DOI: 10.1002/adsc.201000828

N-Heterocyclic Carbene Catalyzed Intramolecular Hydroacylation of Activated Alkynes: Synthesis of Chromones

Seenuvasan Vedachalam,[a] Qian-Ling Wong,[a] Biswajit Maji,[a] Jing Zeng,[a] Jimei Ma,[a] and Xue-Wei Liu[a,*]

[a] Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371
Fax: (+65)-67911961; e-mail: xuewei@ntu.edu.sg

Received: November 4, 2010; Published online: February 8, 2011

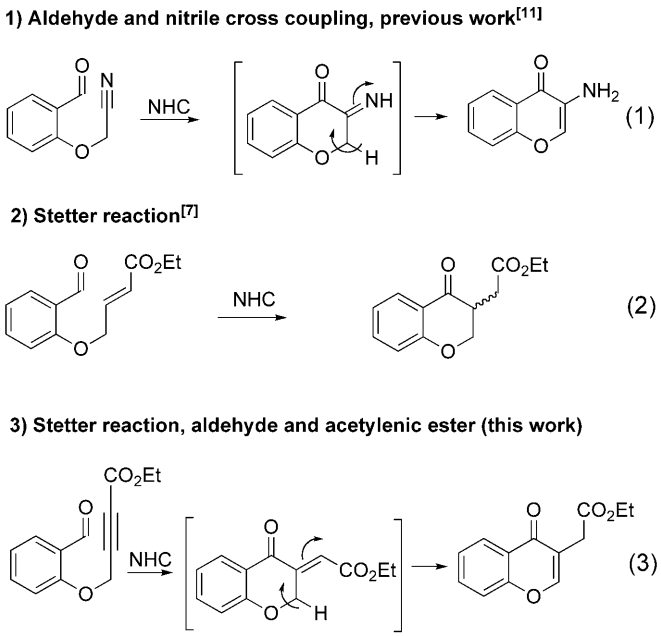
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000828.

Abstract: An organocatalytic intramolecular Stetter-type hydroacylation reaction between an aldehyde and an activated alkyne has been developed. This study induces salicylaldehyde-derived alkyne derivatives to assemble into a series of chromone derivatives using a catalytic amount of thiazolium-based carbene catalyst.

Keywords: chromones; hydroacylation; N-heterocyclic carbenes; organocatalysis; Stetter reaction

Over the past few decades, the development of N-heterocyclic carbenes (NHC) has made important headways due to their extensive applicability in several reactions.[1] Besides the role as excellent ligands in the metal-catalyzed reactions,[2a–c] their ability to efficiently catalyze a number of organic reactions, most notably benzoin condensation,[2d–j] Stetter reaction,[3] transesterification[3h] and homo-enolate addition,[4] has contributed significantly to organic transformations. In 1973, Stetter established the first conjugate addition of aldehydes to α,β-unsaturated ester adopting the cyanide ion as the initial catalyst,[5a] and subsequently using a thiazolium-based carbene catalyst.[5b,c] The recent intermolecular variants of the Stetter reaction set in motion an expanding usage of NHCs as organocatalysts for carbon-carbon bond formation.[6] By exploiting an intramolecular Stetter reaction, Trost[7a] constructed a tricyclic system in order to synthesize hirsutic acid. Pioneering studies carried out by Ciganek,[7b] Enders[7c] and Rovis[7d,e] resulted in the development of intramolecular cyclizations as an access to various chromones. In addition, Glorius[8a,b] and She[8c] embarked on intramolecular acyl anion additions to unactivated olefin to construct the chromone scaffolds.

Chromones are useful heterocyclic motifs found commonly in pharmaceutical compounds and they often exhibit fascinating therapeutic effects.[9] Our interest in drug discovery[10] motivated us to devise new methodologies for the chromone synthesis. Recently, we reported an NHC-catalyzed intramolecular cross-coupling between the aldehyde and the nitrile function to afford 3-aminochromones in high yields[11] [Scheme 1, Eq. (1)]. A comparison of this chemistry to that of the Stetter reaction [Scheme 1, Eq. (2)] prompted us to investigate the possibility of a newly designed carbon-carbon bond forming reaction



Scheme 1. NHC-catalyzed C–C bond formation strategy.

