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# COMMUNICATION

# Organocatalytic tandem three-component reaction of aldehyde, alkyl vinyl ketone, and amide: one-pot syntheses of highly functional alkenes†

**De-Wei Wang, Siang-en Syu, Yi-Ting Hung, Pei-yi Chen, Chia-Jui Lee, Ko-Wei Chen, Yu-Jhang Chen and Wenwei Lin***

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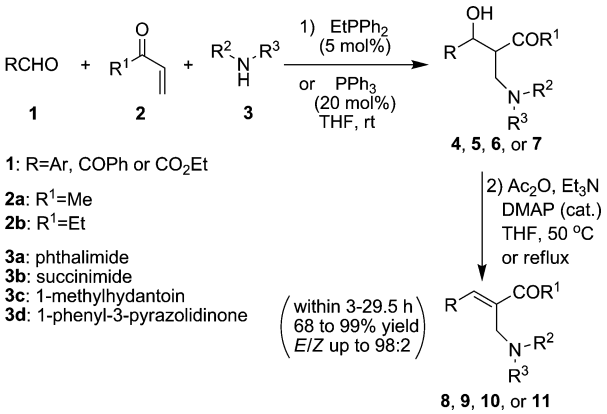
**An $EtPPh_2$- or $PPh_3$-catalyzed tandem three-component reaction of aldehyde, alkyl vinyl ketone, and amide is developed. Its further application in one-pot syntheses of highly functional alkenes starting from aldehydes, alkyl vinyl ketones, and amides is realized. A wide variety of highly functional α,β-unsaturated ketones can be furnished in 68–99% yields with high stereoselectivity (*E*/*Z* up to 98 : 2) within overall 3–29.5 h.**

Carbon–carbon or carbon–heteroatom bond formation is of importance in organic synthesis with numerous interesting studies concerning reactivity, chemoselectivity and stereoselectivity.[1] Among all well-developed methodologies, the multicomponent reaction plays an important role due to its allowance of generation of an adduct in a single operation from three or more reactants with high atom economy and bond-forming efficiency.[2] Successful application of a multicomponent reaction highly relies on the good chemoselectivities in the presence of all the reactants.[3]

The Baylis–Hillman adduct, starting from alkyl vinyl ketone and aldehyde, is a good Michael acceptor according to the ketone function activated by the neighboring hydroxy group.[4,5] Numerous successful applications for syntheses of highly functional compounds were achieved by the Michael addition of nucleophiles toward the Baylis–Hillman adducts as routine protocols.[5] However, the Baylis–Hillman reaction is notorious for its slow reaction with moderate to high yield,[6] and therefore the whole process often takes long time to obtain the final Michael product. Therefore, it remains a strong demand to develop an efficient approach.

Herein, we wish to report a phosphine-catalyzed three-component reaction starting from the Baylis–Hillman reaction of aldehyde **1** and alkyl vinyl ketone **2**, which is followed by Michael addition of amide **3** toward the resulting adduct. Efficient one-pot syntheses of highly functional alkenes **8–11** *via* $EtPPh_2$- or $PPh_3$-catalyzed tandem three-component reactions of **1**, **2** and **3** are also demonstrated (Scheme 1).




**Scheme 1** One-pot syntheses of alkenes **8–11** *via* three-component reactions of aldehydes **1**, alkyl vinyl ketones **2** and amides **3** catalyzed by $EtPPh_2$ or $PPh_3$.

Practically, a more reactive catalyst than $PPh_3$, such as $EtPPh_2$, was seldom used in Morita–Baylis–Hillman reaction of an aldehyde and an α,β-unsaturated ketone due to a significant amount of side reaction resulting from the $EtPPh_2$-catalyzed Michael addition of the α,β-unsaturated ketone toward the corresponding Baylis–Hillman adduct. Besides, dimerization of α,β-unsaturated ketone occurred even when $PPh_3$ was used. Therefore, it is common to use excess amount of α,β-unsaturated ketone (at least 3.0 equiv) in Morita–Baylis–Hillman reactions.[7] Surprisingly, in the presence of $EtPPh_2$ (5 mol%), 4-nitrobenzaldehyde (**1a**) (2.0 mmol) reacted with merely 1.2 equivalent of methyl vinyl ketone (**2a**) and phthalimide (**3a**) (1.1 equiv) in dry THF (2.0 mL) smoothly at room temperature within 1 h, providing the highly functional three-component adduct **4a** in 95% yield (Table 1, entry 1). Even less reactive $PPh_3$ (20 mol%) can effectively catalyze this type of three-component reaction of **1a**, **2a** (1.5 equiv) and **3a** (1.4 equiv), furnishing **4a** in 97% yield within 4.5 h. The reactions of other aryl-substituted aldehydes **1b–i** as well as heteroaryl-substituted aldehydes **1k–n** underwent smoothly with **2a** and **3a** in the presence of $EtPPh_2$ (5 mol%), leading to the corresponding adducts **4b–i** and **4k–n** within 1–7 h (**T1**) in 54–98% yields (entries 2–9 and 11–14). The reactivity of an aldehyde had strong influence on the reaction time, and therefore **2a** (1.3 equiv) and **3a** (1.2 equiv) are necessary for the formation of **4f–h** and **4k–n**.[7,8] $PPh_3$ (20 mol%) also catalyzed the reactions of **1b–n**, **2a** (1.5 or 2.0 equiv) and

