DOI: 10.1002/ejoc.200901483

Simple, One-Pot, and Facile Synthesis of Angularly Fused [6-7-5], [6-7-6], [6-7-7], and [6,7] Ring Systems Using Baylis–Hillman Acetates

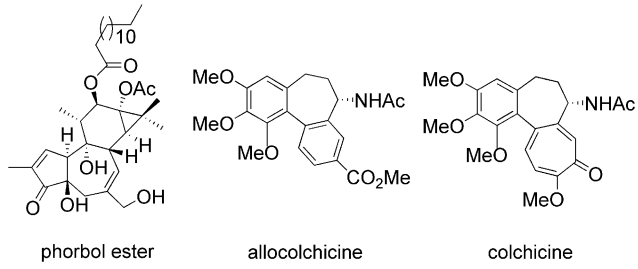
Deevi Basavaiah,*[a] Kunche Aravindu,[a] Katta Santosh Kumar,[a] and Kanumuri Ramesh Reddy[a]

Keywords: Carbocycles / Cyclization / Fused-ring systems / Michael addition

A simple, convenient, and one-pot synthesis of angularly fused [6-7-5], [6-7-6], [6-7-7], and [6,7] carbocyclic ring systems from Baylis–Hillman acetates through a strategy involving alkylation, formation of a vinyl chloride, and intramolecular cyclization (Friedel–Crafts or Michael reaction) is described.

Introduction

The angularly fused tricyclic carbocyclic framework containing cycloheptane as the central ring has a special and respectable place in the history of carbocyclic rings due to the presence of this tricyclic framework in various natural products and bioactive molecules.[1a–1f] For example, an angularly fused [6-7-5] carbocyclic skeleton is the core structure present in several natural products and bioactive molecules such as sphaeroane,[1a] (–)-presphaerene,[1a] frondosin C,[1b] and phorbol esters.[1c] An angularly fused [6-7-6] tricyclic system is present in biologically active compounds such as allocolchicine[1d,1e] and colchinol derivative ZD6126,[1e] whereas an angularly fused [6-7-7] tricyclic ring system is an integral part of the well-known alkaloid colchicine.[1f] Important bioactive compounds such as theaflavin[1g,1h] and TAK-779[1i,1j] contain the [6,7] bicyclic carbocyclic ring framework. Because of the remarkable medicinal importance of these fused-ring frameworks (Figure 1) and also because of unfavorable entropic factors[2] in synthesizing seven-membered rings, the development of efficient protocols for the synthesis of such fused-carbocyclic frameworks having cycloheptane as the key central ring has been and continues to be one of the most attractive and challenging areas in carbocyclic chemistry.[2c,3] In continuation of our interest in the synthesis of heterocyclic/carbocyclic molecules,[4] we herein report a simple one-pot multistep protocol for the synthesis of [6-7-5], [6-7-6], and [6-7-7] tricyclic, as well as [6,7] bicyclic, carbocyclic frameworks from Baylis–Hillman acetates by following a strategy involving alkylation, formation of a vinyl chloride, and intramolecular Friedel–Crafts (or Michael) reaction.



phorbol ester allocolchicine colchicine

Figure 1. Representative biologically active molecules containing a tricyclic carbocyclic framework with cycloheptane as the central ring.

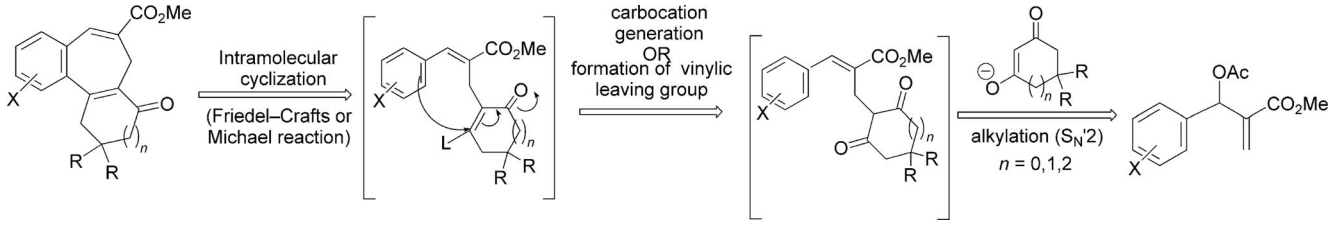
The Baylis–Hillman reaction has become a useful and popular synthetic tool for obtaining diverse classes of densely functionalized molecules (usually referred to as the Baylis–Hillman adducts) through atom-economical carbon–carbon bond-forming reactions involving coupling of the α-position of an activated alkene with an electrophile under the influence of a catalyst/catalytic system.[5,6] Applications of Baylis–Hillman adducts in a variety of organic transformations and also in the synthesis of natural products/bioactive compounds have been well documented over the last several years.[5,7]

