mmol), **2** (0.12 mmol) and 4 Å MS (5 mg) in EtOAc (1.0 mL).

[b] Isolated yield.

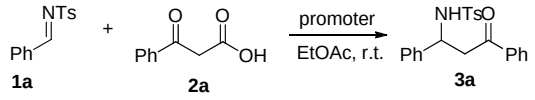
[c] Reaction was performed with 5 mmol of **1a**.

[d] Reaction results with recycled MS: cycle 1, 91% yield; cycle 2, 86% yield; cycle 3, 88% yield; cycle 4, 89% yield; cycle 5, 92% yield. MS = molecular sieves.

The effects of different sulfonamides on the reaction were next examined. Substrates with electron-donating groups on the aryl ring of the sulfonamide reacted slightly better than those with an electron-withdrawing substituent (Table 2, entries 1 3). The reaction tolerated a wide range of aryl imine substrates, regardless of the electronic nature and the substitution pattern of the aromatic rings (entries 4–14). Moreover, the reaction was applicable to linear and branched alkyl tosylimines, although longer reaction times were required for the reactions to reach completion (entries 15 and 16). The -ketoacids could also be varied, and both aryl and alkyl substituted -ketoacids were found to be suitable for the decarboxylative process (entries 17 23). This decarboxylative Mannich reaction could be performed on gram-scale. Under the optimized conditions, the reaction proceeded smoothly to afford the product in high yield (entry 24). The practicality of our method was further demonstrated by the successful recycling of the molecular sieves. The recovered molecular sieves were able to catalyse the reaction for up to five runs without any decrease in reactivity (entry 25).

To gain a better insight into the reaction mechanism, a series of control experiments was performed (Table 3). As expected,[8] the decarboxylative process took place smoothly in the presence of an organic or inorganic base (entries 2−4). We believe the ability of molecular sieves to promote the reaction is independent of their desiccating property, as anhydrous sodium sulfate failed to promote the process (entry 5). The 4 Å molecular sieves without pre-activation worked equally well (entry 6). Moreover, the size of the molecular sieves proved to be important for the reaction: 4 Å and 3 Å molecular sieves were more effective, while 5 Å molecular sieves displayed much lower catalytic activity (entries 7 and 8). Since all the molecular sieves were too small to accommodate the reactants within their cavity, the reaction took place mostly likely on the surface of the molecular sieves. It seems that the basic alkaline metal ions were responsible for the catalytic performance of the molecular sieves, as no catalytic activity was observed when common silica or aluminosilicate (Celite) was used (entries 9 and 10). We also found the basicities of molecular sieves were 4 Å>3 Å>5 Å, which agreed well with the observed catalytic activities (entries 7 and 8).[9] A moderate isolated yield was obtained when the mixture was heated, probably due to significant decomposition of the reactants under the harsh conditions (entry 11).

Table 3. The Effect of Different Promoters[a]



Entry	Promoter	Time (h)	Yield (%)[b]
1	4 Å MS	1	94
2[c]	Et_3N	24	60
3	$NaHCO_3$	12	90

4	Na_2CO_3	1	90
5	Na_2SO_4	24	<20
6[d]	4 Å MS	1	92
7	3 Å MS	3	83
8	5 Å MS	24	72
9[e]	silica gel	24	26
10[f]	Celite	24	<10
11[g]	none	24	58

[a] Reactions were performed with **1a** (0.1 mmol), **2a** (0.12 mmol), promoter (30 mg) in EtOAc (1.0 mL).

[b] Isolated yield.

[c] 10 mol% of Et_3N was used.

[d] 4 Å MS were used without preactivation.

[e] Purchased from Aldrich, technical grade, pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size.

[f] Fluka Analytical, Celite® 500 fine.

[g] Reaction mixture was heated at 50 °C.

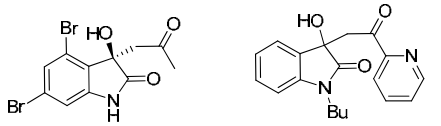
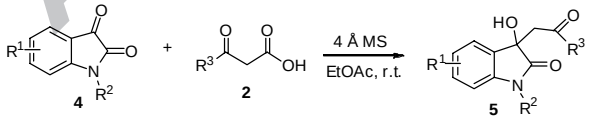


Fig. 1. Selected examples of 3-hydroxy-3-acyloxindole-containing bioactive molecules.