*Department of Chemistry, National Taiwan Normal University, 88, Section 4, Tingchow Road, Taipei 11677, Taiwan, ROC. E-mail: wenweilin@ntnu.edu.tw; Fax: (+886)-2-29324249; Tel: (+886)-2-77346131*

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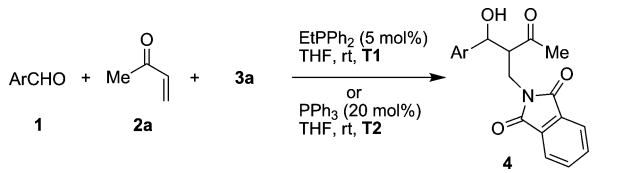
**Table 1** A three-component reaction of **1**, **2a**, and **3a** catalyzed by EtPPh2 or $PPh_3$

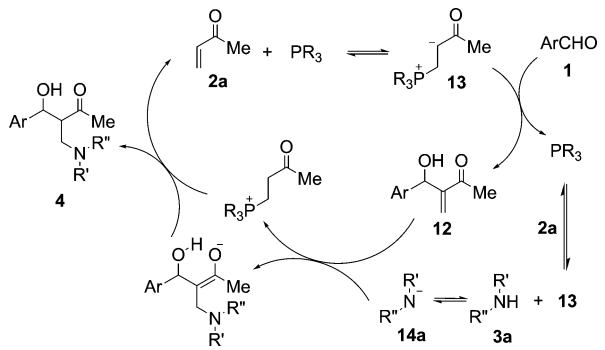



| Entry | Ar | **T1**[a]; **T2**[b]/h | Yield of **4** (%)[c,d] |
|---|---|---|---|
| 1 | 4-$NO_2C_6H_4$ | 1; 4.5 | **4a**[e], 95; 97 |
| 2 | 3-$NO_2C_6H_4$ | 1; 4 | **4b**, 95; 98 |
| 3 | 2-$NO_2C_6H_4$ | 1.5; 24 | **4c**, 88; 96 |
| 4 | 4-$CNC_6H_4$ | 1.5; 5.5 | **4d**, 90; 98 |
| 5 | 4-$CF_3C_6H_4$ | 1.5; 24 | **4e**, 93; 97 |
| 6 | 4-$BrC_6H_4$ | 2[f]; 17[g] | **4f**, 87; 98 |
| 7 | 4-$ClC_6H_4$ | 3[f]; 18[g] | **4g**, 83; 96 |
| 8 | 2-$ClC_6H_4$ | 5[f]; 26[g] | **4h**[e], 91; 98 |
| 9 | $C_6H_5$ | 7; 62[g] | **4i**, 54; 86 |
| 10 | 4-$CH_3C_6H_4$ | –; 62[g] | **4j**, –[h]; 62 |
| 11 | 4-Pyridyl | 1[f]; 7[g] | **4k**, 97; 95 |
| 12 | 3-Pyridyl | 1[f]; 11[g] | **4l**, 98; 92 |
| 13 | 2-Pyridyl | 5[f]; 48[g] | **4m**, 94; 87 |
| 14 | 2-Furyl | 5[f]; 25[g] | **4n**, 77; 98 |

[a] Reactions were carried out with **1** (2.0 mmol), **2a** (1.2 equiv) and **3a** (1.1 equiv) catalyzed by $EtPPh_2$ (5 mol%) in THF (2.0 mL) at rt. [b] **1** (1.0 mmol), **2a** (1.5 equiv) and **3a** (1.4 equiv) were used in the presence of $PPh_3$ (20 mol%) in THF (1.0 mL) at rt. [c] Yield of isolated product. [d] For the diastereomeric ratios of **4**, see the ESI.† [e] The structures of *threo*-**4a** (CCDC no. 778973) and *erythro*-**4h** (CCDC no. 778974) were confirmed by X-ray analysis. [f] **2a** (2.0 equiv) and **3a** (1.3 equiv) were used. [g] **2a** (2.0 equiv) and **3a** (1.5 equiv) were used. [h] The trace amount of **4j** was observed.