Results and Discussion

On the basis of our experience and active involvement in various aspects of this fascinating reaction,[4] we envisioned that Baylis–Hillman acetates would be excellent synthons (or alkylators) for the one-pot, multistep synthesis of all three ([6-7-5], [6-7-6], and [6-7-7]) tricyclic carbocyclic frameworks. Accordingly, we planned a retrosynthetic strategy involving alkylation of suitable cyclic 1,3-diones with

[a] School of Chemistry, University of Hyderabad
Hyderabad 500046, India
Fax: +91-40-23012460
E-mail: dbsc@uohyd.ernet.in

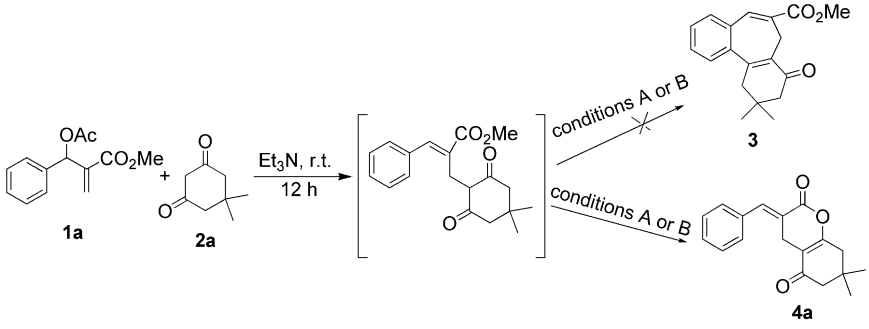
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200901483.



Scheme 1. Retrosynthetic strategy for the synthesis of angularly fused [6-7-5], [6-7-6], and [6-7-7] ring systems.

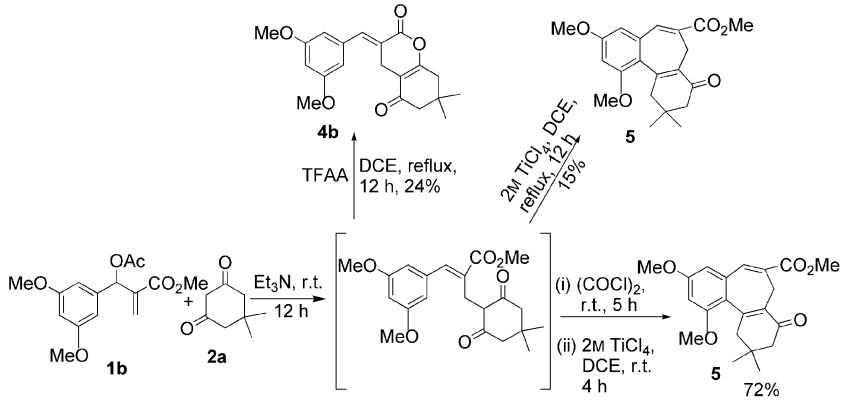
appropriate Baylis–Hillman acetates followed by intramolecular cyclization (by Friedel–Crafts or Michael reaction) after in situ generation of the carbocation according to the reaction sequence described in Scheme 1.

Accordingly, we have first selected methyl 3-acetoxy-2-methylene-3-phenylpropanoate (**1a**; acetate of Baylis–Hillman (BH) alcohol, obtained from the reaction of benzaldehyde with methyl acrylate) and 5,5-dimethyl-1,3-cyclohexanedione (dimedone; **2a**) as reaction partners. Our attempts to obtain desired [6-7-6] tricyclic carbocyclic molecule **3** under various conditions (Scheme 2 and Table 1) were not successful, as (*E*)-4-benzylidene-9,9-dimethyl-2-oxabicyclo-[4.4.0]dec-1(6)-ene-3,7-dione (**4a**)[8] was obtained as the major product. On the basis of our earlier studies[4g,6k] it



Scheme 2. Attempted synthesis of [6-7-6] ring systems by reaction of BH acetate **1a** with dimedone (**2a**). Conditions A: 2 M $TiCl_4$ in DCE, reflux, 12 h, 38%. Conditions B: (i) $(COCl)_2$, r.t., 5 h; (ii) 2 M $TiCl_4$, reflux, 16 h, 32%.

