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DABCO-catalyzed reactions of hydrazones with activated olefins

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Abstract—This paper describes several highly efficient DABCO-catalyzed aza-Michael addition reactions of hydrazones to activated olefins. In most cases, these aza-Michael addition reactions gave the corresponding products in high yields under mild conditions. The plausible reaction mechanism is discussed on the basis of deuterium labeling experiments. Upon treatment with HCl, the corresponding cyclized products can be obtained in high yields from the Michael addition products.

1. Introduction

Great progress has been made in the execution of the Morita–Baylis–Hillman reaction,[1] since Baylis and Hillman first reported the reaction of acetaldehyde with ethyl acrylate and acrylonitrile in the presence of catalytic amounts of strong nucleophilic Lewis base such as 1,4-diazabicyclo[2,2,2]octane (DABCO) in 1972.[2] During our ongoing investigations on the aza-Baylis–Hillman reactions of *N*-tosylated imines (ArCH=NTs) with activated olefins, we found that either 'normal' or 'abnormal' reaction products were formed depending on the employed nucleophilic Lewis base.[3] In this paper, we wish to report DABCO-catalyzed reactions of hydrazones **1** (R–CH=N–NHTs, 4-methylbenzenesulfonic acid *N*-methylidene-hydrazide) and **2** [R–CH=N–NHC(O)Ph, benzoic acid *N*-methylidene-hydrazide] with activated olefins such as methyl vinyl ketone (MVK), methyl acrylate, acrylonitrile and phenyl vinyl ketone (PVK) to give the Michael addition products in good yields. In the present reaction, DABCO served as a Brønsted base or a proton-sponge rather than a nucleophilic Lewis base in Baylis–Hillman reaction.

2. Results and discussion

As initial examination, a variety of organic bases have been examined as catalysts in the reaction of hydrazone **1a** with MVK and the results are summarized in Table 1. As can be seen from Table 1, the reaction proceeded smoothly to give the Michael addition product **3a** in high yields in the presence of nitrogen containing organic bases such as DABCO, 4-(*N*,*N*-dimethylamino)pyridine (DMAP), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or Et_3N (10 mol%) for 10 h (Table 1, entries 2, 8, 9 and 10). The solvent effects have been examined using DABCO as a promoter. We found that tetrahydrofuran (THF) is the solvent of choice. In the presence of 1.0 mol% of DABCO in THF, the reaction also proceeded efficiently to give the addition product **3a** in >99% yield after 24 h (Table 1, entry 6). DMAP (1.0 mol%) and DBU (1.0 mol%) are not as effective as DABCO (1.0 mol%) under the identical conditions (Table 1, entries 8 and 9). Triphenylphosphine or tributylphosphine did not catalyze this reaction (Table 1, entry 7).[4] It should be noted that using inorganic bases such as K_2CO_3, KOAc and KOBu^t in this reaction under the same conditions, the reaction took place as well, but in low yields even after a prolonged reaction time, which is presumably due to their low solubilities in THF.

Under the optimized reaction conditions, we next examined the reactions of a variety of hydrazones **1** with MVK. The results are summarized in Table 2. The corresponding adducts **3** were obtained in good to high yields in the presence of DABCO (1.0 mol%) (Table 2, entries 1–6). For aromatic substrates **1b–f**, the corresponding adducts **3b–f** were obtained in high yields (Table 2, entries 1–5). When the benzene ring bears a strongly electron-withdrawing group such as *p*-nitrobenzenealdehyde, the reaction proceeds quickly to give the adduct within shorter reaction time (Table 1, entry 5). For aliphatic substrate **1g**, the corresponding adduct **3g** was obtained in good yield (Table 2, entry 6).

Under the same conditions, we further examined the

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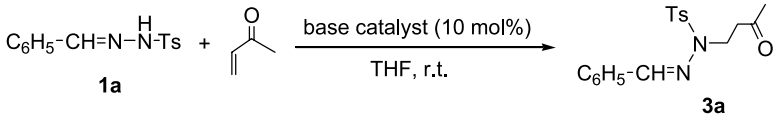
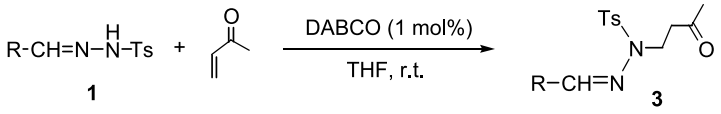
Table 1. Reactions of hydrazone **1a** (1.0 equiv) with MVK (1.2 equiv) in the presence of organic base catalyst (10 mol%) at room temperature



Entry	Base catalyst	Solvent	Time (h)	Yield (%)[a] **3a**
1	—	THF	10	0
2	DABCO	THF	10	>99
3	DABCO	CH_2Cl_2	10	91
4	DABCO	MeCN	10	94
5	DABCO	DMF	10	83
6	DABCO[b]	THF	24	>99
7	PPh_3 or PBu_3	THF	10	0
8	DMAP[c]	THF	10	>99
9	DBU[d]	THF	10	>99
10	Et_3N	THF	10	96

[a] Isolated yields.
[b] DABCO (1.0 mol%) was used.
[c] Using 1.0 mol% of DMAP, **3a** was obtained in 82% yield.
[d] Using 1.0 mol% of DBU, **3a** was obtained in 80% yield.

Table 2. Reactions of hydrazones **1** (1.0 equiv) with MVK (1.2 equiv) in the presence of DABCO (1.0 mol%) at room temperature



Entry	R	Time (h)	Yield (%)[a] **3**
1	*p*-MeC_6H_4 **1b**	36	**3b**, >99
2	*p*-FC_6H_4 **1c**	24	**3c**, 89
3	*p*-ClC_6H_4 **1d**	24	**3d**, >99
4	*p*-BrC_6H_4 **1e**	24	**3e**, >99
5	*p*-$NO_2C_6H_4$ **1f**	12	**3f**, 84
6	$(CH_3)_2CH$ **1g**	24	**3g**, 70

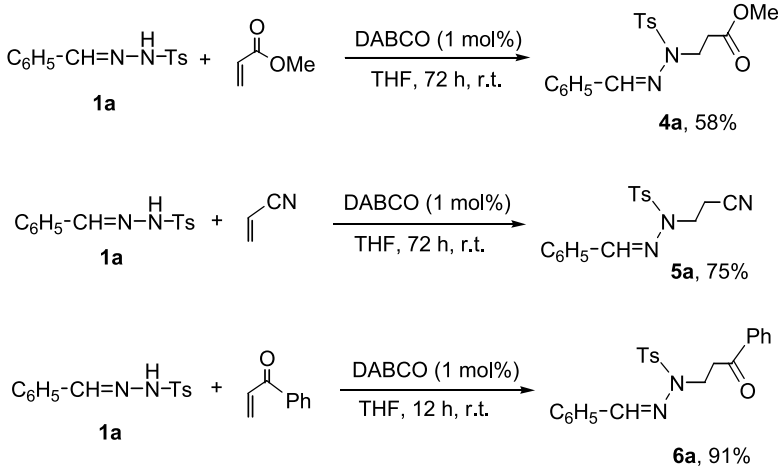
[a] Isolated yields.

reaction of **1a** with other activated olefins such as methyl acrylate, acrylonitrile, and phenyl vinyl ketone (PVK) and found that the corresponding adducts **4a**, **5a** and **6a** were also obtained in good to high yields (Scheme 1).

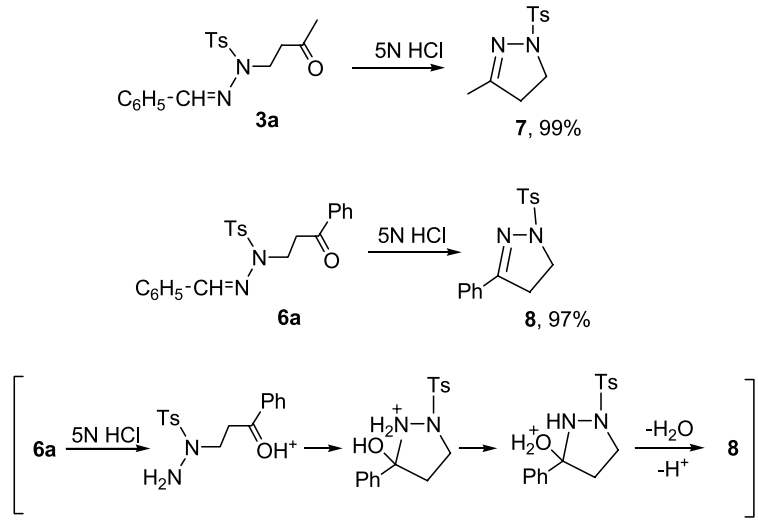
It should be emphasized here that treatment of **3a** or **6a** with 5 N HCl for 2 h gave the cyclized product **7** or **8** in high yield at room temperature (Scheme 2).