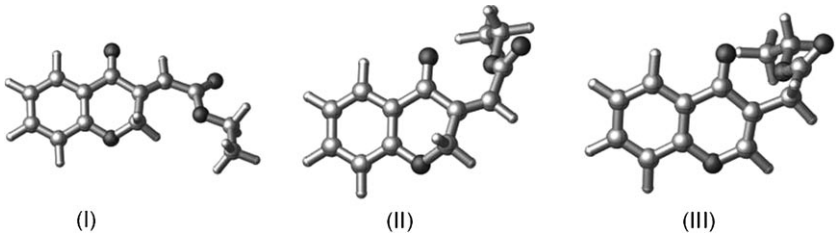
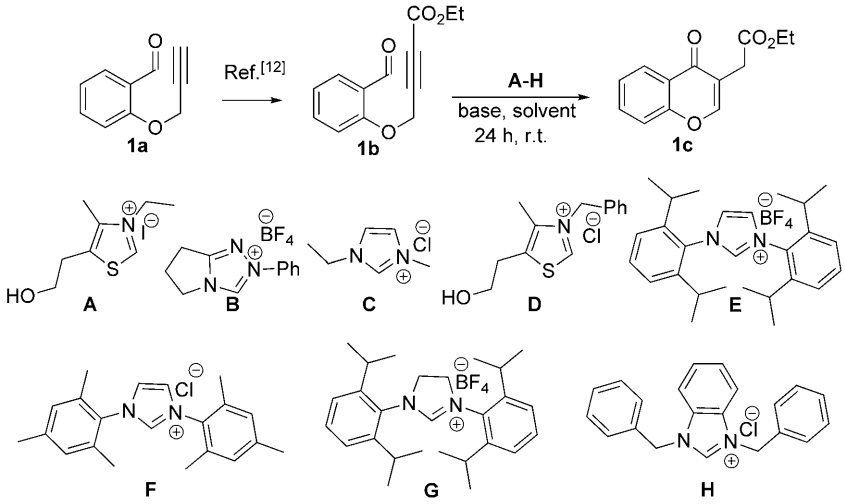


Figure 1. Conformational analysis of the exocyclic-Stetter type products (**I** and **II**) and the stable aromatized product (**III**).

[Scheme 1, Eq. (3)]. Our proposed strategy involves the intramolecular reaction of an aldehyde and an activated alkyne (e.g., acetylenic ester) based on our previous work[10] and a DFT calculation, in which aromatized chromones are formed from the less favored *exo*-cyclic double bond. The calculated energy profiles[12] (Figure 1, DFT, B3LYP/6-31G* level) of the exocyclic Stetter product and the aromatized product

Table 1. Optimization of reaction conditions.



Entry[a]	Catalyst (equiv.)	Base[b]	Sovent (0.1 M)	Yield [%][c]
1	A (0.2)	DBU	DCM	53
2	B (0.2)	DBU	DCM	30
3	C (0.2)	DBU	DCM	-
4	**D (0.2)**	**DBU**	**DCM**	**64**
5	E (0.2)	DBU	DCM	-
6	F (0.2)	DBU	DCM	-
7	G (0.2)	DBU	DCM	-
8	H (0.2)	DBU	DCM	20
9	D (0.2)	DBU	THF	58
10	D (0.2)	DBU	*t*-BuOH	53
11	D (0.2)	DBU	toluene	35
12	D (0.2)	DBU	CH_3CN	52
13	**D (0.2)**	**DBU**	**DMF**	**77**
14	D (0.2)	DIPEA	DMF	78
15	**D (0.2)**	**Et_3N**	**DMF**	**83**
16	D (0.2)	Cs_2CO_3	DMF	74
17	D (0.2)	KHMDS	DMF	62