Table 1. Reaction optimization: Synthesis of angularly fused [6-7-6] ring systems by the reaction of **1b** with **2a**.[a]



Entry	Conditions	Product	Yield [%]
1	(i) Et_3N, r.t., 12 h; (ii) TFAA, r.t., 6 h[b]	–	–
2	(i) Et_3N, r.t., 12 h; (ii) TFAA, reflux, 12 h	**4b**	24
3	(i) Et_3N, r.t., 12 h; (ii) $MeSO_3H$, r.t., 6 h[b]	–	–
4	(i) Et_3N, r.t., 12 h; (ii) $MeSO_3H$, reflux, 12 h[c]	–	–
5	(i) Et_3N, r.t., 12 h; (ii) triflic acid, r.t., 6 h[b]	–	–
6	(i) Et_3N, r.t., 12 h; (ii) triflic acid, reflux, 12 h[c]	–	–
7	(i) Et_3N, r.t., 12 h; (ii) $POCl_3$, r.t., 6 h[b]	–	–
8	(i) Et_3N, r.t., 12 h; (ii) $POCl_3$, reflux, 10 h[c]	–	–
9	(i) Et_3N, r.t., 12 h; (ii) 2 M $TiCl_4$, reflux,12 h	**5**	15
10	(i) Et_3N, r.t., 12 h; (ii) $(COCl)_2$, r.t., 5 h; (iii) 2 M $TiCl_4$, r.t., 4 h	**5**	72

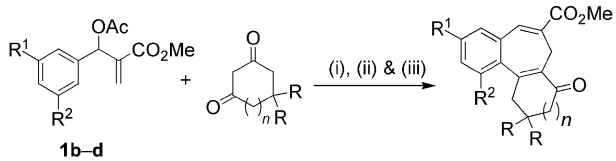
[a] All reactions were carried out on 1-mmol scale of Baylis–Hillman acetate **1b** with 1 mmol of dimedone (**2a**). [b] At room temperature, almost all the alkylated product was intact as evidenced by TLC examination. [c] Reaction was not clean.

occurred to us that the presence of an electron-donating group on the aromatic ring of the BH acetate would help to facilitate the intramolecular cyclization (Friedel–Crafts or Michael reaction).

Accordingly, we selected methyl 3-acetoxy-3-(3,5-dimethoxyphenyl)-2-methylenepropanoate (**1b**) as the reaction partner with dimedone (**2a**). We performed this reaction under different conditions (Table 1) and realized that BH acetate **1b** provided the expected [6-7-6] tricyclic carbocyclic framework (Table 1, Entry 10). Thus, treatment of **1b** (1 mmol) with **2a** (1 mmol) in the presence of Et_3N provided the alkylated product, which (after removal of excess triethylamine) upon reaction with oxalyl chloride (5 mmol) in situ afforded the corresponding vinyl chloride. Subsequent intramolecular cyclization (Friedel–Crafts or Michael reaction) was performed by using $TiCl_4$ (2 mmol, 2 M in DCE) in 1,2-dichloroethane (DCE) as the Lewis acid at room temperature for 4 h (after removal of DCM and oxalyl chloride under reduced pressure) to provide the desired [6-7-6] tricyclic carbocyclic molecule, i.e., {13,15-dimethoxy-4,4-dimethyl-9-methoxycarbonyltricyclo-[9.4.0.0^{2,7}]pentadeca-1(15),2(7),9,11,13-pentaen-6-one (**5**)} in 72% isolated yield after usual workup followed by column chromatography (Table 2, Entry 1). The structure of this molecule was further confirmed by single-crystal X-ray data (Figure 2).[9]

To examine the generality of this strategy, we subjected acetates, **1b**–**d**, of Baylis–Hillman alcohols (derived from the reaction of 3,5-dimethoxy and 3-alkoxybenzaldehydes with methyl acrylate) to the reaction with 5,5-dimethyl-1,3-cyclohexanedione (**2a**), 1,3-cyclohexanedione (**2b**), 1,3-cycloheptanedione (**2c**), and 1,3-cyclopentanedione (**2d**) as nucleophiles, which gave the desired [6-7-6], [6-7-7], and [6-7-5] tricyclic carbocyclic derivatives **5**–**15** in 50–75% isolated yields (Table 2, Entries 2–11). We further confirmed the structures of molecules **10** and **13** (Figures 2 and 3) by single-crystal X-ray analysis.[9]

Table 2. Synthesis of angularly fused [6-7-6], [6-7-7], and [6-7-5] frameworks by the reaction of **1b**–**d** with **2a**–**d**.[a]



1b–d

R = Me, *n* = 1 (**2a**);
R = H, *n* = 1 (**2b**),
R = H, *n* = 2 (**2c**);
R = H, *n* = 0 (**2d**)[c]

(i) Et_3N, r.t., 12 h-14 h or Et_3N / DMF, 80 °C, 8 h
(ii) $(COCl)_2$ / DCM, r.t., 5 h
(iii) $TiCl_4$ / DCE, r.t. or reflux, 4–14 h

