Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron Letters 46 (2005) 2593–2597
Tetrahedron Letters

Synthesis of arenediynes via the vinylidenecarbene–acetylene rearrangement

Bichismita Sahu,[a] Irishi N. N. Namboothiri[a,*] and Rachel Persky[b]

[a]*Department of Chemistry, Indian Institute of Technology, Bombay, Mumbai 400 076, India*
[b]*Department of Chemistry, Bar-Ilan University, Ramat Gan 52900, Israel*

Received 26 December 2004; revised 7 February 2005; accepted 15 February 2005

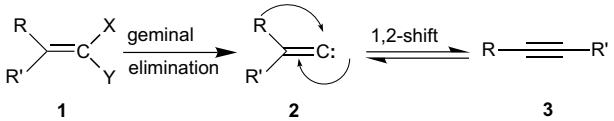
Dedicated to Professor A. P. Marchand on the occasion of his 65th birthday

Abstract—A convenient method for the two-step synthesis of arenediynes from 1,2-arenedialdehydes is reported. Dibromomethylenation of dialdehydes under Corey–Fuchs conditions (CBr_4, Ph_3P, Zn) provides the tetrabromides in excellent yields. Treatment of the tetrabromides with *n*-BuLi or LDA affords 3,4-unsaturated 1,5-diynes, the key structural moiety present in several naturally occurring antitumour antibiotics, in varying yields. The key intermediates in these transformations appear to be vinylidenecarbenes or carbenoids, generated in situ via metal–halogen exchange and elimination.

The enediyne natural products containing a (*Z*)-3-hexen-1,5-diyne moiety belong to five different classes of natural products such as calicheamicin, esperamicin, dynemicin, kedarcidin and C-1027 and are amongst the most potent antitumour agents known to date.[1] The key steps in the antitumour activity of enediynes are Bergman cyclization[1,2] to give 1,4-dehydroarene biradicals and abstraction of hydrogen from DNA by the latter thereby inflicting permanent damage on the genetic material.

Given the structural complexity of the naturally occurring enediyne antitumour agents, design and synthesis of simple structures that can mimic the biological activity of these natural products is important. The methods available for the construction of *Z*-enediyne subunits, in both linear and cyclic form, include the Pd catalyzed alkynylation[3] of 1,2-dihalides[3,4] or 1,2-ditriflates[5,6] of alkenes or arenes. While 1,2-dihalides are often expensive and/or difficult to prepare, complex mixtures are often encountered in the case of triflates.[5] Other related metal-mediated methods[7] are essentially multistep reaction sequences and are complicated by the requirement for highly sensitive and often toxic organometallic reagents. Thermal (Diels–Alder),[8] photochemical (Norrish type II)[9] and several elimination[10] methods employed to introduce a double bond between and in conjugation with a 1,5-diyne are specific to a narrow range of substrates.

In this context, a fundamentally novel approach to the synthetic analogues of the enediyne antibiotics based on the rearrangement of a vinylidenecarbene to its corresponding acetylene (Fritsch–Buttenberg–Wiechell rearrangement)[11] is reported here. Although the FBW rearrangement (Scheme 1),[11–14] has been employed for the synthesis of acetylenes[15] and its applications to numerous systems in which the migrating group is an alkyl, aryl or heteroaryl group have been reported,[16,17] there is no report, to our knowledge, of the synthesis of 3,4-unsaturated 1,5-diynes (enediynes) **7** from

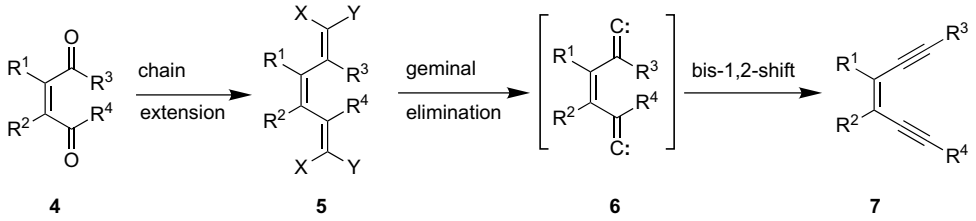


1a: X = H, Y = Br, NH_2, OTf, N=NTs; **1b:** X = $SiMe_3$, Y = Cl, OTf, IPhOTf; **1c:** X = Cl, Y = S (O)Tol; **1d:** X = Y = Br; **1e**: XY = N_2; **1f**: XY = -$COOC(CH_3)_2OCO$-

Scheme 1. 1a–f: R, R′ = alkyl, aryl, heteroaryl or H.