By a sequential treatment of **1** with MVK in the presence of DABCO (1.0 mmol) in THF for 24–36 h and then with 5 N HCl for 2 h, the cyclized product **7** was also obtained in good yields. The results are summarized in Table 3.

We next examined the reactions of hydrazone **2a** having a *N*-benzoyl protecting group with MVK in a variety of solvents in the presence of various organic base catalysts to

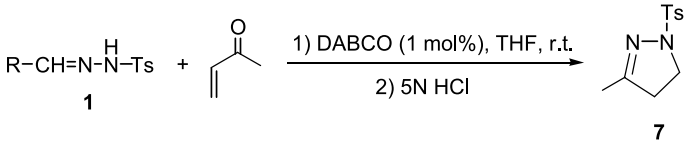


Scheme 1. Reactions of hydrazone **1a** (1.0 equiv) with other activated olefins (1.2 equiv) in the presence of DABCO (1 mol%) in THF.



Scheme 2. Cyclization of **3a** or **6a** with 5 N HCl.

Table 3. Reactions of hydrazones **1** (1.0 equiv) with MVK (1.2 equiv) in the presence of DABCO (1 mol%) and then with 5 N HCl



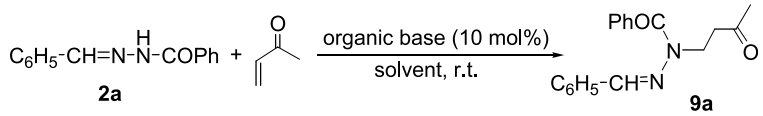
Entry	R	Time (h)	Yield (%)[a] of **7** (two steps)
1	C_6H_5 **1a**	24, 2	>99
2	*p*-MeC_6H_4 **1b**	36, 2	89
3	*p*-FC_6H_4 **1c**	24, 2	78
4	*p*-ClC_6H_4 **1d**	24, 2	>99
5	*p*-BrC_6H_4 **1e**	24, 2	95
6	$(CH_3)_2CH$ **1g**	24, 2	92

[a] Isolated yields.

optimize the reaction conditions. The result are shown in Table 4 (entries 1–9). We were pleased to find that using hydrazone **2a** as a substrate and DABCO (10 mol%) as the base catalyst in *N*,*N*-dimethylformamide (DMF), the Michael addition product **9a** can be obtained in 91% yield after a prolonged reaction time (Table 4, entry 6). The results of hydrazones **2b** and **2c** combined with **2a** under the optimized reaction conditions are summarized in Table 5. For aliphatic hydrazone **2c**, the corresponding Michael addition product **9c** was formed in 56% yield (Table 5, entry 3).

Accordingly, treatment of **2a** with MVK in the presence of DABCO in DMF for 96 h and then with 5 N HCl for 12 h, the corresponding cyclized product **10** was obtained in 98% yield (Scheme 3).

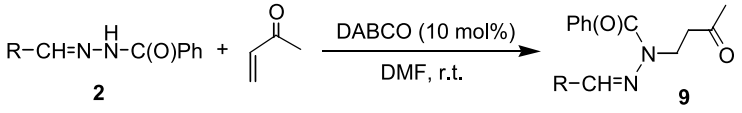
Table 4. Reactions of hydrazone **2a** (1.0 equiv) with MVK (1.2 equiv) in the presence of nitrogen containing organic base (10 mol%) at room temperature



Entry	Organic base	Solvent	Time (h)	Yield (%)[a] of **9a**
1	DABCO	THF	96	0
2	DABCO	DME	96	0
3	DABCO	EtOH[b]	96	0
4	DABCO	CH_3CN	96	Trace
5	DABCO	CH_3COCH_3	96	Trace
6	DABCO	DMF	96	91
7	DMAP	DMF	96	71
8	DBU	DMF	96	68
9	Et_3N	DMF	96	Trace

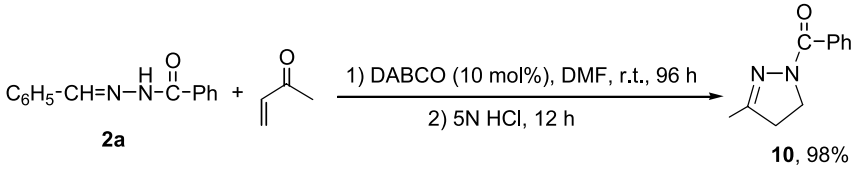
[a] Isolated yields.
[b] The reaction was carried under reflux.

Table 5. Reactions of hydrazones **2** (1.0 equiv) with MVK (1.2 equiv) in the presence of DABCO (10 mol%) at room temperature



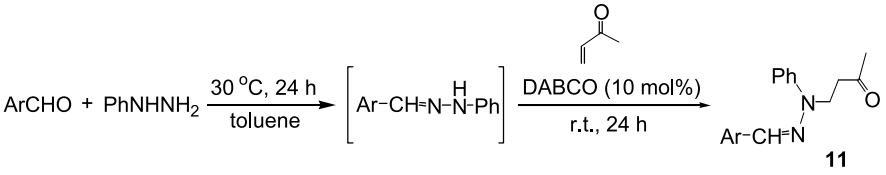
Entry	R	Time (h)	Yield (%)[a] of **9**
1	C_6H_5 **2a**	96	**9a**, 91
2	*p*-ClC_6H_4 **2b**	72	**9b**, 90
3	$(CH_3)_2CH$ **2c**	96	**9c**, 56

[a] Isolated yields.



Scheme 3. Reaction of hydrazone **2a** (1.0 equiv) with MVK (1.2 equiv) in the presence of DABCO (10 mol%) at room temperature and then with 5 N HCl.

Table 6. Reactions of aryladehyde (1.0 equiv) with phenyl hydrazine and MVK (1.2 equiv) in the presence of DABCO (10 mol%)



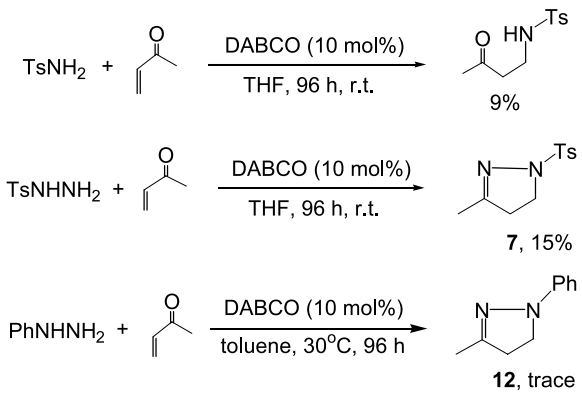
Entry	Ar	Yield (%)[a] of **11** (two steps)
1	C_6H_5	**11a**, 34
2	*p*-$CH_3C_6H_4$	**11b**, 20
3	*p*-ClC_6H_4	**11c**, 39

[a] Isolated yields.

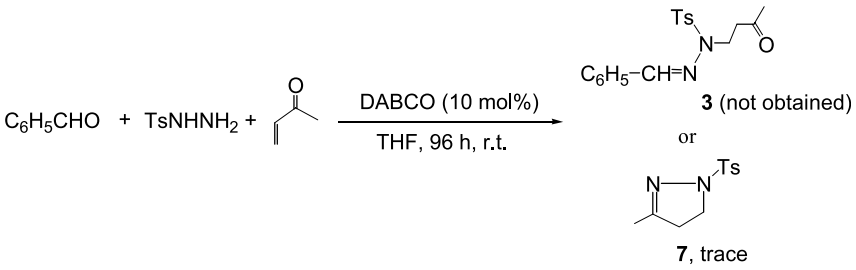
Scheme 4. Cyclization of **11a** with 5 N HCl.

Next, we examined the reactions of *N*-arylmethylidene-*N′*-phenylhydrazine (Ar–CH=N–NH–Ph)[5] prepared in situ with MVK under the similar conditions. The results are summarized in Table 6. The Michael addition adducts **11** could be obtained, but in lower yields. Cyclization of **11a** could also take place upon treating with 5 N HCl to give the cyclized product **12** in 31% yield (Scheme 4).