Entry	Acetate	R^1	R^2	Dione	Product[b]	Yield [%]
1	**1b**	OMe	OMe	**2a**	**5**[d]	72
2	**1c**	OMe	H	**2a**	**6**	67
3	**1b**	OMe	OMe	**2b**	**7**	75
4	**1c**	OMe	H	**2b**	**8**	64
5	**1d**	OEt	H	**2b**	**9**	61
6	**1b**	OMe	OMe	**2c**	**10**[d]	63
7	**1c**	OMe	H	**2c**	**11**	59
8	**1d**	OEt	H	**2c**	**12**	57
9	**1b**	OMe	OMe	**2d**[c]	**13**[d]	52
10	**1c**	OMe	H	**2d**[c]	**14**	53
11	**1d**	OEt	H	**2d**[c]	**15**	50

[a] All reactions were carried out on 1-mmol scale of Baylis–Hillman acetates (**1b**–**d**) with 1 mmol of cyclic dione (**2a**–**d**) in the presence of Et_3N (1 mL) at room temperature for 12–14 h followed by treatment with $(COCl)_2$ at room temperature for 5 h in DCM and then reaction of the resulting vinyl chloride with 2 M $TiCl_4$ in DCE at r.t. (or reflux) for 4–14 h. [b] All compounds were fully characterized (see Supporting Information). [c] Reaction was carried out at 80 °C in Et_3N/DMF for 8 h. [d] Structures of these molecules were further confirmed by single-crystal X-ray data (see Supporting Information).[9]

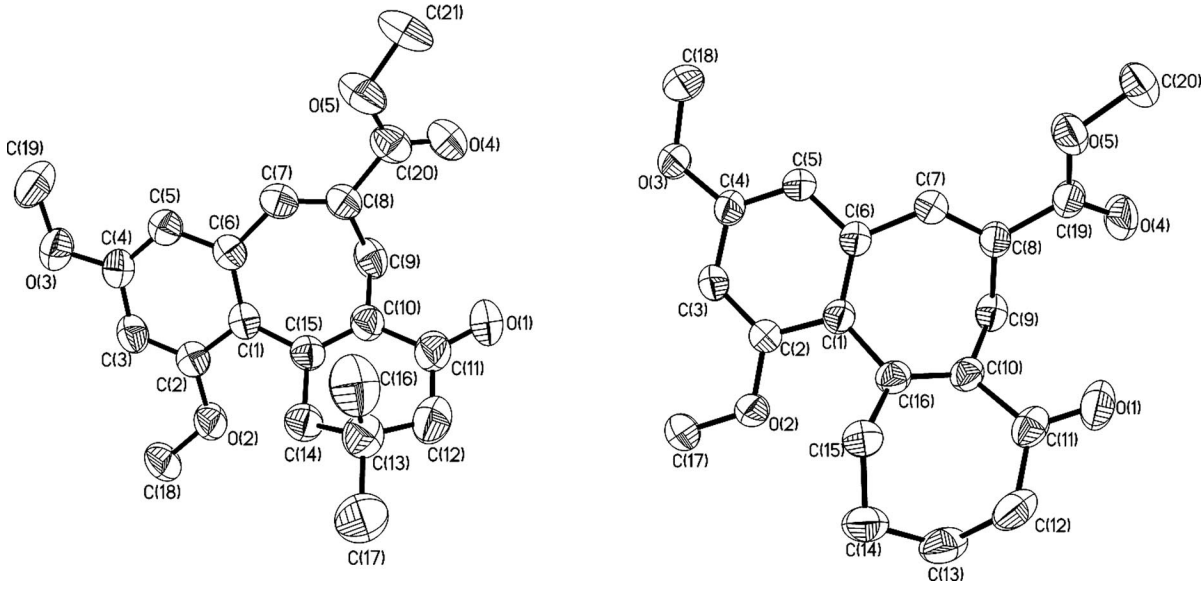


Figure 2. ORTEP diagrams of compounds **5** and **10** (hydrogen atoms were omitted for clarity).