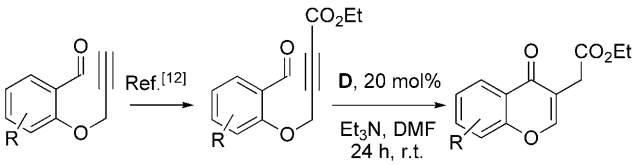
[a] Unless otherwise specified, all of the reactions were carried out with freshly distilled dry solvents at room temperature for 24 h.
[b] Equal mol% with respect to catalyst.
[c] Yield of isolated product.

show that the exocyclic double bond **I** is higher in energy (ΔE, 12.8 kcal mol^{-1}) than the aromatized **III**, thus providing a driving force for the isomerization to chromone **III**. Indeed, the exocyclic double bond could be as in conformation **I**, because the conformation **II** is associated with a higher energy (ΔE, 3.5 kcal mol^{-1}) than conformation **I**. To test the feasibility of the above reaction [Scheme 1, Eq. (3)], a number of NHC catalysts were screened and the results are summarized in Table 1.

We began our investigation by using simple phenyl substrate **1b** as a control variable in order to optimize the reaction conditions. The initial screening was conducted at room temperature for 24 h with 20 mol% of the imidazolium, triazolium or thiazolium catalysts (**A**–**H**) utilizing 20 mol% of DBU as the base and dichloromethane (DCM, 0.1 M) as the solvent (Table 1, entries 1–8). Thiazolium salt **D** (entry 4) afforded the chromones in highest yield (64%) among the catalyst precursors. Subsequently, the effects of various solvents on the reaction were examined using catalyst **D** as a control (entries 9–13). The use of DMF exhibited a promising yield of 77% (entry 13). Using catalyst **D** and DMF as the solvent, we varied the bases (entries 14–17) and found that mild bases afforded higher yields than strong bases. Et_3N was observed to be the most suitable base (entry 15). Thus, the optimized conditions were established to be as follows: thiazolium salt **D** as the pre-catalyst, Et_3N as the base, DMF as the solvent and stirring at room temperature for 24 h.

We found that the aforementioned optimized conditions are applicable for the vast majority of substrates tested in the chromone-forming Stetter-type hydroacylation reaction. The access to the starting materials,[12] that is, activated alkyne derivatives was developed from corresponding salicylaldehyde derivatives which dramatically expanded the substrate scope (Table 2 and Table 3). In preliminary efforts, a range of substrates with varied alkyl substituents on the phenyl group of the salicylaldehyde-derived acetylenic esters afford good yields (Table 2, entries 1–5). While investigating the substrate scope, we extended the study to electron-donating substituents and these

Table 2. Reaction scope for chromone derivatives.