Keywords: Enediynes; Vinylidenecarbene; Fritsch–Buttenberg–Wiechell rearrangement.
* Corresponding author. Tel.: +91 22 2576 7196; Fax: +91 22 2576 7152; e-mail: irishi@iitb.ac.in

0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.02.101



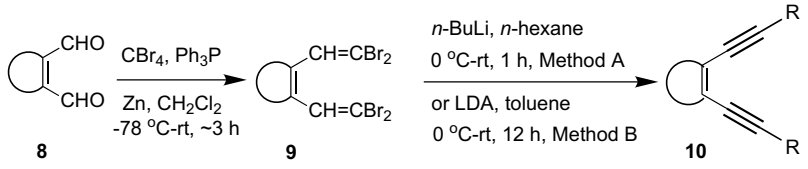
Scheme 2.

2,3-unsaturated 1,4-dicarbonyl compounds **4** via a 2,3-unsaturated 1,4-bis-vinylidenecarbene **6** (Scheme 2).[18] The use of complex organometallic reagents and cumbersome reaction conditions are also obviated in this method.

In fact, a variety of geminal elimination methods such as deprotonation–elimination from **1a**, desilylation–elimination from **1b**, metal–halogen exchange–elimination from **1c**[19] or **1d**, elimination of N_2 from **1e**,[20] cycloelimination via pyrolysis from **1f**, etc., is available for the generation of vinylidenecarbenes **2**.[12,13] Among these, the metal–halogen exchange–elimination from **1d** appears to be the most convenient method as **1d** is easily accessible via dihalomethylenation of an aldehyde[21–23] or a ketone.[24]

In view of the above, we have subjected a variety of symmetrical and unsymmetrical 1,2-arenedialdehydes **8a–g** to the dibromomethylenation conditions (Table 1, columns 1–3). Optimization of the dibromomethylenation procedure using phthalaldehyde **8a** as the model substrate showed that 4 equiv of CBr_4, 8 equiv of Ph_3P and 8 equiv of Zn dust were necessary to obtain the best yield (94%) of the tetrabromide **9a** (Table 1, entry a, columns 1–3). Exclusion of Zn dust or lowering the amount of the reagents (e.g., 3 equiv of CBr_4, 6 equiv of Ph_3P and 6 equiv of Zn dust) led to substantial reduction in the yields (68% and 56%, respectively). Subsequently, 1,2-dialdehydes **8b–g** were converted to their corresponding tetrabromides **9b–g** under the optimized conditions in good to excellent yields (Table 1, entries b–g, columns 1–3).

Table 1. Preparation of tetrabromides **9** from 1,2-dialdehydes **8** and subsequent *n*-BuLi- and LDA-mediated transformation to enediynes **10**[a]