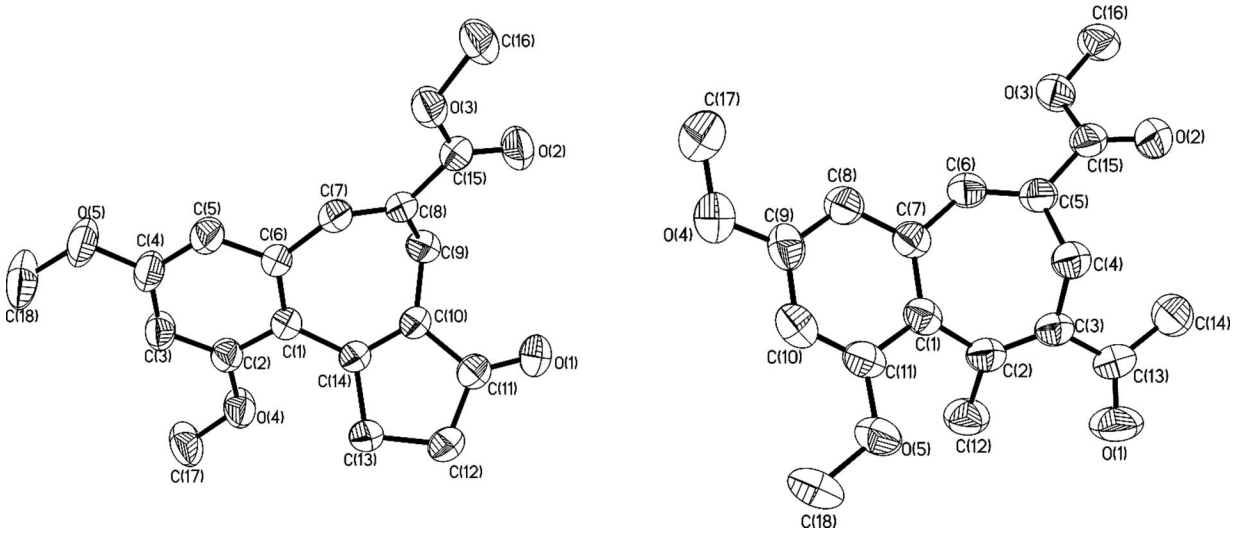
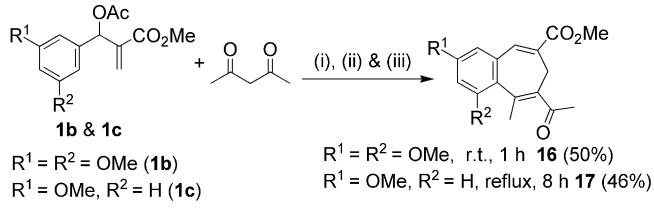


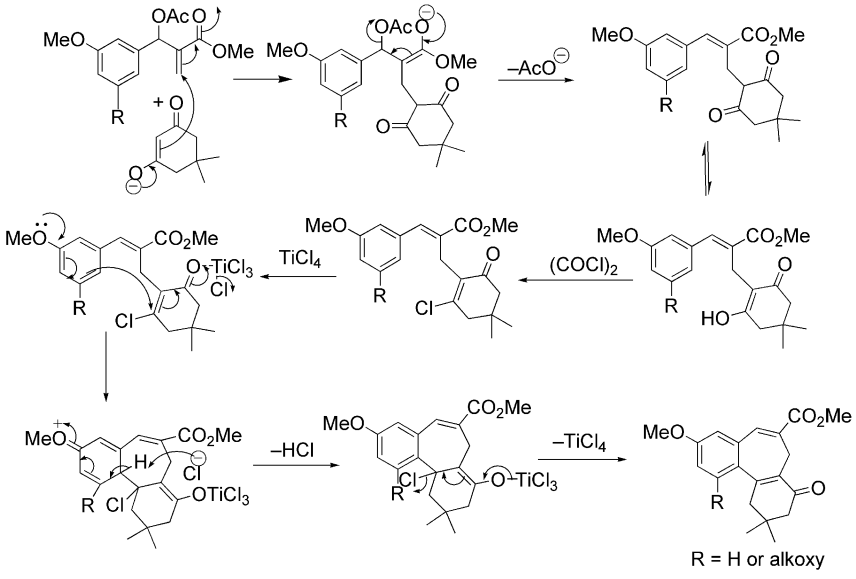
Figure 3. ORTEP diagrams of compounds **13** and **16** (hydrogen atoms were omitted for clarity).

With a view to extend this strategy to acyclic diones we employed 2,4-pentanedione (**2e**) as a nucleophile. Thus, reaction of 2,4-pentanedione with Baylis–Hillman acetate **1b** followed by treatment of the resulting trisubstituted alkene–esters with oxalyl chloride and then with $TiCl_4$ provided desired [6,7] bicyclic framework **16** in 50% isolated yield (Scheme 3). The structure of molecule **16** was also confirmed by single-crystal X-ray analysis (Figure 3).[9] Similarly, Baylis–Hillman acetate methyl 3-acetoxy-3-(3-methoxyphenyl)-2-methylenepropanoate (**1c**) upon reaction with 2,4-pentanedione (**2e**) provided [6,7] bicyclic derivative **17** in 46% isolated yield.



Scheme 3. One-pot synthesis of the [6,7] bicyclic carbocyclic framework by the reaction of **1b** and **1c** with **2e**. Reagents and conditions: (i) Et_3N, reflux, 10 h; (ii) $(COCl)_2$/DCM, r.t., 8 h; (iii) $TiCl_4$/DCE, r.t. or reflux, 1–8 h.