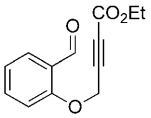
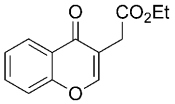
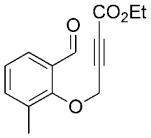
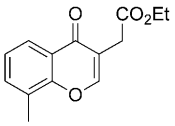
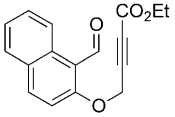
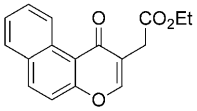
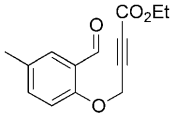
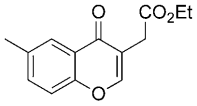
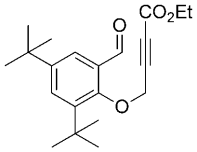
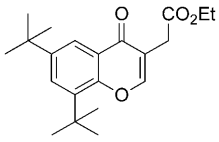
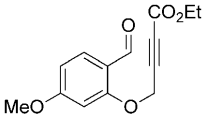
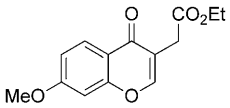
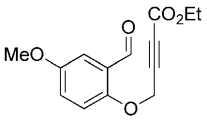
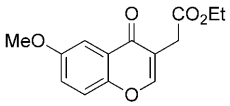
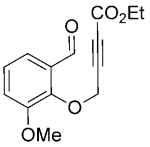
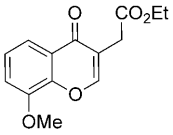
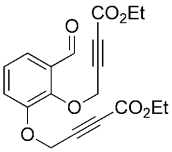
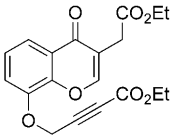
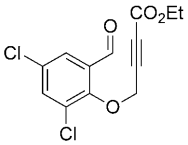
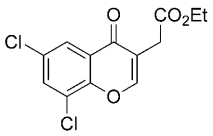
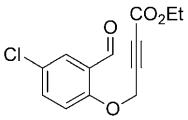
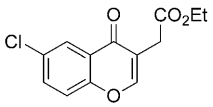
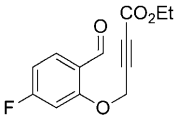
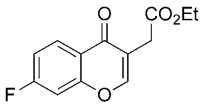
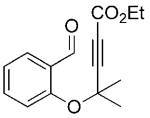
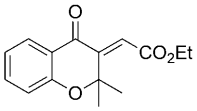
Entry	Substrate[a]		Product		Yield [%][b]
1		**1b**		**1c**	83
2		**2b**		**2c**	86
3		**3b**		**3c**	84
4		**4b**		**4c**	90
5		**5b**		**5c**	76

Table 2. (Continued)

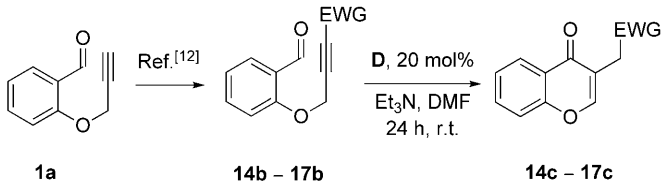
Entry	Substrate[a]		Product		Yield [%][b]
6		**6b**		**6c**	92
7		**7b**		**7c**	88
8		**8b**		**8c**	85
9		**9b**		**9c**	80
10		**10b**		**10c**	78
11		**11b**		**11c**	76
12		**12b**		**12c**	80
13		**13b**		**13c**	78

[a] See the Supporting Information for a detailed experimental procedure.
[b] Yield of isolated product.

delivered chromones in good to excellent yields (80–92%, entries 6–9). Similar extension of the present methodology to electron-withdrawing substituents, such as the halides, also gave the desired chromones in good yields (75–82%, entries 10–12). However, we were not able to synthesize nitro-substituted reactants to investigate their reactivities, although current data suggest that variations made to the phenyl motif have minimal impact on this carbon-carbon bond forming reaction. Substituting the two α-hydrogens of the alkyne moiety with two methyl groups also has little impact on the product yield (Table 2, entry 13). As highlighted in Table 3, we were pleased to find that the reaction was also suitable for the substrates possessing a ketone moiety as the electron-withdrawing group such as acetyl, trimethylacetyl, benzoyl and phenylacetyl functionalities, which were found to furnish products to further broaden the synthetic utility and tolerance of the NHC-catalyzed reaction (Table 3, entries 1–4). All in all, this new method allows the preparation of a range of chromone derivatives in a straightforward manner.

With our current synthetic methodology, the success of the reaction mainly relies on the electron-withdrawing group of the propargyl moiety. We had attempted to use the simple propargyl surrogate **1a**[8a] without electron-withdrawing groups but it was observed that the intermolecular benzoin product in-

Table 3. Reaction scope of carbonyl Michael acceptors.