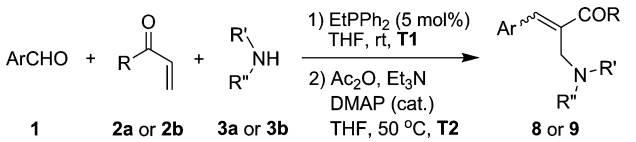
**3a** (1.4 or 1.5 equiv), providing the corresponding adducts **4b–n** within 4–62 h (**T2**) in 62–98% yields (entries 2–14). DABCO (20 mol%), one of the best catalysts for the Baylis–Hillman reaction, also catalyzed the reaction of **1a**, **2a** (1.3 equiv) and **3a** (1.2 equiv). However, the reaction rate was very slow (7 days, 86% conversion), indicating DABCO was not effective for our designed reaction.[9]

Based on experimental‡ results (Table 1), a plausible reaction mechanism for this highly chemoselective three-component reaction was proposed (Scheme 2). First, an $EtPPh_2$- or $PPh_3$-catalyzed Morita–Baylis–Hillman reaction took place, giving rise to the corresponding adduct **12**. The *in situ* formed basic intermediate **13**, which was the nucleophile in the Morita–Baylis–Hillman reaction, deprotonated an amide **3a**, and then **14a** underwent the Michael addition toward **12** followed by protonation, affording the corresponding adduct **4** with the regeneration of $EtPPh_2$ or $PPh_3$.




**Scheme 2** A proposed mechanism of the three-component reaction of **1**, **2a** and **3a** catalyzed by $EtPPh_2$ or $PPh_3$.

**Table 2** One-pot syntheses of **8** and **9**[a]



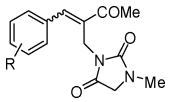
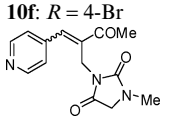
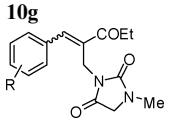
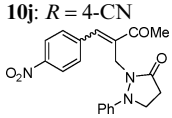
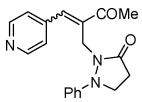

| Entry | **1**/**2**/**3** | **T1**[a];**T2**[b]/h | Product **8** or **9** | *E*/*Z*[c]; Yield (%)[d] |
|---|---|---|---|---|
| 1 | **1a**/**2a**/**3a** | 1[e]; 3 | **8a**: $R$ = 4-$NO_2$ | 92/8; 81[f] |
| 2 | **1b**/**2a**/**3a** | 1[e]; 3 | **8b**: $R$ = 3-$NO_2$ | 91/9; 83 |
| 3 | **1e**/**2a**/**3a** | 1.5[g]; 4.5 | **8c**: $R$ = 4-$CF_3$ | 93/7; 81[h] |
| 4 | **1g**/**2a**/**3a** | 3; 5 | **8d**: $R$ = 4-Cl | 94/6; 77 |
| 5 | **1h**/**2a**/**3a** | 5; 4[i] | **8e**: $R$ = 2-Cl | 97/3; 76 |
| 6 | **1k**/**2a**/**3a** | 1; 2 | **8f**: $R$ = 4-pyridyl | 92/8; 96 |
| 7 | **1l**/**2a**/**3a** | 1; 3 | **8g**: $R$ = 3-pyridyl | 91/9; 99 |
| 8 | **1m**/**2a**/**3a** | 5; 6[i] | **8h**: $R$ = 2-pyridyl | 98/2; 90[f] |
| 9 | **1d**/**2b**/**3a** | 1.5[e]; 5 | **8i** | 92/8; 76 |
| 10 | **1a**/**2a**/**3b** | 1[e]; 3 | **9a**: $R$ = 4-$NO_2$ | 88/12; 76[f] |
| 11 | **1d**/**2a**/**3b** | 1.5[e]; 4.5 | **9b**: $R$ = 4-CN | 90/10; 68[f] |