In order to clarify the scope and limitation of this interesting DABCO-catalyzed aza-Michael addition reaction, the reactions of $TsNH_2$,[6] $TsNHNH_2$, or $PhNHNH_2$[7] with MVK were carried out under the similar conditions in the presence of DABCO (10 mol%) (Scheme 5). However, we found that all these reactions were sluggish and the corresponding adducts were obtained in trace to only low yields even after a prolonged reaction time. Attempts to perform the one-pot reaction of aldehydes, tosylhydrazine, and MVK (Scheme 6) produced trace of cyclized product **7**, and no aza-Michael addition product **3** were obtained. These results suggest that the acidity of N–H proton in hydrazones **1** and **2** plays a significant role in this DABCO-catalyzed reaction. The *N*-tosylated or *N*-acylated hydrazones **1** and **2** can react with MVK and other activated olefins in the presence of DABCO to give the corresponding Michael addition products in good yields. This synthetic method can



Scheme 5. Reactions of $TsNH_2$, $TsNHNH_2$ $PhNHNH_2$ (1.0 equiv) with MVK (1.2 equiv) in the presence of DABCO (10 mol%).



Scheme 6. The one-pot reaction of PhCHO (1.0 equiv), $TsNHNH_2$ (1.0 equiv) with MVK (1.2 equiv) in the presence of DABCO (10 mol%).

produce pyrazoline derivatives in high yields comparing to previously reported methods.[8]

The mechanism of this interesting organic nitrogen base promoted reaction has not been unequivocally established, but on the basis of previous investigations[1,9,10] and our deuterium labeling experiments (Figs. 1–8, Schemes 7 and 8), one plausible explanation is proposed in Scheme 9.

We first carried out the following deuterium labeling experiment to clarify this mechanism. In the presence of DABCO (0.1 mmol), we found that the H/D exchange of 3-pentanone (0.1 mmol) took place rapidly in D_2O (0.5 mL)

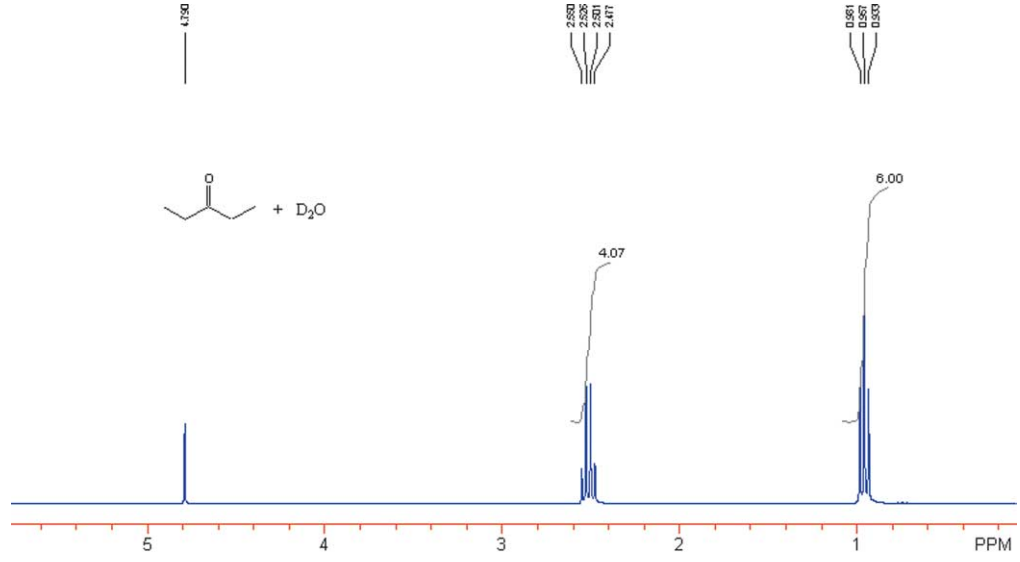


Figure 1. The ^1H NMR spectrum of 3-pentanone in D_2O.

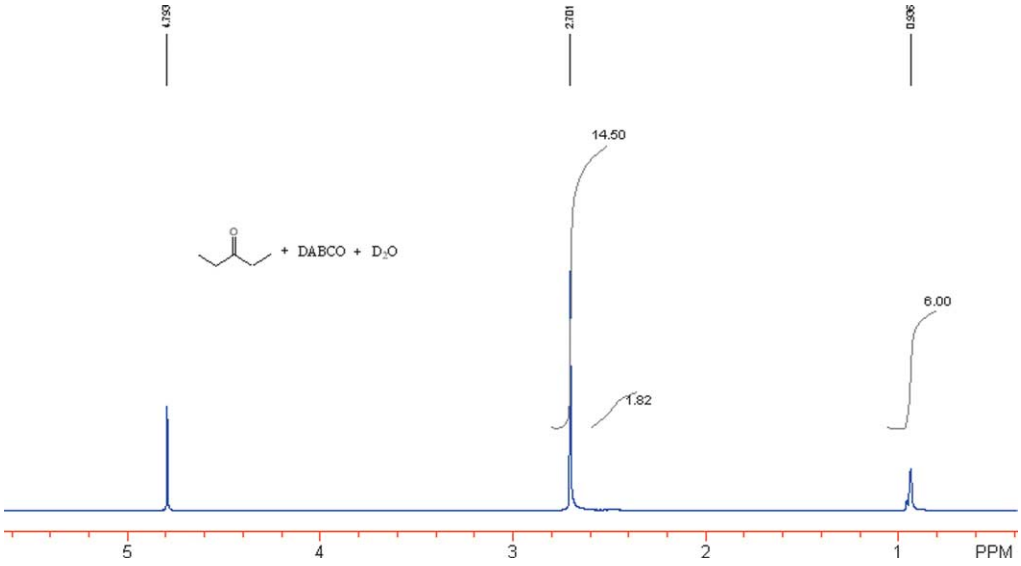


Figure 2. The ^1H NMR spectrum of 3-pentanone (0.1 mmol) and DABCO (0.1 mmol) in D_2O.

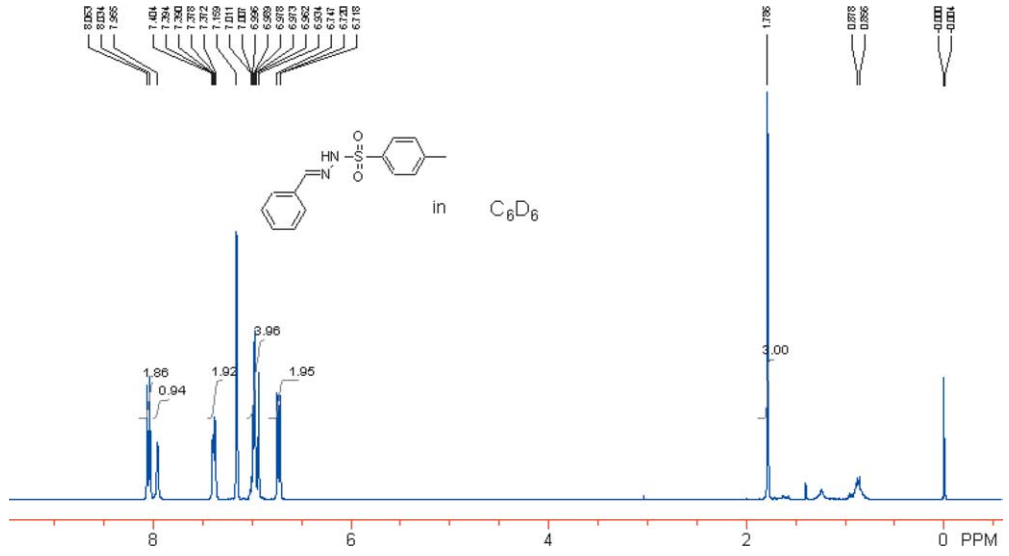


Figure 3. The ^{1}H NMR spectrum of hydrazone **1a** in C_6D_6.