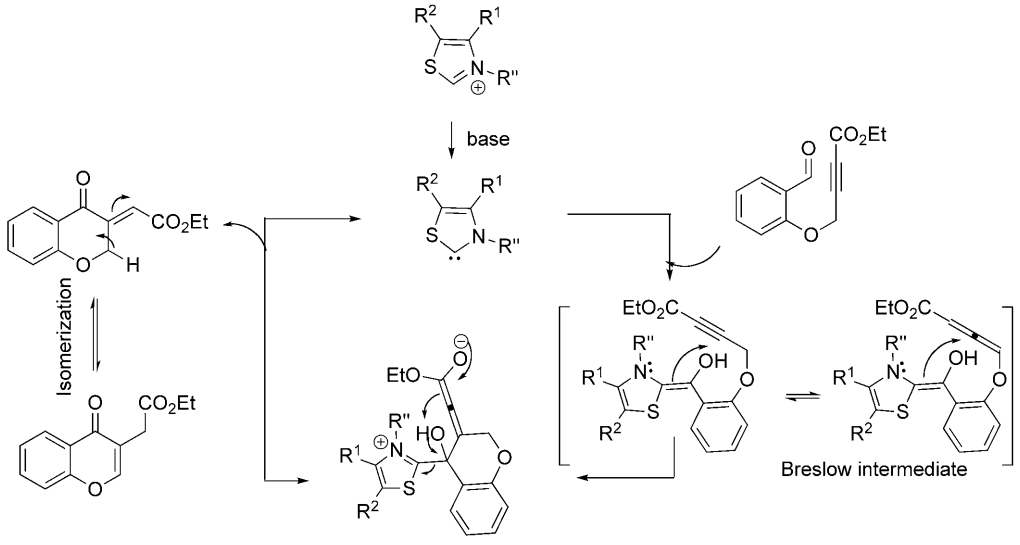
1a 14b – 17b 14c – 17c

Entry	Substrate[a]	EWG	Product	Yield [%][b]
1	**14b**	CH_3CO-	**14c**	74
2	**15b**	*t*-BuCO−	**15c**	72
3	**16b**	PhCO−	**16c**	66
4	**17b**	$PhCH_2CO-$	**17c**	68

[a] See the Supporting Information for a detailed experimental procedure.
[b] Yield of isolated product.

stead of the desired hydroacylation product was formed. However, Glorius et al. recently reported a hydroacylation reaction using a hindered carbene from the same surrogate (**1a**) and salicylaldehyde-derived unactivated olefin which might involve a Coniaene-type reaction at higher temperature.[8a,b] In contrast to our reaction system, the reaction progress does not terminate in the exocyclic Stetter-type product and subsequent isomerization forms the aromatized chromone at room temperature. Indeed, several control experiments were carried out with the intermolecular reaction between benzaldehyde and methyl phenylpropiolate or dimethyl acetylenedicarboxylate (DMAD) under the optimized conditions and which could not support the viability of this pathway. Apparently, Nair and Ma[13] demonstrated the intermolecular reaction between an activated alkyne (DMAD) and an aldehyde using a quantitative amount of imidazolium or thiazolium NHC catalyst to obtain highly functionalized furanone derivatives which highlights the absence of Stetter-type products in the reaction. Based on our system, we infer that both reactive species are in close proximity to each other, allowing the formation of the Stetter-type product instead of other products which arises from the hydroxy enamine having a harder oxygen or the alkyne as the first reacting species. Significantly, this type of intramolecular hydroacylation reaction allowed us to develop a new class of heterocycles at room temperature. A reasonable mechanism may be formulated as shown in Scheme 2. We propose that the carbene first performs a nucleophilic attack on the electrophilic carbonyl carbon of the aldehyde. Subsequent proton transfer results in an acyl anion equivalent[14] (Breslow intermediate) which acts as a nucleophilic carbon to attack the Michael acceptor (activated alkyne) thus forming a carbon-carbon bond. Proton exchange followed by elimination of the catalyst results in the *exo*cyclic kinetic product. This exocyclic hydroacylation product undergoes isomerization to give the aromatized product, driven by the energetics of the system as previously discussed.