[a] Reactions were carried out with **1** (2.0 mmol), **2** (2.0 equiv) and **3** (1.3 equiv) catalyzed by $EtPPh_2$ (5 mol%) in THF (2.0 mL) at rt. [b] Without further purification, reactions were carried out using $Ac_2O$ (1.2 equiv), $Et_3N$ (2.5 equiv), DMAP (10 mol %), and additional THF (2.0 mL) at 50 °C. [c] Determined by $^1H$ NMR analysis of the crude product. [d] Yield of isolated products. [e] **2a** (1.3 equiv) and **3b** (1.01 equiv) were used. [f] Yield of (*E*)-form isomer. [g] **2a** (1.5 equiv) and **3b** (1.01 equiv) were used. [h] The structure of (*E*)-form of **8c** (CCDC no. 769605) was confirmed by X-ray analysis. [i] Reactions were carried out in refluxing THF.

Highly functional α,β-unsaturated ketones are bioactive compounds as well as interesting building blocks for organic synthesis, and the three-component adduct such as **4a** can be further transformed into **8a** successfully in our preliminary study.[10,11] Encouraged by this result, we envisioned that it should be possible to develop one-pot procedure for the syntheses of polyfunctional α,β-unsaturated ketones *via* our designed three-component reactions and acylation of the corresponding adducts followed by elimination. Thus, the reaction of **1a** (2.0 mmol), **2a** (1.3 equiv) and **3a** (1.01 equiv) catalyzed by $EtPPh_2$ (5 mol%) proceeded in THF at rt within 1 h, followed by the addition of $Ac_2O$ (1.2 equiv), $Et_3N$ (2.5 equiv) and DMAP (10 mol%), and then underwent smoothly at 50 °C within 3 h, providing the highly functional alkene (*E*)-**8a** in 81% yield (Table 2, entry 1). Other aryl-substituted aldehydes, such as **1b**, **1d–e**, **1g–h**, and **1k–m**, worked nicely with **2a** (or **2b**)

**Table 3** One-pot syntheses of **10** and **11**[a]

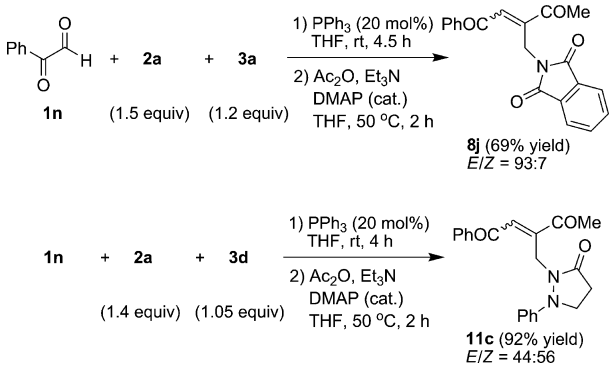

| Entry | 1/2/3 | T1[a];T2[b]/h | Product **10** or **11** | *E*/*Z*[c]; Yield (%)[d] |
|---|---|---|---|---|
| | | |  | |
| 1 | **1a/2a/3c** | 3; 3.5 | **10a**: $R$ = 4-$NO_2$ | 84/16; 84 |
| 2 | **1b/2a/3c** | 3; 3.5 | **10b**: $R$ = 3-$NO_2$ | 83/17; 88 |
| 3 | **1c/2a/3c** | 15; 6 | **10c**: $R$ = 2-$NO_2$ | 92/8; 92 |
| 4 | **1d/2a/3c** | 4.5; 3.5 | **10d**: $R$ = 4-CN | 89/11; 92 |
| 5 | **1e/2a/3c** | 23; 6.5 | **10e**: $R$ = 4-$CF_3$ | 90/10; 90 |
| 6 | **1f/2a/3c** | 24; 5[e] | **10f**: $R$ = 4-Br | 89/11; 83[f] |
| | | |  | |
| 7 | **1k/2a/3c** | 12[g]; 4 | **10g** | 89/11; 92 |
| | | |  | |
| 8 | **1a/2b/3c** | 3.5; 3[e] | **10h**: $R$ = 4-$NO_2$ | 86/14; 80 |
| 9 | **1b/2b/3c** | 6; 3[e] | **10i**: $R$ = 3-$NO_2$ | 87/13; 86 |
| 10 | **1d/2b/3c** | 3.5; 4[e] | **10j**: $R$ = 4-CN | 85/15; 83 |
| | | |  | |
| 11 | **1a/2a/3d** | 1[h]; 2 | **11a** | 97/3; 83 |
| | | |  | |
| 12 | **1k/2a/3d** | 7[i]; 2 | **11b** | 92/8; 98 |