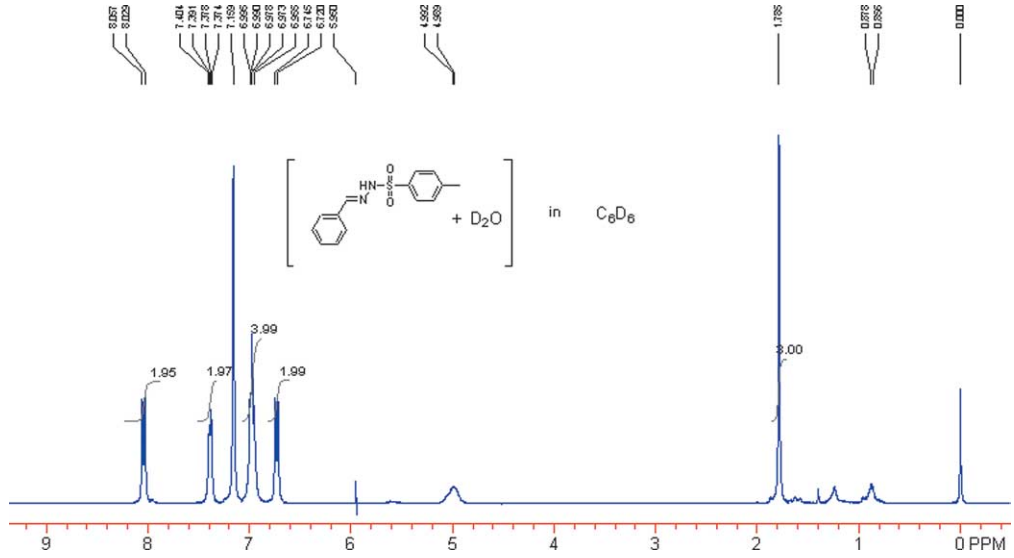


Figure 4. The ^{1}H NMR spectrum of hydrazone **1a** with D_2O in C_6D_6.

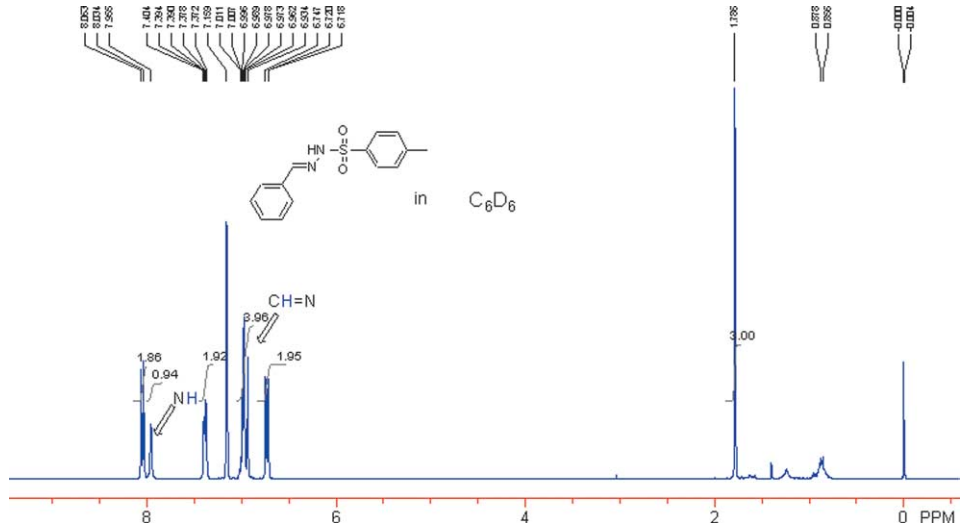


Figure 5. The ^{1}H NMR spectrum of hydrazone **1a** in C_6D_6.

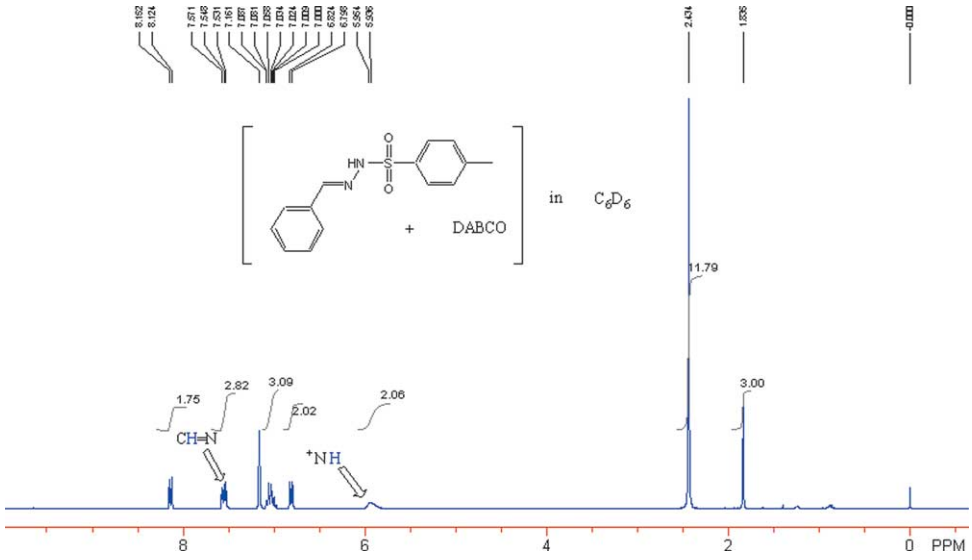


Figure 6. The ^{1}H NMR spectrum of hydrazone **1a** (0.05 mmol) with DABCO (0.05 mmol) in C_6D_6.

(Scheme 7), which could be clearly observed from ^{1}H NMR spectra shown in Figures 1 and 2. The methylene protons at 2.53 ppm (q) in Figure 1 completely disappeared in Figure 2 and the signal at δ 2.70 ppm (s) in Figure 2 was DABCO.

The deuterium labeling experiment of hydrazone **1a** (0.05 mmol) with DABCO (0.05 mmol) in C_6D_6 (0.5 mL) was also examined. Their ^{1}H NMR spectra were shown in Figures 3–6. From Figures 3, 4 and 5, we can assign the exact chemical shift of NH and CH in the ^{1}H NMR spectrum of **1a** because the signal at δ 7.97 ppm completely disappeared with the addition of deuterium oxide (D_2O) in C_6D_6. Their chemical shifts have been clearly shown in Figure 5 (δ_{NH} at 7.97 ppm and δ_{CH} at 6.93 ppm).

Next, we examined the ^{1}H NMR spectrum of **1a** in C_6D_6 with the addition of DABCO. This spectroscopic chart is shown in Figure 6. From Figure 6, we observed that the N–H proton of **1a** disappeared and a new signal appeared at 5.95 ppm which can be supposed to be $[DABCOH]^+$ (the signal at δ 2.43 ppm (s) is DABCO). Thus, we believe that DABCO functions as a base to abstract the N–H proton in **1a** directly.

Moreover, the following deuterium labeling experiment was also performed (Scheme 8). The deuterium labeled nucleophilic reagent **1a**-*d* was prepared with DCl in D_2O according to Scheme 8, which was used in the DABCO-catalyzed aza-Michael addition reaction with MVK under the similar conditions as those described above. The deuterium incorporated Michael addition product **3a**-*d* was obtained in 89% yield (D content 94%). The ^{1}H and ^{13}C NMR spectra of **3a**-*d* are given in Figures 7 and 8.

Overall, on the basis of the above spectroscopic investigations, we believe that DABCO acts as a Brønsted base

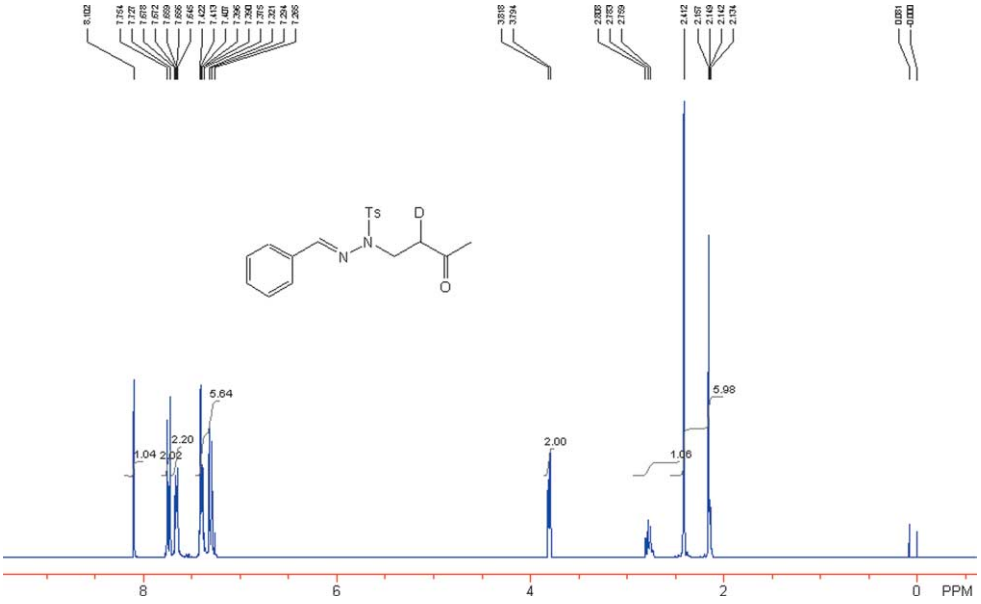


Figure 7. The ^{1}H NMR spectrum of **3a**-*d* in $CDCl_3$.