Having developed the above efficient decarboxylative Mannich reaction of -ketoacids, our next goal was to extend this process to the analogous aldol reaction. When benzaldehyde was employed as an acceptor, only a trace amount of the desired aldol product was obtained. Given the high reactivity of isatins and the prevalence of 3-hydroxyoxindoles[10] in natural products and bioactive molecules (Figure 1), we examined the feasibility of molecular sieves in promoting the aldol reaction of isatins. To our delight, the aldol reaction of -ketoacid **2a** with isatin proceeded very rapidly in the presence of 4 Å molecular sieves, affording 3-hydroxyoxindole **5a** in 93% yield (Table 4, entry 1). Different protecting groups on the NH of isatin worked equally well (entries 2 5). The reaction was also applicable to isatins with different aromatic moieties, including those with electron-donating and electron-withdrawing groups and halogen atoms on the phenyl ring (entries 6 10). The -ketoacid substrates could also be varied, both aryl and alkyl -ketoacids were well-tolerated, and the desired aldol products were obtained in excellent yields in all the examples examined (entries 11 19).

Table 4. Molecular sieve mediated decarboxylative aldol reaction of -ketoacids with isatins[a]



Entry	R^1	R^2	R^3	Product	Time (h)	Yield (%)[b]
1	H	H	C_6H_5	**5a**	1	93
2	H	Boc	C_6H_5	**5b**	1	96
3	H	Ac	C_6H_5	**5c**	1	95
4	H	Bn	C_6H_5	**5d**	3	93
5	H	C_6H_5	C_6H_5	**5e**	4	87
6	5-OMe	H	C_6H_5	**5f**	12	82
7	5-Br	H	C_6H_5	**5g**	2	94
8	5-NO_2	H	C_6H_5	**5h**	2	91
9	7-Cl	H	C_6H_5	**5i**	6	83
10	7-F	H	C_6H_5	**5j**	6	85
11	H	H	4-F-C_6H_4	**5k**	1	95
12	H	H	4-Me-C_6H_4	**5l**	1	96
13	H	H	3-Cl-C_6H_4	**5m**	6	71
14	H	H	2-MeO-C_6H_4	**5n**	2	93
15	H	H	2-naphthyl	**5o**	1	98
16	H	H	2-thienyl	**5p**	1	95
17	H	H	Me	**5q**	2	91
18	H	H	Pr	**5r**	4	88
19	H	H	*t*Bu	**5s**	12	83

[a] Reactions were performed with **4** (0.1 mmol), **2** (0.12 mmol) and 4 Å MS (5 mg) in EtOAc (1.0 mL).

[b] Isolated yield. MS = molecular sieves.

In conclusion, we have successfully developed a molecular sieve mediated decarboxylative Mannich reaction of -ketoacids with sulfonylimines. We have also developed a decarboxylative aldol reaction between -ketoacids and isatins. The described synthetic protocols were highly efficient, and were also broad in substrate scope, affording the desired products in high yields. Notably, the above reactions were carried out under very mild, base-free conditions, and molecular sieves were the sole activator for the reaction. We believe our methods represent highly efficient protocols for the practical synthesis of useful molecular scaffolds.