A plausible mechanism taking dimedone as a model case (nucleophile) for the formation of angularly fused tricyclic carbocyclic frameworks is presented in Scheme 4. Intramolecular cyclization of the in situ generated vinyl chloride might involve either a Friedel–Crafts or a Michael reaction.



Scheme 4. Plausible mechanism [taking dimedone as a model case (nucleophile)].

Conclusions

In conclusion, we have developed a simple, facile, and convenient synthesis of angularly fused [6-7-5], [6-7-6], and [6-7-7] tricyclic and [6,7] bicyclic carbocyclic frameworks, thus demonstrating the application of Baylis–Hillman adducts as a valuable source of a one-pot, multistep protocol for the synthesis of important and useful structural frameworks.

Experimental Section

General Experimental Procedure: A mixture of methyl 3-acetoxy-3-(3,5-dimethoxyphenyl)-2-methylenepropanoate (**1b**; 1 mmol, 0.294 g) and 5,5-dimethyl-1,3-cyclohexanedione (**2a**; 1 mmol, 0.140 g) in triethylamine (1 mL) was stirred at room temperature for 12 h. Then, the excess amount of triethylamine was removed under reduced pressure, and the reaction mixture was diluted with dichloromethane (3 mL). Oxalyl chloride (5 mmol, 0.635 g, 0.42 mL) was then added dropwise, and the mixture was stirred at room temperature for 5 h. The excess amount of oxalyl chloride and dichloromethane were evaporated, and the reaction mixture was diluted with DCE (3 mL). A solution of $TiCl_4$ (2 mmol, 1 mL, 2 M in DCE) was then added dropwise at 0 °C and stirring was continued at room temperature for 4 h. The reaction mixture was diluted with water (10 mL) and extracted with diethyl ether (3 × 15 mL). The combined organic layer was dried with anhydrous Na_2SO_4. The solvent was evaporated, and the residue thus obtained was purified by silica gel column chromatography (20% EtOAc in hexanes) to provide compound **5** as a colorless solid in 72% (0.256 g) isolated yield.

Supporting Information (see footnote on the first page of this article): All the experimental details, spectroscopic data, and the ^1H and ^{13}C NMR spectra for all the compounds.

Acknowledgments

We thank the Department of Science and Technology (DST, New Delhi) for funding this project. K.A., K.S.K., and K.R.R. thank the Council of Scientific and Industrial Research (CSIR, New Delhi) for their research fellowships. We thank the University Grants Commission (UGC, New Delhi) for support and for providing some instrumental facilities. We thank the National Single-Crystal X-ray facility funded by the Department of Science and Technology (DST, New Delhi). We also thank Professor S. Pal, School of Chemistry, University of Hyderabad, for helpful discussions regarding X-ray data analysis.

[1] a) J. Lee, J. Hong, *J. Org. Chem.* **2004**, *69*, 6433–6440; b) A. D. Patil, A. J. Freyer, L. Killmer, P. Offen, B. Carte, A. J. Jurewicz, R. K. Johnson, *Tetrahedron* **1997**, *53*, 5047–5060; c) G. Goel, H. P. S. Makkar, G. Francis, K. Becker, *Int. J. Toxicol.* **2007**, *26*, 279–288; d) O. Boye, A. Brossi, H. J. C. Yeh, E. Hamel, B. Wegrzynski, V. Toome, *Can. J. Chem.* **1992**, *70*, 1237–1249; e) P. D. Davis, G. J. Dougherty, D. C. Blakey, S. M. Galbraith, G. M. Tozer, A. L. Holder, M. A. Naylor, J. Nolan, M. R. L. Stratford, D. J. Chaplin, S. A. Hill, *Cancer Res.* **2002**, *62*, 7247–7253; f) A. Brossi, *J. Med. Chem.* **1990**, *33*, 2311–2319; g) T. Tanaka, Y. Miyata, K. Tamaya, R. Kusano, Y. Matsuo, S. Tamaru, K. Tanaka, T. Matsui, M. Maeda, I. Kouno, *J. Agric. Food Chem.* **2009**, *57*, 5816–5822; h) C. S. Yang, J. D. Lambert, J. Ju, G. Lu, S. Sang, *Toxicol. Appl. Pharmacol.* **2007**, *224*, 265–273; i) M. Baba, O. Nishimura, N. Kanzaki, M. Okamoto, H. Sawada, Y. Iizawa, M. Shiraishi, Y. Aramaki, K. Okonogi, Y. Ogawa, K. Meguro, M. Fujino, *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 5698–5703; j) M. Shiraishi, Y. Aramaki, M. Seto, H. Imoto, Y. Nishikawa, N. Kanzaki, M. Okamoto, H. Sawada, O. Nishimura, M. Baba, M. Fujino, *J. Med. Chem.* **2000**, *43*, 2049–2063.