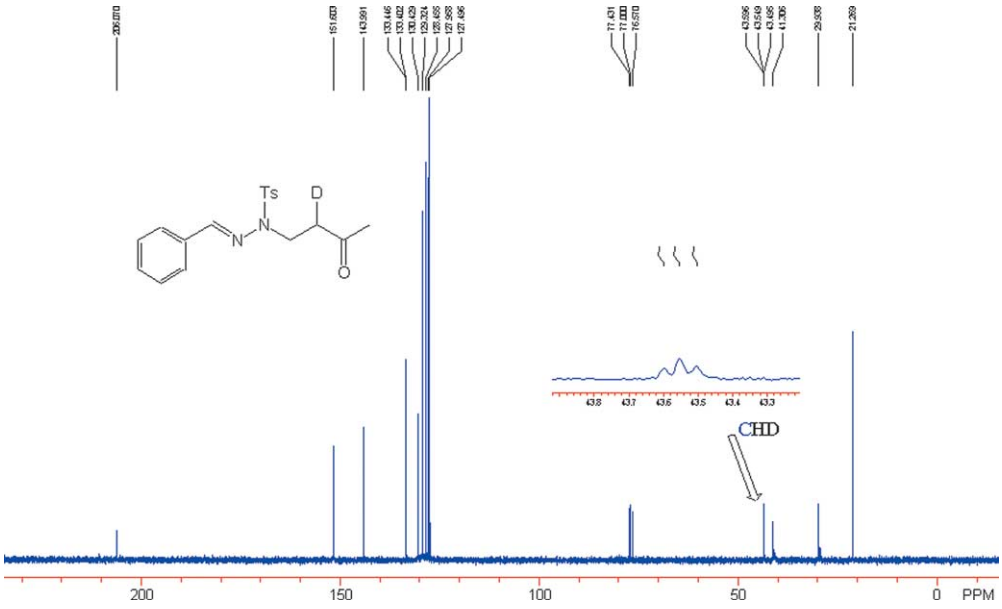
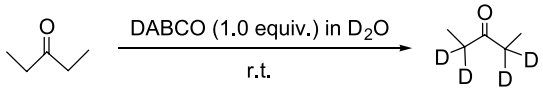
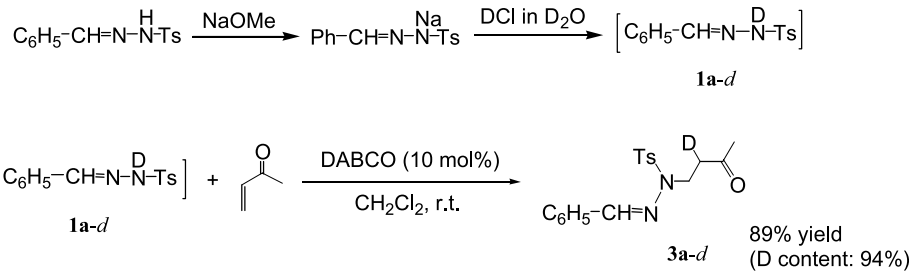


Figure 8. The ^{13}C NMR spectrum of **3a**-*d* in $CDCl_3$.



Scheme 7. DABCO-catalyzed H/D exchange of 3-pentanone in D_2O.

catalytic cycle (Scheme 9). The N–H proton of *N*-sulfonated group has higher acidity because SO_2R is a strongly electron-withdrawing group. Therefore, its proton can be easily removed by DABCO. This is why the reaction rate of **1** is remarkably higher than that of **2** and only 1.0 mol% of DABCO is enough to accomplish this catalytic reaction under otherwise identical conditions.

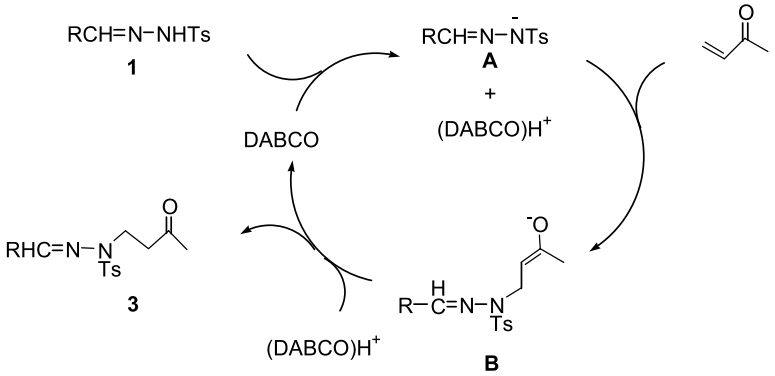


Scheme 8. The reaction of deuterium labeled **1a** (1.0 equiv) with MVK (1.2 equiv) in the presence of DABCO (10 mol%).

which abstracts a proton from hydrazone **1** or **2** to produce nucleophilic intermediate **A**. The subsequent conjugate addition of **A** to MVK generates enolate **B**. Reprotonation of enolate **B** affords **3** and regenerates DABCO to complete the

3. Conclusion

We disclosed an interesting organic nitrogen base DABCO promoted aza-Michael addition reaction of **1** or **2** with



Scheme 9. Proposed reaction mechanism of DABCO catalyzed reaction of hydrazone **1** or **2** with activated olefins.

activated olefins. The transformation is in contrast to the recently reported DABCO catalyzed aza-Baylis–Hillman reaction[3] and the reaction mechanism is different from phosphine Lewis base catalyzed Michael addition of alcohols to activated olefins.[11] Additionally, this finding can open new ways for the design of new reactions and synthesis of novel compounds by the organocatalysts in the future. The scope and limitations of this reaction have been disclosed along with the detailed investigation on the plausible reaction mechanism. Efforts are underway to elucidate the mechanistic details of this reaction and to extend the scope of those reactions in other C–C bond forming transformations thereof.

4. Experimental

4.1. General remarks

MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 200–300 mesh silica gel at medium pressure. The starting materials hydrazones **1** and **2** were prepared according to the literature.

4.2. Typical reaction procedure for the nitrogen Lewis base-catalyzed reaction of 4-methylbenzenesulfonic acid *N*-methylidene-hydrazide 1a with methyl vinyl ketone (MVK)

To a Schlenk tube with **1a** (274 mg, 1.0 mmol) and DABCO (1.0 mg, 0.01 mmol) in THF (1.0 mL) was added methyl vinyl ketone (MVK) (70 mg, 83 μL, 1.0 mmol) under an argon atmosphere and the reaction mixture was stirred for 24 h at room temperature (20 °C). The reaction mixture was diluted with dichloromethane (20 mL). The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: EtOAc/petroleum=1/2) to give **3a** (341 mg, 99%) as a colorless solid.

4.2.1. 4-Methylbenzenesulfonic acid *N′*-benzylidene-*N*-(3-oxobutyl)hydrazide 3a. Colorless solid; mp 55–58 °C (recrystallized from dichloromethane and petroleum ether); IR (CH_2Cl_2) ν 3296, 3062, 1716 (C=O), 1676, 1358, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.16 (3H, s, CH_3), 2.41 (3H, s, CH_3), 2.79 (2H, t, J=7.2 Hz, CH_2), 3.82 (2H, t, J=7.2 Hz, CH_2), 7.31 (2H, d, J=8.4 Hz, ArH), 7.39–7.41 (3H, m, ArH), 7.64–7.68 (2H, m, ArH), 7.74 (2H, d, J=8.4 Hz, ArH), 8.10 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.5, 30.2, 41.6, 43.9, 127.7, 128.2, 128.6, 129.3, 129.5, 130.6, 133.5, 144.2, 152.5, 206.3; MS (EI) *m/z* 344 (M^+, 6.54), 189 (M^+-155, 47.72), 147 (M^+-197, 52.01), 131 (M^+-213, 73.05), 119 (M^+-225, 100); HRMS (MALDI) calcd for $C_{18}H_{20}N_2O_3SNa^{+1}$ (M^+ + Na): 367.1087. Found: 367.1074.