Acknowledgments

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References and notes

1. (a) Baktharaman, S.; Hili R.; Yudin, A. K. *Aldrichim. Acta* **2008**, *41*, 109; (b) Joshi, N. S.; Whitaker, L. R.; Francis, M. B. *J. Am. Chem. Soc.* **2004**, *126*, 15942.
2. For selected reviews, see: (a) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069; (b) Liu, M.; Sibi, M. P. *Tetrahedron* **2002**, *58*, 7991; (c) Arend, M.; Westermann B.; Risch, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 1044; (d) Xu, L-W.; Xia, C.-G. *Eur. J. Org. Chem.* **2005**, 633; (e) Weiner, B.; Szymański, W.; Janssen, D. B.; Minnaard A. J.; Feringa, B. L. *Chem. Soc. Rev.* **2010**, *39*, 1656; (f) Cai, X.-H.; Guo H.; Xie, B. *Eur. J. Chem.* **2012**, *3*, 258.
3. (a) Ojima, I.; Inaba, S.; Yoshida, K. *Tetrahedron Lett.* **1977**, *18*, 3643; (b) Ishitani, H.; Ueno, M.; Kobayashi, S. *J. Am. Chem. Soc.* **1997**, *119*, 7153; (c) Hagiwara, E.; Fujii, A.; Sodeoka, M. *J. Am. Chem. Soc.* **1998**, *120*, 2474; (d) Taggi, A. E.; Hafez, A. M.; Leckta, T. *Acc. Chem. Res.* **2003**, *36*, 10; (e) Akiyama, T.; Itoh, J.; Yokota, K.; Fuchibe, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1566; (f) Fujisawa, H.; Takahashi, E. and Mukaiyama, T. *Chem. Eur. J.* **2006**, *12*, 5082.
4. Pan. Y.; Tan, C.-H. *Synthesis,* **2011**, 2044.
5. (a) Lalic, G.; Aloise, A. D.; Shair, M. D. *J. Am. Chem. Soc.* **2003**, *125*, 2852; (b) Orlandi, S.; Benaglia, M.; Cozzi, F. *Tetrahedron*

Lett. **2004**, *45*, 1747; (c) Magdziak, D.; Lalic, G.; Lee, H. M.; Fortner, K. C.; Aloise, A. D.; Shair, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 7284; (d) Fortner, K. C.; Shair, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 1032; (e) Furutachi, M.; Mouri, S.; Matsunaga, S.; Shibasaki, M. *Chem. Asian J.* **2010**, *5*, 2351. For examples of other decarboxylative additions, see: (f) van Tamelen, E. E.; Baran, J. S. *J. Am. Chem. Soc.* **1956**, *78*, 2913; (g) Yin, L.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2009**, *131*, 9610; (h) Yin, L.; Kanai, M.; Shibasaki, M. *Tetrahedron* **2012**, *68*, 3497; (i) Albrecht, S.; Adam, J.-M.; Bromberger, U.; Diodone, R.; Fettes, A.; Fischer, R.; Goeckel, V.; Hildbrand, S.; Moine, G.; Weber, M. *Org. Proc. Res. Develop.* **2011**, *15*, 503.