In conclusion, the present methodology demonstrates the unique reactivity of these catalytically generated nucleophilic precursors and their subsequent Stetter character with activated alkynes. This versatile mechanistic platform can be applied not only to chromone products, but can also be further extended for use in other novel synthetic methodologies. The catalytic activity of the catalyst **D** is remarkable especially in view of its low cost and commercial availability. This method also adds to the expanding use of organocatalyst-based heterocycle synthesis which has been



Scheme 2. Plausible reaction mechanism.

investigated less than the metal-catalyzed counterparts.

Experimental Section

Typical Procedure for the Intramolecular Chromone-Forming Stetter-Type Hydroacylation Reaction, as Exemplified for the Formation of Ethyl 2-(4-Oxo-4*H*-chromen-3-yl)acetate (1c)

Precatalyst **D** (12 mg, 0.043 mmol, 0.2 equiv.) and **1b** (50 mg, 0.216 mmol, 1 equiv.) were suspended with anhydrous DMF (1 mL) in an oven-dried, round-bottom flask under a nitrogen atmosphere at room temperature. Et_3N (6 μL, 0.043 mmol, 0.2 equiv.) was added *via* micro syringe to the reaction mixture which was then allowed to stir for 24 h at room temperature. The progress of the reaction was monitored using TLC. Upon completion, the reaction mixture was diluted with ethyl acetate (20 mL), washed with water (3×20 mL), followed by brine (2×10 mL), and then dried over Na_2SO_4. The solvent was removed and the crude product was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate 5:1) to afford **1c** as a pale white solid; yield: 41.5 mg (83%); m.p. 79–81 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.21$ (dd, $J_1=8.0$ Hz, $J_2=1.6$ Hz, 1H), 7.94 (s, 1H), 7.68–7.63 (m, 1H), 7.45–7.36 (m, 2H), 4.18 (q, $J=7.1$ Hz, 2H), 3.47 (s, 2H), 1.27 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=176.9$, 170.6, 156.5, 153.7, 133.6, 125.9, 125.1, 123.6, 118.4, 118.0, 61.0, 30.9, 14.1; FT-IR (KBr): $\nu_{max}=3078$, 2978, 1739, 1610, 1477, 1344, 1205, 1028, 759 cm^{-1}; HR-MS (ESI): $m/z=233.0815$, calcd. for $C_{13}H_{13}O_4$ $[M+H]^+$: 233.0814.

Acknowledgements

Financial supports from Nanyang Technological University (RG50/08) and the Ministry of Health, Singapore (NMRC/H1N1R/001/2009) are gratefully acknowledged. We thank Dr. Yong-Xin Li for X-ray analyses and also thank Drs. Guan Leong Chua and Guofu Zhong for proofreading this manuscript.

References

[1] a) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746; b) V. Nair, S. Vellalath, B. P. Babu, *Chem. Soc. Rev.* **2008**, *37*, 2691; c) N. Marion, S. Díez-González, S. P. Nolan, *Angew. Chem.* **2007**, *119*, 3046; *Angew. Chem. Int. Ed.* **2007**, *46*, 2988; d) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606; e) C. Burstein, F. Glorius, *Angew. Chem.* **2004**, *116*, 6331; *Angew. Chem. Int. Ed.* **2004**, *43*, 6205; f) A. H. Wolfgang, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162; g) A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361; h) D. Seebach, *Angew. Chem.* **1979**, *91*, 259; *Angew. Chem. Int. Ed. Engl.***1979**, *18*, 239; i) H. W. Wanzlick, *Angew. Chem.* **1962**, *74*, 129; *Angew. Chem. Int. Ed.* Zeitschrift wurde noch nicht gegründet! **1962**, *1*, 75.