[a] Reactions were carried out with **1** (1.0 mmol), **2** (1.4 equiv) and **3** (1.05 equiv) catalyzed by $PPh_3$ (20 mol%) in THF (1.0 mL) at rt. [b] Without further purification, reactions were carried out using $Ac_2O$ (1.2 equiv), $Et_3N$ (2.5 equiv), DMAP (10 mol %), and additional THF (1.0 mL) at 50 °C. [c] Determined by $^1H$ NMR analysis of the crude product. [d] Yield of isolated products. [e] Reactions were carried out in refluxing THF. [f] The structure of (*E*)-**10f** (CCDC no. 770519) was confirmed by X-ray analysis. [g] **1j** (1.01 equiv) and **2a** (1.4 equiv) were used. [h] **1a** (1.05 equiv) and **2a** (1.4 equiv) were used. [i] **2a** (1.4 equiv) and **3d** (1.05 equiv) were used.

and **3a** according to our protocol, furnishing the corresponding adducts **8b–i** within 3–11 h (**T1**+**T2**) in overall 76–99% yields with high stereoselectivities (*E*/*Z* = 91/9 to 98/2) (entries 2–9). The other amide, like succinimide (**3b**), was also successfully applied in our one-pot procedure with **2a** and **1a** or **1d**, affording the corresponding alkene (*E*)-**9a** or (*E*)-**9b** within 4 or 6 h in overall 76% or 68% yields, respectively (entries 10 and 11).[12]

The broad reaction scope of our one-pot protocol was demonstrated by further studies disclosed in Table 3. It showed that the syntheses of **10** and **11** starting from the reactions of aldehydes **1**, **2a–b**, and amides, such as 1-methylhydantoin (**3c**) and 1-phenyl-3-pyrazolidinone (**3d**), in the presence of $PPh_3$ (20 mol%) were achieved in overall 3–29.5 h (**T1**+**T2**) with high yields (80–98%) and good stereoselectivities (*E*/*Z* = 83/17 to 97/3) according to our procedure (Table 3, entries 1–12). However, $EtPPh_2$, which showed better catalytic ability than $PPh_3$ for the three-component reaction of **1**, **2** and **3a–b**, gave poor results in case of **3c** and **3d**, and was not a suitable catalyst for the preparation of **10** and **11**.

Not only aryl-substituted aldehydes **1a–m** but also the other interesting aldehyde, like **1n**, reacted successfully with **2a** and **3a** according to our one-pot protocol, giving the corresponding highly functional alkene **8j** in 69% yield with good stereoselectivity (*E*/*Z* = 93 : 7) (Scheme 3). The amide **3d** worked also nicely with **1n** and **2a**, furnishing the corresponding alkene **11c** within 6 h in 92% yield (*E*/*Z* = 44 : 56).[13]




**Scheme 3** One-pot syntheses of **8j** or **11c**.

In summary, we have developed a general procedure for one-pot syntheses of highly functional α,β-unsaturated ketones **8–11** *via* tandem $EtPPh_2$- or $PPh_3$-catalyzed three-component reaction of aldehydes **1**, alkyl vinyl ketones **2** and amides **3**, and acylation of the corresponding adducts followed by elmination. The reaction condition is very mild, and numerous polyfunctional alkenes **8–11** can be efficiently afforded in good yields with high stereoselectivities. The reaction mechanism of our tandem three-component reaction is proposed to undergo the Morita–Baylis–Hillman reaction of **1** and **2** followed by the Michael addition of **3** toward the corresponding adduct. Further studies and the extensions of this work in imines as well as the use of other nucleophilic reagents, are currently underway.

The authors thank the National Science Council of the Republic of China (NSC Grant No. 97-2113-M-003-003-MY2) and National Taiwan Normal University (99T3030-6) for financial support.