6. (a) List, B.; Doehring, A.; Fonseca, M.; Wobser, K.; van Thienen, H.; Torres, R.; Galilea, P. *Adv. Synth. Catal.* **2005**, *347*, 1558; (b) Blanchet, J.; Baudoux, J.; Amere, M.; Lasne, M. C.; Rouden, J. *Eur. J. Org. Chem.* **2008**, 5493; (c) Blaquiere, N.; Shore, D. G.; Rousseaux, S.; Fagnou, K. *J. Org. Chem.* **2009**, *74*, 6190; (d) Ricci, A.; Pettersen, D.; Bernardi, L.; Fini, F.; Fochi, M.; Herrera, R. P.; Sgarzani, V. *Adv. Synth. Catal.* **2007**, *349*, 1037; (e) Lubkoll, J.; Wennemers, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 6841; (f) Pan, Y.; Kee, C. W.; Jiang, Z.; Ma, T.; Zhao, Y.; Yang, Y.; Xue, H.; Tan, C.-H. *Chem. Eur. J.* **2011**, *17*, 8363; (g) Bae, H. Y.; Some, S.; Lee, J. H.; Kim, J.-Y.; Song, M. J.; Lee, S. ; Zhang Y. J.; Song, C. E. *Adv. Synth. Catal.* **2011**, *353*, 3196; (h) Baudoux, J.; Lefebvre, P.; Legay, R.; Lasne M.-C.; Rouden, J. *Green Chem.* **2010**, *12*, 252; (i) Hara, N.; Nakamura, S.; Funahashi Y.; Shibata, N. *Adv. Synth. Catal.* **2011**, *353*, 2976.
7. (a) Stiles, M.; Wolf, D.; Hudson, G. V. *J. Am. Chem. Soc.* **1959**, *81*, 628; (b) Kourouli, T.; Kefalas, P.; Ragoussis, N.; Ragoussis, V. *J. Org. Chem.* **2002**, *67*, 4615; (c) Tsuda, T.; Okada, M.; Nishi, S.; Saegusa, T. *J. Org. Chem.* **1986**, *51*, 421; (d) Tsuda, T.; Tokai, M.; Ishida, T.; Saegusa, T. *J. Org. Chem.* **1986**, *51*, 5216; (e) Yang, C.-Y.; Wang, J.-Y.; Tian, S.-K. *Chem. Commun.* **2011**, *47*, 8343; (f) Evans, D. A.; Mito, S.; Seidel, D. *J. Am. Chem. Soc.* **2007**, *129*, 11583; (g) Rohr, K.; Mahrwald, R. *Org. Lett.* **2011**, *13*, 1878; (h) Yang, C.-F.; Shen, C.; Wang, J.-Y.; Tian, S.-K. *Org. Lett.* **2012,** *14,* 3092**;** (i) Zhong, F.; Yao, W.; Dou, X.; Lu, Y. *Org. Lett.* **2012**, *14*, 4018; (j) Zheng, Y.; Xiong, H.-Y.; Nie, J.; Hua, M.-Q.; Ma, J.-A. *Chem. Commun.* **2012**, *48*, 4308; (k) Jiang, C.; Zhong, F.; Lu, Y. *Beilstein J. Org. Chem.* **2012**, *8*, 1279; (l) Yuan, H.-N.; Wang, S.; Nie, J.; Meng, W.; Yao, Q.; Ma, J.-A. *Angew. Chem., Int. Ed.* **2013**, 52, 2869.
8. (a) Singh, G. S.; Desta, Z. Y. *Chem. Rev.* **2012**, *112*, 6104. (b) Guo, Q.; Bhanushali, M.; Zhao, C.-G. *Angew. Chem., Int. Ed.* **2010**, *49*, 9460. (c) Allu, S.; Molleti, N.; Panem, R.; Singh, V. K. *Tetrahedron Lett.* **2011**, *52*, 4080. (d) Chen, W.-B.; Liao, Y.-H.; Du, X.-L.; Zhang, X.-M.; Yuan, W.-C. *Green Chem.* **2009**, *11*, 1465.
9. The pH values of the molecular sieves were measured by stirring a suspension of molecular sieves (50 mg) in H_2O (1 mL) for 1 h prior to measurements with pH paper. The results are: 3 Å molecular sieves, 9<pH<10; 4 Å molecular sieves, pH~10; 5 Å molecular sieves, 7<pH<8. The basicities agreed well with their catalytic reactivities.
10. For reviews on oxindoles, see: (*a*) Marti, C.; Carreira, E. M. *Eur. J. Org. Chem.* **2003**, 2209; (*b*) Galliford, C. V.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8748; (*c*) Dounay, A. B.; Overman, L. E. *Chem. Rev.* **2003**, *103*, 2945; (*d*) Zhou, F.; Liu, Y.-L.; Zhou, J. *Adv. Synth. Catal.* **2010**, *352*, 1381; (*e*) Lin, H.; Danishefsky, S. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 36; (*f*) Ball-Jones, N. R.; Badillo, J. J.; Franz, A. K. *Org. Biomol. Chem.* **2012**, *10*, 5165. For examples reported by us, see: (*g*) Zhu, Q. Lu, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 7753; (*h*) Zhong, F.; Chen, G.-Y.; Lu, Y. *Org. Lett.* **2011**, *13*, 82; (*i*) Zhong, F.; Han, X.; Wang, Y.; Lu, Y. *Angew. Chem., Int. Ed.* **2011**, *50*, 7837; (*j*) Han, X.; Wang, S.-X.; Zhong, F.; Lu, Y. *Synthesis* **2011**, 1859; *(k)* F. Zhong, X. Han, Y. Wang, Y. Lu, *Chem. Sci.,* 2012, **3**, 1231; (*l*) Chen, G.-Y.; Zhong, F.; Lu, Y. *Org. Lett.* **2012**, *14*, 3955; (*m*) Dou, X.; Lu, Y. *Chem. Eur. J.* **2012**, *18*, 8315; (*n*) Zhong, F.; Dou, X.; Han, X.; Yao, W.; Zhu, Q.; Meng, Y.; Lu, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 943.