[2] a) L. Yet, *Chem. Rev.* **2000**, *100*, 2963–3007; b) G. A. Molander, *Acc. Chem. Res.* **1998**, *31*, 603–609; c) M. A. Battiste, P. M. Pelphrey, D. L. Wright, *Chem. Eur. J.* **2006**, *12*, 3438–3447.

[3] a) N. Nicolaus, S. Strauss, J.-M. Neudorfl, A. Prokop, H.-G. Schmalz, *Org. Lett.* **2009**, *11*, 341–344; b) L. F. Silva Jr., R. S. Vasconcelos, M. A. Nogueira, *Org. Lett.* **2008**, *10*, 1017–1020; c) K. M. Brummond, D. Chen, M. M. Davis, *J. Org. Chem.* **2008**, *73*, 5064–5068; d) F.-D. Boyer, I. Hanna, *Org. Lett.* **2007**, *9*, 715–718; e) F.-D. Boyer, I. Hanna, *Org. Lett.* **2007**, *9*, 2293–2295; f) X. Li, R. E. Kyne, T. V. Ovaska, *Org. Lett.* **2006**, *8*, 5153–5156; g) T. Graening, H.-G. Schmalz, *Angew. Chem.* **2004**, *116*, 3292–3318; *Angew. Chem. Int. Ed.* **2004**, *43*, 3230–3256; h) T. Ikemoto, A. Nishiguchi, H. Mitsudera, M. Wakimasu, K. Tomimatsu, *Tetrahedron* **2001**, *57*, 1525–1529; i) T. V. Ovaska, J. L. Roark, C. M. Shoemaker, J. Bordner, *Tetrahedron Lett.* **1998**, *39*, 5705–5708; j) P. A. Wender, K. D. Rice, M. E. Schnute, *J. Am. Chem. Soc.* **1997**, *119*, 7897–7898.

[4] a) D. Basavaiah, B. Devendar, D. V. Lenin, T. Satyanarayana, *Synlett* **2009**, 411–416; b) D. Basavaiah, D. V. Lenin, B. Devendar, *Tetrahedron Lett.* **2009**, *50*, 3538–3542; c) D. Basavaiah, R. J. Reddy, *Org. Biomol. Chem.* **2008**, *6*, 1034–1039; d) D. Basavaiah, S. Roy, *Org. Lett.* **2008**, *10*, 1819–1822; e) D. Basavaiah, K. Aravindu, *Org. Lett.* **2007**, *9*, 2453–2456; f) D. Basavaiah, K. R. Reddy, *Org. Lett.* **2007**, *9*, 57–60; g) D. Basavaiah, T. Satyanarayana, *Chem. Commun.* **2004**, 32–33; h) D. Basavaiah, D. S. Sharada, A. Veerendhar, *Tetrahedron Lett.* **2004**, *45*, 3081–3083.

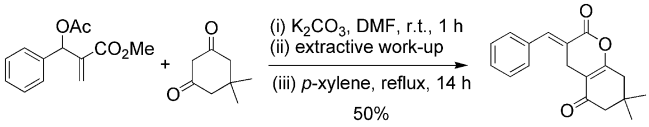
[5] For leading reviews on the Baylis–Hillman reaction, see: a) V. Declerck, J. Martinez, F. Lamaty, *Chem. Rev.* **2009**, *109*, 1–48; b) V. Singh, S. Batra, *Tetrahedron* **2008**, *64*, 4511–4574; c) D. Basavaiah, K. V. Rao, R. J. Reddy, *Chem. Soc. Rev.* **2007**, *36*, 1581–1588; d) G. Masson, C. Housseman, J. Zhu, *Angew. Chem.* **2007**, *119*, 4698–4712; *Angew. Chem. Int. Ed.* **2007**, *46*, 4614–4628; e) D. Basavaiah, A. J. Rao, T. Satyanarayana, *Chem. Rev.* **2003**, *103*, 811–891; f) E. Ciganek in *Organic Reactions* (Ed.: L. A. Paquette), Wiley, New York, **1997**, vol. 51, pp. 201–350; g) D. Basavaiah, P. D. Rao, R. S. Hyma, *Tetrahedron* **1996**, *52*, 8001–8062; h) S. E. Drewes, G. H. P. Roos, *Tetrahedron* **1988**, *44*, 4653–4670.