## Notes and references

‡ Experimental procedure: Preparation of **8a**: A dry and nitrogen-flushed 10-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of **1a** (302 mg, 2 mmol) and **3a** (297 mg, 1.01 equiv) in dry THF (2 mL). MVK (**2a**) (211 μL, 1.3 equiv) and $EtPPh_2$ (20.4 μL, 5 mol%) were added, and the reaction mixture was stirred for 1 h (**T1**) at rt. Without further purification, $Ac_2O$ (0.23 mL, 1.2 equiv), $Et_3N$ (0.70 mL, 2.5 equiv), DMAP (24.4 mg, 10 mol%), and additional THF (2.0 mL) were added, and the resulting mixture was stirred at 50 °C for 3 h (**T2**) Thereafter, the solvent was removed by evaporation in vacuo. Purification by recrystallization (hexanes/$CH_2Cl_2$) furnished the alkene (*E*)-**8a** as a yellow solid (568 mg, 81%).

1 (*a*) P. I. Dalko and L. Moisan, *Angew. Chem., Int. Ed.*, 2004, **43**, 5138; (*b*) P. I. Dalko and L. Moisan, *Angew. Chem., Int. Ed.*, 2001, **40**, 3726; (*c*) *Handbook of functionalized organometallics*, ed. P. Knochel, Wiley-VCH, Weinheim, Germany, 2005.

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4 Reviews for Morita–Baylis–Hillman reactions, see: (*a*) D. Basavaiah, A. J. Rao and T. Satyanarayana, *Chem. Rev.*, 2003, **103**, 811, and references cited therein; (*b*) P. Langer, *Angew. Chem., Int. Ed.*, 2000, **39**, 3049; (*c*) D. Basavaiah, K. V. Rao and R. J. Reddy, *Chem. Soc. Rev.*, 2007, **36**, 1581; (*d*) C. Menozzi and P. I. Dalko, Organocatalytic Enantioselective Morita–Baylis–Hillman Reactions. In *Enantioselective Organocatalysis, Reactions and Experimental Procedures*, ed. P. I. Dalko, Wiley-VCH, Weinheim, Germany, 2007; recent reviews for application of Baylis–Hillman adduct, see: (*e*) G. Masson, C. Housseman and J. Zhu, *Angew. Chem., Int. Ed.*, 2007, **46**, 4614; (*f*) S. Batra and V. Singh, *Tetrahedron*, 2008, **64**, 4511; (*g*) D. Basavaiah, B. S. Reddy and S. S. Badsara, *Chem. Rev.*, 2010, **110**, 5447.

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7 For double transitional Morita–Baylis–Hillman reactions, please see: (*a*) G.-N. Ma, J.-J. Jiang, M. Shi and Y. Wei, *Chem. Commun.*, 2009, 5496, and references cited therein; for the *p*-$NO_2C_6H_4OH$ and $PPh_3$-catalyzed Baylis–Hillman reaction of **1a** and **2a** (3.0 equiv) (98% yield, rt, 18 h), see: (*b*) M. Shi and Y.-H. Liu, *Org. Biomol. Chem.*, 2006, **4**, 1468.

8 The dimerization of methyl vinyl ketone (**2a**) occurred during the reaction progress, and therefore it is necessary to use increasing amount of **2a** when the reaction time of the whole reaction progress was getting longer. In case of preparation of **4i**, there was no further improvement when increasing amount of **2a** was used.

9 The Baylis–Hillman adduct resulting from **1a** and **2a** was furnished efficiently (5 h, 100% conversion). However, the further addition of **3a** toward the Baylis–Hillman adduct in the presence of DABCO proceeded very slowly (7 days, 86% conversion), leading to the expected adduct **4a** in 84% yield.

10 For recent application of functionalized $\alpha,\beta$-unsaturated ketones as inhibitors of specific classes of cysteine proteases, see: Z. Yang, M. Fonović, S. H. L. Verhelst, G. Blum and M. Bogyo, *Bioorg. Med. Chem.*, 2009, **17**, 1071.

11 In our preliminary study, the three-component adduct **4a** can be successfully converted into the corresponding $\alpha,\beta$-unsaturated ketone **8a** in the presence of $Ac_2O$, $Et_3N$ and DMAP at rt.

12 Interestingly, the alkenes, such as **8a–i**, were afforded with high stereoselectivities ($E/Z$ = 91/9 to 98/2) after acylation of the three-component adducts **4a–b**, **4d–e**, **4g–h**, **4j–k**, and **4l** followed by elimination according to our one-pot protocol. However, **4a–b**, **4d–e**, **4g–h**, **4j–k**, and **4l** were furnished in poor diastereoselectivities (dr = 1 : 1 to 1 : 4.6).

13 The structure of (*E*)-form of **11c** (CCDC no. 775300) was confirmed by X-ray analysis.


 