[2] a) R. Corberán, E. Mas-Marzá, E. Peris, *Eur. J. Inorg. Chem.* **2009**, 1700; b) N. Marion, R. S. Ramón, S. P. Nolan, *J. Am. Chem. Soc.* **2009**, *131*, 448; c) T. W. Hudnall, C. W. Bielawski, *J. Am. Chem. Soc.* **2009**, *131*, 16039; d) L. Baragwanath, C. A. Rose, K. Zeitler, S. J. Connon, *J. Org. Chem.* **2009**, *74*, 9214; e) D. Enders, O. Niemeier, G. Raabe, *Synlett* **2006**, 2431; f) D. Enders, O. Niemeier, T. Balensiefer, *Angew. Chem.* **2006**, *118*, 1491; *Angew. Chem. Int. Ed.* **2006**, *45*, 1463; g) Y. Hachisu, J. W. Bode, K. Suzuki, *Adv. Synth. Catal.* **2004**, *346*, 1097; h) T. Dudding, K. N. Houk, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5770; i) Y. Hachisu, J. W. Bode, K. Suzuki, *J. Am. Chem. Soc.* **2003**, *125*, 8432; j) D. Enders, U. Kallfass, *Angew. Chem.* **2002**, *114*, 1822; *Angew. Chem. Int. Ed.* **2002**, *41*, 1743.

[3] a) J. R. deAlaniz, T. Rovis, *Synlett* **2009**, 1189; b) K. J. Hawkes, B. F. Yates, *Eur. J. Org. Chem.* **2008**, 5563; c) D. Enders, J. Han, *Synthesis* **2008**, 3864; d) A. E. Mattson, A. M. Zuhl, T. E. Reynolds, K. A. Scheidt, *J. Am. Chem. Soc.* **2006**, *128*, 2552; e) J. Read deAlaniz, T. Rovis, *J. Am. Chem. Soc.* **2005**, *127*, 6284; f) S. M. Mennen, J. T. Blank, M. B. Tran-Dubé, J. E. Imbriglio, S. J. Miller, *Chem. Commun.* **2005**, 195; g) A. G. M. Barrett, A. C. Love, L. Tedeschi, *Org. Lett.* **2004**, *6*, 3377; h) R. S. A. Grasa, R. Singh, S. P. Nolan, *Synthesis* **2004**, 971; i) M. S. Kerr, J. Read deAlaniz, T. Rovis, *J. Am. Chem. Soc.* **2002**, *124*, 10298; j) R. U. Braun, K. Zeitler, T. J. J. Muller, *Org. Lett.* **2001**, *3*, 3297.

[4] a) C. Burstein, F. Glorius, *Angew. Chem.* **2004**, *116*, 6331; *Angew. Chem. Int. Ed.* **2004**, *43*, 6205; b) S. S. Sohn, E. L. Rosen, J. W. Bode, *J. Am. Chem. Soc.* **2004**, *126*, 14370; c) V. Nair, C. R. Sinu, B. P. Babu, V. Varghese, A. Jose, E. Suresh, *Org. Lett.* **2009**, *11*, 5570; d) P.-C. Chiang, M. Rommel, J. W. Bode, *J. Am. Chem. Soc.* **2009**, *131*, 8714; e) E. M. Phillips, T. E. Reynolds, K. A. Scheidt, *J. Am. Chem. Soc.* **2008**, *130*, 2416; f) V. Nair, S. Vellalath, M. Poonoth, E. Suresh, *J. Am. Chem. Soc.* **2006**, *128*, 8736.

[5] a) H. Stetter, M. Schreckenberg, *Angew. Chem.* **1973**, *85*, 89; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 81; b) H. Stetter, *Angew. Chem.* **1976**, *88*, 695; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 639; c) H. Stetter, H. Kuhlmann, *Synthesis* **1975**, 379.

[6] a) Q. Liu, T. Rovis, *Org. Lett.* **2009**, *11*, 2856; b) Y. Li, F.-Q. Shi, Q.-L. He, S.-L. You, *Org. Lett.* **2009**, *11*, 3182; c) D. A. DiRocco, K. M. Oberg, D. M. Dalton, T. Rovis, *J. Am. Chem. Soc.* **2009**, *131*, 10872; d) Q. Liu, S. P. Perreault, T. Rovis, *J. Am. Chem. Soc.* **2008**, *130*, 14066.