4.2.2. 4-Methylbenzenesulfonic acid *N′*-(4-methylbenzylidene)-*N*-(3-oxobutyl) hydrazide 3b. Colorless solid; mp 102–105 °C (recrystallized from dichloromethane and petroleum ether); IR (CH_2Cl_2) ν 3463, 3055, 1690, (C=O), 1357, 1170, 896 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.16 (3H, s, CH_3), 2.39 (3H, s, CH_3), 2.42 (3H, s, CH_3), 2.76 (2H, t, J=7.2 Hz, CH_2), 3.74 (2H, t, J=7.2 Hz, CH_2), 7.21 (2H, d, J=7.8 Hz, ArH), 7.31 (2H, d, J=7.8 Hz, ArH), 7.56 (2H, d, J=7.8 Hz, ArH), 7.71 (2H, d, J=7.8 Hz, ArH), 8.16 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.5, 21.5, 30.2, 41.8, 44.5, 127.9, 128.3, 129.4, 129.5, 130.7, 133.3, 141.3, 144.1, 154.9, 206.3; MS (EI) *m/z* 358 (M^+, 5.19), 203 (M^+-155, 22.71), 161 (M^+-197, 20.25), 145 (M^+-213, 77.31), 133 (M^+-225, 100); HRMS (MALDI) calcd for $C_{19}H_{22}N_2O_3SNa^{+1}$ (M^+ + Na): 381.1243. Found: 381.1251.

4.2.3. 4-Methylbenzenesulfonic acid *N′*-(4-fluorobenzylidene)-*N*-(3-oxobutyl) hydrazide 3c. Colorless oil; IR (CH_2Cl_2) ν 3512, 3251, 1714 (C=O), 1644, 1357, 1233, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.17 (3H, s, CH_3), 2.42 (3H, s, CH_3), 2.78 (2H, t, J=7.2 Hz, CH_2), 3.78 (2H, t, J=7.2 Hz, CH_2), 7.06–7.12 (2H, m, ArH), 7.31 (2H, d, J=8.1 Hz, ArH), 7.63–7.68 (2H, m, ArH), 7.72 (2H, d, J=8.1 Hz, ArH), 8.10 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.3, 30.0, 41.4, 43.8, 115.6 (d, J=21.8 Hz), 128.0, 129.4, 129.5 (d, J=8.0 Hz), 129.7 (d, J=2.9 Hz), 133.3, 144.1, 150.8, 163.9 (d, J=250.1 Hz), 206.1; MS (EI) *m/z* 362 (M^+, 7.08), 207 (M^+-155, 57.49), 165 (M^+-197, 65.52), 149 (M^+-213, 30.54), 137 (M^+-225, 100), 108 (M^+-254, 57.31); HRMS (MALDI) calcd for $C_{18}H_{19}N_2O_3FSNa^{+1}$ (M^++ Na): 385.0993. Found: 385.1012.

4.2.4. 4-Methylbenzenesulfonic acid *N′*-(4-chlorobenzylidene)-*N*-(3-oxobutyl) hydrazide 3d. Colorless solid; mp 78–80 °C (recrystallized from dichloromethane and petroleum ether); IR (CH_2Cl_2) ν 2922, 1701 (C=O), 1677, 1597, 1492, 1355, 1167, 1093 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.17 (3H, s, CH_3), 2.41 (3H, s, CH_3), 2.80 (2H, t, J=6.9 Hz, CH_2), 3.84 (2H, t, J=6.9 Hz, CH_2), 7.31 (2H, d, J=8.1 Hz, ArH), 7.36 (2H, d, J=8.1 Hz, ArH), 7.59 (2H, d, J=8.1 Hz, ArH), 7.73 (2H, d, J=8.1 Hz, ArH), 8.00 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.4, 30.1, 41.5, 43.4, 128.0, 128.7, 128.8, 129.5, 132.1, 133.5, 136.2, 144.2, 148.9, 206.1; MS (EI) *m/z* 378 (M^+, 4.55), 223 (M^+-155, 27.43), 181 (M^+-197, 33.44), 165 (M^+-213, 30.54), 153 (M^+-225, 52.04), 43 (M^+-335, 100); HRMS (MALDI) calcd for $C_{18}H_{20}N_2O_3SCl^{+1}$ (M^++H): 379.0878. Found: 379.0887.

4.2.5. 4-Methylbenzenesulfonic acid *N′*-(4-bromobenzylidene)-*N*-(3-oxobutyl) hydrazide 3e. Colorless solid; mp 105–108 °C (recrystallized from dichloromethane and petroleum ether); IR (CH_2Cl_2) ν 3052, 2927, 1699 (C=O), 1674, 1356, 1093, 818 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.17 (3H, s, CH_3), 2.41 (3H, s, CH_3), 2.80 (2H, t, J=7.2 Hz, CH_2), 3.84 (2H, t, J=7.2 Hz, CH_2), 7.31 (2H, d, J=8.1 Hz, ArH), 7.51 (4H, s, ArH), 7.73 (2H, d, J=8.1 Hz, ArH), 7.97 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz,

TMS) δ 21.4, 30.1, 41.3, 43.2, 124.5, 127.9, 128.8, 129.4, 131.7, 132.5, 133.5, 144.2, 148.2, 206.1; MS (EI) *m/z* 424 (M^++2, 9.57), 422 (M^+, 9.34), 269 (M^+−153, 46.51), 267 (M^+−155, 48.85), 199 (M^+−123, 77.35), 197 (M^+−125, 81.39), 89 (M^+−333, 100); HRMS (MALDI) calcd for $C_{18}H_{19}N_2O_3SBr^{+1}$: 422.0294. Found: 422.0290.

4.2.6. 4-Methylbenzenesulfonic acid *N′*-(4-nitrobenzylidene)-*N*-(3-oxobutyl) hydrazide 3f. Colorless solid; mp 155–157 °C (recrystallized from dichloromethane and petroleum ether); IR (CH_2Cl_2) *ν* 3449, 1713 (C=O), 1639, 1343, 1166, 851 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.21 (3H, s, CH_3), 2.43 (3H, s, CH_3), 2.90 (2H, t, *J*=6.9 Hz, CH_2), 4.00 (2H, t, *J*=6.9 Hz, CH_2), 7.34 (2H, d, *J*=7.8 Hz, ArH), 7.76–7.86 (5H, m, ArH, CH), 8.24 (2H, d, *J*=9.0 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.5, 30.3, 41.3, 42.2, 123.9, 127.7, 128.0, 129.7, 134.0, 139.9, 141.4, 144.6, 148.2, 206.1; MS (EI) *m/z* 389 (M^+, 4.35), 234 (M^+−155, 100), 192 (M^+−197, 86.00), 91 (M^+−298, 43.70), 43 (M^+−346, 84.65); HRMS (MALDI) calcd for $C_{18}H_{19}N_3O_5SNa^{+1}$: 412.0938. Found: 412.0939.

4.2.7. 4-Methylbenzenesulfonic acid *N′*-isobutylidene-*N*-(3-oxobutyl)hydrazide 3g. Colorless oil; IR (CH_2Cl_2) *ν* 3426, 2971, 2877, 1717 (C=O), 1597, 1434, 1352, 816 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.09 (3H, s, CH_3), 1.11 (3H, s, CH_3), 2.14 (3H, s, CH_3), 2.41 (3H, s, CH_3), 2.53–2.59 (1H, m, CH), 2.63 (2H, t, *J*=7.2 Hz, CH_2), 3.51 (2H, t, *J*=7.2 Hz, CH_2), 7.29–7.31 (2H, m, ArH), 7.61–7.66 (3H, m, ArH, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.1, 21.4, 29.9, 31.9, 41.7, 44.9, 128.3, 129.2, 132.7, 144.0, 168.2, 206.2; MS (EI) *m/z* 310 (M^+, 0.25), 155 (M^+−155, 49.89), 113 (M^+−197, 23.72), 91 (M^+−219, 36.09), 43 (M^+−267, 100); HRMS (MALDI) calcd for $C_{15}H_{23}N_2O_3S^{+1}$ (M^++H): 311.1424. Found: 311.1432.