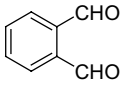
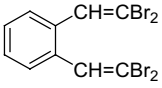
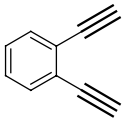
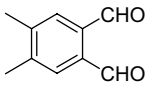
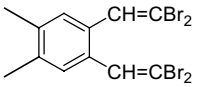
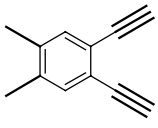
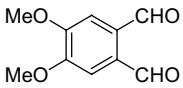
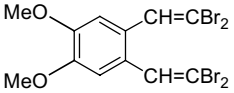
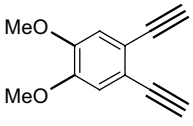
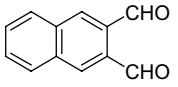
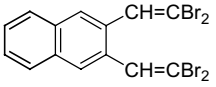
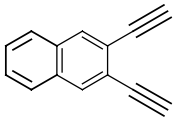
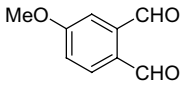
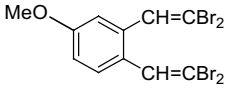
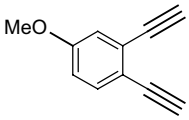
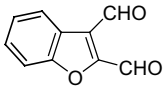
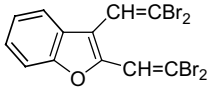
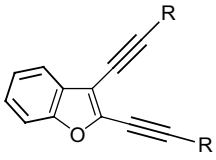
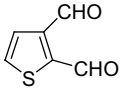
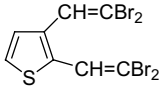
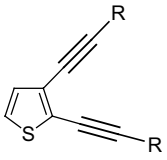
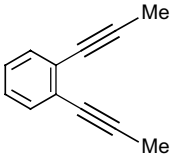
Entry	1 1,2-Dialdehydes **8**[b]	2 Tetrabromides **9**	3 % Yield of **9**	4 Enediynes **10**	5 % Yield of **10**	6
					Method A	Method B
a			94		96	88
b			62		84	68
c[c]			46		71	84
d			88		67	44

Table 1. (*continued*)

Entry	1 1,2-Dialdehydes **8**[b]	2 Tetrabromides **9**	3 % Yield of **9**	4 Enediynes **10**	5 % Yield of **10**	6
					Method A	Method B
e			66		91	87
f[d]			73		33	26
g[d]			95		43	31
h[e]	—	—	—		62	—

[a] All tetrabromides **9a–g** and enediynes **10a–h** provided satisfactory IR, ^{1}H NMR, ^{13}C NMR and HRMS data. Enediynes **10a–e** and **10g–h** are known compounds; see Ref. 26.

[b] The dialdehydes **8a** and **8g** are commercially available. All other dialdehydes, that is, **8b–f**, were prepared in the laboratory following published procedures; see Ref. 25.

[c] Heated at 70 °C for 4 h.

[d] The parent enediyne, due to its instability, was isolated as its bis-trimethylsilyl derivative (R = TMS).

[e] **10h** was formed after **10a** was treated with an additional amount of *n*-BuLi (2 equiv) and then quenched with MeI (R = Me).

The transformation of tetrabromides **9a–g** to enediynes **10a–g** was performed under two different sets of conditions, viz. using *n*-BuLi (Method A, Table 1, column 5) and LDA (Method B, Table 1, column 6). Under the optimized conditions of Method A, that is, with 6 equiv of *n*-BuLi in *n*-hexane as solvent at −78 °C, tetrabromide **9a** afforded the desired enediyne **10a** in excellent yield (96%, Table 1, entry a, column 5). While the yield was 23% when THF was used as solvent, toluene provided the enediyne **10a** in 78% yield. Similarly, the yields were <20% and 55% when 2 and 4 equiv of *n*-BuLi, respectively, were used. Other tetrabromides **9b–g** were subsequently subjected to the *n*-BuLi mediated transformation to enediynes **10b–g** (Table 1, entries b–g, column 5). Although tetrabromides **9b–e** provided the corresponding enediynes **10b–e**, respectively, in very high yields (Table 1, entries b–e, column 5), complex mixtures were isolated in the cases of tetrabromides **9f** and **9g** due to poor stability of the parent enediynes. The enediynes were subsequently isolated as their bis-trimethylsilyl derivatives by quenching the reaction mixtures with TMSCl (R = TMS, Table 1, entries f–g, column 5).

Comparable results were obtained when tetrabromides **9a–g** were reacted with LDA (Method B, Table 1, column 6). Optimization of the LDA-mediated transformation of tetrabromide **9a** to enediyne **10a**, was carried out by screening different solvents and by varying the amount of LDA. Among the solvents screened (THF, toluene and *n*-hexane), toluene was found to give the best yield (88%, Table 1, entry a, column 6). Excess LDA (6 equiv) was also necessary to achieve complete conversion of the starting material. Therefore, LDA (6 equiv) in toluene at –78 °C–rt was employed for the conversion of tetrabromides **9b–g** to enediynes **10b–g**. As in the case of the *n*-BuLi-mediated reactions of **9f** and **9g** (Table 1, entries f–g, column 5), the parent enediynes were transformed in situ to their TMS derivatives for isolation and characterization.