[7] a) B. M. Trost, C. D. Shuey, F. DiNinno, *J. Am. Chem. Soc.* **1979**, *101*, 1284; b) E. Ciganek, *Synthesis* **1995**, 1311; c) D. Enders, K. Breuer, J. Runsink, J. H. Teles, *Helv. Chim. Acta* **1996**, *79*, 1899; d) J. R. deAlaniz, M. S. Kerr, J. L. Moore, T. Rovis, *J. Org. Chem.* **2008**, *73*, 2033; e) M. S. Kerr, T. Rovis, *J. Am. Chem. Soc.* **2004**, *126*, 8876.

[8] For reports on hydroacylation of unactivated alkynes and alkene using sterically hindered carbenes, see: a) A. T. Biju, N. E. Wurz, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 5970; b) K. Hirano, A. T. Biju, I. Piel, F. Glo-

rius, *J. Am. Chem. Soc.* **2009**, *131*, 14190; c) J. He, S. Tang, J. Liu, Y. Su, X. Pan, X. She, *Tetrahedron* **2008**, *64*, 8797.

[9] a) S. Gobbi, A. Cavalli, A. Rampa, F. Belluti, L. Piazzi, A. Paluszcak, R. W. Hartmann, M. Recanatini, A. Bisi, *J. Med. Chem.* **2006**, *49*, 4777; b) B. P. Nutley, N. F. Smith, A. Hayes, L. R. Kelland, L. Brunton, B. T. Golding, G. C. M. Smith, N. M. B. Martin, P. Workman, F. I. Raynaud, *Br. J. Cancer* **2005**, *93*, 1011.

[10] a) R. Lorpitthaya, Z. Z. Xie, K. B. Sophy, J. L. Luo, X.-W. Liu, *Chem. Eur. J.* **2010**, *16*, 588; b) B. K. Gorityala, R. Lorpitthaya, Y. Bai, X.-W. Liu, *Tetrahedron* **2009**, *65*, 5844; c) R. Y. Yang, K. K. Pasunooti, F. Li, X.-W. Liu, C.-F. Liu, *J. Am. Chem. Soc.* **2009**, *131*, 13592; d) B. K. Gorityala, S. T. Cai, R. Lorpitthaya, J. M. Ma, K. K. Pasunooti, X.-W. Liu, *Tetrahedron Lett.* **2009**, *50*, 676; e) X.-W. Liu, T. N. Le, Y. P. Lu, Y. J. Xiao, J. M. Ma, X. Li, *Org. Biomol. Chem.* **2008**, *6*, 3997; f) R. Lorpitthaya, Z. Z. Xie, J. L. Kuo, X.-W. Liu, *Chem. Eur. J.* **2008**, *14*, 1561; g) R. Lorpitthaya, K. B. Sophy, J. L. Luo, X.-W. Liu, *Org. Biomol. Chem.* **2009**, *7*, 1284.

[11] S. Vedachalam, J. Zeng, B. K. Gorityala, M. Antonio, X.-W. Liu, *Org. Lett.* **2010**, *12*, 352.

[12] See the detailed experimental procedure and calculation data in the Supporting Information. CCDC 793190 and CCDC 793191 contain the supplementary crystallographic data for the compounds **8c** and **15c** of this paper, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[13] a) V. Nair, V. Sreekumar, S. Bindu, E. Suresh, *Org. Lett.* **2005**, *7*, 2297; b) C. Ma, Y. Yang, *Org. Lett.* **2005**, *7*, 1343; c) C. Ma, H. Ding, G. Wu, Y. Yang, *J. Org. Chem.* **2005**, *70*, 8919; d) V. Nair, S. Bindu, V. Sreekumar, N. P. Rath, *Org. Lett.* **2003**, *5*, 665.

[14] a) R. Breslow, C. Schmuck, *Tetrahedron Lett.* **1996**, *37*, 8241; b) R. Breslow, R. Kim, *Tetrahedron Lett.* **1994**, *35*, 699; c) R. Breslow, E. Kool, *Tetrahedron Lett.* **1988**, *29*, 1635; d) R. Breslow, *J. Am. Chem. Soc.* **1958**, *80*, 3719.