4.2.8. 3-(*N*-(4-Methylbenzenesulfonyl)-*N′*-benzylidene-hydrazino)-propionic acid methyl ester 4a. Colorless oil; IR (CH_2Cl_2) *ν* 2953, 1743 (C=O), 1598, 1439, 1352, 1162, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.42 (3H, s, CH_3), 2.63 (2H, t, *J*=7.2 Hz, CH_2), 3.67 (3H, s, OCH_3), 3.83 (2H, t, *J*=7.2 Hz, CH_2), 7.31 (2H, d, *J*=8.4 Hz, ArH), 7.39–7.43 (3H, m, ArH), 7.66–7.69 (2H, m, ArH), 7.74 (2H, d, *J*=8.4 Hz, ArH), 8.19 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.1, 32.3, 44.5, 51.4, 127.4, 127.9, 128.3, 129.2, 130.4, 133.2, 133.3, 143.9, 152.6, 170.9; MS (EI) *m/z* 360 (M^+, 9.73), 205 (M^+−155, 40.85), 173 (M^+−187, 57.13), 131 (M^+−229, 100); 90 (M^+−270, 90.78); HRMS (MALDI) calcd for $C_{18}H_{21}N_2O_4S^{+1}$ (M^++H): 361.1217. Found: 361.1239.

4.2.9. 4-Methylbenzenesulfonic acid *N′*-benzylidene-*N*-(2-cyano-ethyl)-hydrazide 5a. A yellow oil; IR (CH_2Cl_2) *ν* 3060, 2923, 2850, 1598, 1356, 1266, 1168 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.38 (3H, s, CH_3), 2.57 (2H, t, *J*=6.9 Hz, CH_2), 3.61 (2H, t, *J*=6.9 Hz, CH_2), 7.27 (2H, d, *J*=8.4 Hz, ArH), 7.37–7.41 (3H, m, ArH), 7.59 (2H, d, *J*=8.4 Hz, ArH), 7.63–7.65 (2H, m, ArH), 8.46 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 17.5, 21.6, 46.5, 117.1, 128.4, 128.5, 128.9, 129.8, 131.8, 132.7, 132.9, 144.8, 161.5; MS (EI) *m/z* 327 (M^+, 0.92), 222 (M^+−105, 2.25), 172 (M^+−155, 4.47), 119 (M^+−208, 26.08), 84 (M^+−243, 100); HRMS (MALDI) calcd for $C_{17}H_{18}N_3O_2S^{+1}$ (M^++H): 328.1114. Found: 328.1121.

4.2.10. 4-Methylbenzenesulfonic acid *N′*-benzylidene-*N*-(3-oxo-3-phenyl-propyl)hydrazide 6a. A yellow oil; IR (CH_2Cl_2) *ν* 3059, 1691 (C=O), 1597, 1449, 1356, 1266, 1169 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.43 (3H, s, CH_3), 3.35 (2H, t, *J*=7.2 Hz, CH_2), 4.06 (2H, t, *J*=7.2 Hz, CH_2), 7.33 (2H, d, *J*=7.8 Hz, ArH), 7.40–7.49 (5H, m, ArH), 7.56–7.58 (1H, m, ArH), 7.66–7.69 (2H, m, ArH), 7.76 (2H, d, *J*=8.4 Hz, ArH), 7.92–7.95 (2H, m, ArH), 8.12 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.3, 36.7, 44.1, 127.5, 127.8, 128.0, 128.4, 128.5, 129.4, 130.4, 133.3, 133.5, 133.7, 136.0, 144.0, 150.8, 197.4; MS (EI) *m/z* 406 (M^+, 0.09), 300 (M^+−106, 23.02), 159 (M^+−247, 36.20), 145 (M^+−261, 89.02), 105 (M^+−301, 100), 77 (M^+−329, 96.97); HRMS (MALDI) calcd for $C_{23}H_{23}N_2O_3S^{+1}$ (M^++H): 407.1424. Found: 407.1408.

4.3. Typical reaction procedure for the one-pot reaction of 4-methylbenzenesulfonic acid *N*-methylidene-hydrazide 1a with methyl vinyl ketone (MVK)

To a Schlenk tube with **1a** (274 mg, 1.0 mmol) and DABCO (1.0 mg, 0.01 mmol) in THF (1.0 mL) was added methyl vinyl ketone (MVK) (70 mg, 83 μL, 1.0 mmol) under an argon atmosphere and the reaction mixture was stirred for 24 h at room temperature (20 °C). Then 5 N HCl (2 mL) was added and the reaction mixture was stirred for another 2 h at room temperature. Then the reaction mixture was extracted with dichloromethane (2×20 mL). The organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the residue purified by silica gel column chromatography (eluent: EtOAc/petroleum=1/1) to give **7** (236 mg, 99%) as a white solid.

4.3.1. 3-Methyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1*H*-pyrazole 7. Mp >300 °C (recrystallized from dichloromethane and petroleum ether); IR (CH_2Cl_2) *ν* 3434, 1712 (C=O), 1633, 1348, 988 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.96 (3H, s, CH_3), 2.43 (3H, s, CH_3), 2.65 (2H, t, *J*=9.6 Hz, CH_2), 3.50 (2H, t, *J*=9.6 Hz, CH_2), 7.32 (2H, d, *J*=8.4 Hz, ArH), 7.76 (2H, d, *J*=8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.9, 21.5, 36. 7, 47.9, 128.7, 129.3, 130.8, 144.1, 160.0; MS (EI) *m/z* 238 (M^+, 47.54), 155 (M^+−83, 30.26), 139 (M^+−99, 23.99), 91 (M^+−147, 100), 83 (M^+−155, 42.70). Anal. Calcd for $C_{11}H_{14}N_2O_2S$ requires C, 55.44; H, 5.92; N, 11.76%. Found: C, 55.27; H, 5.87; N, 11.63%.

4.3.2. 3-Phenyl-1-(toluene-4-sulfonyl)-4,5-dihydro-1*H*-pyrazole 8. A yellow oil; IR (CH_2Cl_2) *ν* 3055, 2986, 1356, 1266, 1171, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.60 (3H, s, CH_3), 3.28 (2H, t, *J*=9.6 Hz, CH_2), 3.88 (2H, t, *J*=9.6 Hz, CH_2), 7.48 (2H, d, *J*=7.2 Hz, ArH), 7.58–7.61 (3H, m, ArH), 7.87–7.90 (2H, m, ArH), 8.03 (2H, d, *J*=7.2 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.5, 32.7, 48.6, 126.8, 128.5, 128.7, 129.4, 130.4, 130.7, 130.9, 144.3, 158.3; MS (EI) *m/z* 300 (M^+, 24.11), 219 (M^+−81, 14.13), 197 (M^+−103, 38.18), 145 (M^+−155, 100), 91 (M^+−209, 75.80). Anal. Calcd for $C_{16}H_{16}N_2O_2S$ requires C, 63.98; H, 5.37; N, 9.33%. Found: C, 63.95; H, 5.30; N, 9.28%.

4.3.3. Benzoic acid *N′*-benzylidene-*N*-(3-oxobutyl)hydrazide 9a. Colorless solid; mp 107–110 °C (recrystallized from dichloromethane and petroleum ether); IR (CH_2Cl_2) ν 3441, 1713 (C=O), 1608, 1414, 1340, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.24 (3H, s, CH_3), 2.89 (2H, t, $J=7.5$ Hz, CH_2), 4.43 (2H, t, $J=7.5$ Hz, CH_2), 7.32–7.35 (3H, m, ArH), 7.43–7.50 (5H, m, ArH), 7.71–7.74 (2H, m, ArH), 7.82 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 30.2, 35.8, 39.2, 127.1, 127.2, 128.6, 129.6, 129.8, 130.3, 134.4, 134.8, 142.5, 170.9, 206.5; MS (EI) *m/z* 294 (M^+, 3.13), 188 (M^+-106, 6.52), 148 (M^+-146, 17.03), 105 (M^+-189, 100), 77 (M^+-217, 37.85). Anal. Calcd for $C_{18}H_{18}N_2O_2$ requires C, 73.45; H, 6.16; N, 9.52%. Found: C, 73.40; H, 6.26; N, 9.35%.