[6] a) G.-N. Ma, J.-J. Jiang, M. Shi, Y. Wei, *Chem. Commun.* **2009**, 5496–5514; b) G. W. Amarante, H. M. S. Milagre, B. G. Vaz, B. R. V. Ferreira, M. N. Eberlin, F. Coelho, *J. Org. Chem.* **2009**, *74*, 3031–3037; c) A. Trofimov, V. Gevorgyan, *Org. Lett.* **2009**, *11*, 253–255; d) I. Deb, P. Shanbhag, S. M. Mobin, I. N. N. Namboothiri, *Eur. J. Org. Chem.* **2009**, 4091–4101; e) M. E. Krafft, T. F. N. Haxell, K. A. Seibert, K. A. Abboud, *J. Am. Chem. Soc.* **2006**, *128*, 4174–4175; f) T. Turki, J. Villieras, H. Amri, *Tetrahedron Lett.* **2005**, *46*, 3071–3072; g) T. G. Back, D. A. Rankic, J. M. Sorbetti, J. E. Wulff, *Org. Lett.* **2005**, *7*, 2377–2379; h) V. Nair, K. G. Abhilash, *Synthesis* **2005**, 1967–1970; i) B. G. Jellerichs, J.-R. Kong, M. J. Krische, *J. Am. Chem. Soc.* **2003**, *125*, 7758–7759; j) D. Basavaiah, B. Sreenivasalu, A. J. Rao, *J. Org. Chem.* **2003**, *68*, 5983–5991; k) D. Basavaiah, M. Bakthadoss, G. Jayapal Reddy, *Synthesis* **2001**, 919–923; l) G. Li, J. Gao, H.-X. Wei, M. Enright, *Org. Lett.* **2000**, *2*, 617–620; m) K.-S. Yang, K. Chen, *Org. Lett.* **2000**, *2*, 729–731; n) D. Basavaiah, V. V. L. Gowriswari, T. K. Bharathi, *Tetrahedron Lett.* **1987**, *28*, 4591–4592; o) H. Amri, J. Villieras, *Tetrahedron Lett.* **1986**, *27*, 4307–4308.

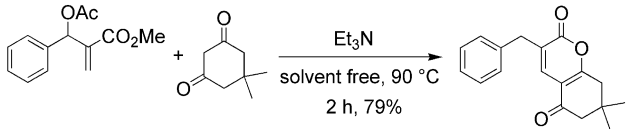
[7] a) T. Gendrineau, N. Demoulin, L. Navarre, J.-P. Genet, S. Darses, *Chem. Eur. J.* **2009**, *15*, 4710–4715; b) M. Bakthadoss, G. Sivakumar, D. Kannan, *Org. Lett.* **2009**, *11*, 4466–4469; c) L. D. S. Yadav, C. Awasthi, *Tetrahedron Lett.* **2009**, *50*, 3801–3804; d) V. Singh, V. Singh, S. Batra, *Eur. J. Org. Chem.* **2008**,

5446–5460; e) Z. Shafiq, L. Liu, Z. Liu, D. Wang, Y.-J. Chen, *Org. Lett.* **2007**, *9*, 2525–2528; f) P. Shanmugam, B. Viswambharan, S. Madhavan, *Org. Lett.* **2007**, *9*, 4095–4098; g) S. I. Lee, G.-S. Hwang, S. C. Shin, T. G. Lee, R. H. Jo, D. H. Ryu, *Org. Lett.* **2007**, *9*, 5087–5089; h) S. Gowrisankar, K. Y. Lee, C. G. Lee, J. N. Kim, *Tetrahedron Lett.* **2004**, *45*, 6141–6146; i) G. W. Kabalka, B. Venkataiah, G. Dong, *J. Org. Chem.* **2004**, *69*, 5807–5809; j) D. Basavaiah, R. M. Reddy, *Tetrahedron Lett.* **2001**, *42*, 3025–3027; k) D. Basavaiah, P. K. S. Sarma, *J. Chem. Soc., Chem. Commun.* **1992**, 955–957; l) M. L. Bode, P. T. Kaye, *J. Chem. Soc. Perkin Trans. 1* **1990**, 2612–2613.

[8] a) Kim and co-workers prepared (*E*)-4-benzylidene-9,9-dimethyl-2-oxabicyclo[4.4.0]dec-1(6)-ene-3,7-dione according to the equation given below. Its melting point and its ^{1}H and ^{13}C NMR spectroscopic data are reported. Our data is in agreement with that of the literature data (S. C. Kim, H. S. Lee, J. N. Kim, *Bull. Korean Chem. Soc.* **2007**, *28*, 147–150).



b) Su and co-workers reported the synthesis of 4-benzyl-9,9-dimethyl-2-oxabicyclo[4.4.0]deca-1(6),4-diene-3,7-dione by following the procedure given below (W. Zhong, Y. Zhao, W. Su, *Tetrahedron* **2008**, *64*, 5491–5496).



[9] CCDC-750184 (for **5**), -750185 (for **10**), -750186 (for **13**), and -750187 (for **16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: December 20, 2009
Published Online: March 1, 2010