4.3.4. Benzoic acid *N′*-(4-chlorobenzylidene)-*N*-(3-oxobutyl)hydrazide 9b. Colorless solid; mp 133–135 °C (recrystallized from dichloromethane and petroleum ether); IR (CH_2Cl_2) ν 3441, 3055, 2987, 1716 (C=O), 1658, 1414, 896 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.24 (3H, s, CH_3), 2.89 (2H, t, $J=7.2$ Hz, CH_2), 4.41 (2H, t, $J=7.2$ Hz, CH_2), 7.27–7.32 (2H, m, ArH), 7.38–7.52 (5H, m, ArH), 7.68–7.71 (2H, m, ArH), 7.79 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 30.3, 35.9, 39.3, 127.3, 128.2, 128.9, 129.8, 130.4, 133.0, 134.7, 135.4, 137.8, 170.9, 206.5; MS (EI) *m/z* 328 (M^+, 3.53), 223 (M^+-105, 0.43), 188 (M^+-140, 8.38), 105 (M^+-223, 100), 77 (M^+-251, 29.77). Anal. Calcd for $C_{18}H_{17}N_2O_2Cl$ requires C, 65.75; H, 5.21; N, 8.52%. Found: C, 65.58; H, 5.14; N, 8.61%.

4.3.5. Benzoic acid *N′*-isobutylidene-*N*-(3-oxobutyl)-hydrazide 9c. Colorless oil; IR (CH_2Cl_2) ν 2965, 1716 (C=O), 1655, 1417, 1326, 1051, 715 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.01 (3H, s, CH_3), 1.03 (3H, s, CH_3), 2.21 (3H, s, CH_3), 2.46–2.52 (1H, m, CH), 2.78 (2H, t, $J=7.5$ Hz, CH_2), 4.24 (2H, t, $J=7.5$ Hz, CH_2), 7.12 (1H, d, $J=4.5$ Hz, CH), 7.32–7.41 (3H, m, ArH), 7.63–7.66 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.4, 30.0, 31.6, 35.6, 39.1, 127.0, 129.5, 129.8, 134.8, 148.2, 170.4, 206.4; MS (EI) *m/z* 261 ($M^+ +1$, 3.28), 217 (M^+-43, 57.84), 188 (M^+-72, 8.37), 105 (M^+-155, 100), 77 (M^+-183, 53.44); HRMS (MALDI) calcd for $C_{15}H_{21}N_2O_2^{+1}$ ($M^+ +H$): 261.1598. Found: 261.1599.

4.3.6. (3-Methyl-4,5-dihydropyrazol-1-yl)phenylmethanone 10. Colorless solid; mp 90–93 °C (recrystallized from dichloromethane and petroleum ether); IR (CH_2Cl_2) ν 3460, 1634 (C=O), 1454, 1375, 1169, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.04 (3H, s, CH_3), 2.85 (2H, t, $J=9.9$ Hz, CH_2), 4.09 (2H, t, $J=9.9$ Hz, CH_2), 7.37–7.45 (3H, m, ArH), 7.84–7.86 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 16.1, 35.2, 44.7, 127.5, 129.4, 130.6, 134.4, 158.4, 166.5; MS (EI) *m/z* 188 (M^+, 27.72), 105 (M^+-83, 100), 77 (M^+-111, 47.82), 51 (M^+-137, 14.09). Anal. Calcd for $C_{11}H_{12}N_2O$ requires C, 70.19; H, 6.43; N, 14.88%. Found: C, 70.13; H, 6.09; N, 14.71%.

4.3.7. 4-(*N*-Benzylidene-*N*-phenyl-hydrazino)-butan-2-one 11a. A yellow oil; IR (CH_2Cl_2) ν 3059, 3027, 1713 (C=O), 1592, 1496, 1394, 1266, 1164, 1144 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.20 (3H, s, CH_3), 2.81 (2H, t, $J=7.5$ Hz, CH_2), 4.24 (2H, t, $J=7.5$ Hz, CH_2), 6.93–6.97 (1H, m, ArH), 7.24–7.40 (7H, m, ArH), 7.50 (1H, s, CH), 7.67–7.70 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 30.46, 38.15, 39.31, 115.03, 120.79, 126.00, 127.83, 128.50, 129.13, 131.65, 136.35, 146.42, 206.88; MS (EI) *m/z* 266 (M^+, 39.39), 209 (M^+-57, 38.54), 119 (M^+-147, 41.73), 106 (M^+-160, 81.61), 77 (M^+-189, 100); HRMS (MALDI) calcd for $C_{17}H_{18}N_2O$: 266.1419. Found: 266.1413.

4.3.8. 4-[*N*-(4-Methylbenzylidene)-*N*-phenylhydrazino]-butan-2-one 11b. A yellow oil; IR (CH_2Cl_2) ν 3002, 2921, 1712 (C=O), 1592, 1498, 1363, 1221, 1143 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.19 (3H, s, CH_3), 2.36 (3H, s, CH_3), 2.80 (2H, t, $J=7.5$ Hz, CH_2), 4.23 (2H, t, $J=7.5$ Hz, CH_2), 6.92–6.96 (1H, m, ArH), 7.18 (2H, d, $J=7.8$ Hz, ArH), 7.32–7.36 (4H, m, ArH), 7.49 (1H, s, CH), 7.58 (2H, d, $J=7.8$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.3, 30.5, 38.3, 39.4, 115.0, 120.6, 126.0, 129.1, 129.3, 132.0, 133.6, 137.8, 146.6, 206.9; MS (EI) *m/z* 280 (M^+, 100), 223 (M^+-57, 69.40), 119 (M^+-161, 51.14), 106 (M^+-174, 90.55), 77 (M^+-203, 62.31); HRMS (MALDI) calcd for $C_{18}H_{21}N_2O^{+1}$ ($M^+ +H$): 281.1648. Found: 281.1655.

4.3.9. 4-[*N′*-(4-Chlorobenzylidene)-*N*-phenylhydrazino]-butan-2-one 11c. A yellow oil; IR (CH_2Cl_2) ν 3061, 2922, 1714 (C=O), 1596, 1497, 1404, 1145, 1087 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.21 (3H, s, CH_3), 2.82 (2H, t, $J=7.8$ Hz, CH_2), 4.24 (2H, t, $J=7.8$ Hz, CH_2), 6.96–7.00 (1H, m, ArH), 7.31–7.37 (6H, m, ArH), 7.45 (1H, s, CH), 7.60 (2H, d, $J=8.4$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 30.5, 38.2, 39.5, 115.2, 121.1, 127.1, 128.7, 129.2, 130.3, 133.3, 135.0, 146.3, 206.7; MS (EI) *m/z* 300 (M^+, 51.47), 243 (M^+-57, 48.44), 119 (M^+-181, 67.18), 106 (M^+-194, 71.59), 77 (M^+-223, 78.15); HRMS (MALDI) calcd for $C_{17}H_{18}N_2OCl^{+1}$ ($M^+ +H$): 301.1102. Found: 301.1114.

4.3.10. 1,3-Diphenyl-4,5-dihydro-1*H*-pyrazole 12. This a known compound.[11] ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.08 (3H, s, CH_3), 2.83 (2H, t, $J=9.6$ Hz, CH_2), 3.66 (2H, t, $J=9.6$ Hz, CH_2), 6.78–6.83 (1H, m, ArH), 6.98–7.01 (2H, m, ArH), 7.23–7.28 (2H, m, ArH); This ^1H NMR spectroscopic data is in consistent with those reported in literature.[12]

The ^1H and ^{13}C NMR spectroscopic data of **3a**-*d*: ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.16 (3H, s, CH_3), 2.41 (3H, s, CH_3), 2.76–2.81 (1H, m, CHD), 3.82 (2H, m, CH_2), 7.31 (2H, d, $J=8.4$ Hz, ArH), 7.39–7.41 (3H, m, ArH), 7.64–7.68 (2H, m, ArH), 7.74 (2H, d, $J=8.4$ Hz, ArH), 8.10 (1H, s, CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.3, 29.9, 41.3, 43.5 (t, $J=3.75$ Hz, CHD), 127.5, 128.0, 128.5, 129.3, 130.4, 133.4, 133.4, 144.0, 151.6, 205.1.

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Supplementary data

Supplementary data associated with this article can be found at 10.1016/j.tet.2005.04.071

^{1}H NMR spectra for aza-Michael addition products **3**–**6**, **9**, **11**, and cyclized products **7**, **8**, **10**, and **12**. This material is available free of charge via internet.

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