Finally, the enediynes synthesized by our methodology could be transformed to 1,6-disubstituted enediynes by generation and trapping of the acetylides in the same reaction vessel with appropriate electrophiles. For instance, enediyne **10a**, after generation from tetrabromide **9a**, was treated in situ with an additional amount of *n*-BuLi (2 equiv) and then the reaction mixture was quenched with MeI (Table 1, entry h, column 5). The resultant dimethylated enediyne **10h** was isolated in 62% yield.

In conclusion, an easy synthesis of arenediynes from 1,2-arenedialdehydes has been developed. Efforts towards expanding the scope of this strategy for the synthesis

of enediynes in which the ene moiety is part of open chain and alicyclic systems are currently in progress.

Acknowledgements

The authors thank DST, India, for financial assistance and SAIF, IIT Bombay, for NMR data. B.S. thanks CSIR, India, for a scholarship.

References and notes

1. For recent reviews: (a) Basak, A.; Mandal, S.; Bag, S. S. *Chem. Rev.* **2003**, *103*, 4077–4094; (b) Wenk, H. H.; Winkler, M.; Sander, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 502–528.
2. (a) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255–263; (b) Biggins, J. B.; Onwueme, K.; Thorson, J. S. *Science* **2003**, *301*, 1537–1541.
3. Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627–630.
4. (a) Selected recent articles: Kraft, B. J.; Coalter, N. L.; Nath, M.; Clark, A. E.; Siedle, A. R.; Huffman, J. C.; Zaleski, J. M. *Inorg. Chem.* **2003**, *42*, 1663–1672; (b) Alabugin, I. V.; Manoharan, M.; Kovalenko, S. V. *Org. Lett.* **2002**, *4*, 1119–1122; (c) Miljanic, O. S.; Vollhardt, K. P. C.; Whitener, G. D. *Synlett* **2003**, 29–34; (d) König, B.; Pitsch, W.; Klein, M.; Vasold, R.; Prall, M.; Schreiner, P. R. *J. Org. Chem.* **2001**, *66*, 1742–1746; (e) Boydston, A. J.; Haley, M. M.; Williams, R. V.; Armantrout, J. R. *J. Org. Chem.* **2002**, *67*, 8812–8819; (f) Spence, J. D.; Cline, E. D.; LLagostera, D. M.; O'Toole, P. S. *Chem. Commun.* **2004**, 180–181.
5. Powel, N. A.; Rychnovsky, S. D. *Tetrahedron Lett.* **1996**, *37*, 7901–7904.
6. Nicolaou, K. C.; Dai, W. M.; Hong, Y. P.; Tsay, S. C.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7944–7953.
7. For coupling of vinyl/alkynyl stannanes: (a) Magriotis, P. A.; Scott, M. E.; Kim, K. D. *Tetrahedron Lett.* **1991**, *32*, 6085–6088; (b) Wang, Z.; Wang, K. K. *J. Org. Chem.* **1994**, *59*, 4738–4742; boranes: (c) Wang, K. K.; Wang, Z.; Gu, Y. G. *Tetrahedron Lett.* **1993**, *34*, 8391–8394; cuprates: (d) Feng, L.; Kumar, D.; Kerwin, S. M. *J. Org. Chem.* **2003**, *68*, 2234–2242; (e) Miki, Y.; Momotake, A.; Arai, T. *Org. Biomol. Chem.* **2003**, *1*, 2655–2660; (f) Stang, P. J.; Blume, T.; Zhdankin, V. V. *Synthesis* **1993**, 35–36; (g) Semmelhack, M. F.; Wu, L.; Pascal, R. A.; Ho, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 10496–10497; Li compounds: (h) Jones, G. B.; Hynd, G.; Wright, J. M.; Purohit, A.; Plourde, G. W., II; Huber, R. S.; Mathews, J. E.; Li, A.; Kilgore, M. W.; Bubley, G. J.; Yancisin, M.; Brown, M. A. *J. Org. Chem.* **2001**, *66*, 3688–3695; Mg compounds: (i) Wang, G. X.; Iguchi, S.; Hirama, M. *J. Org. Chem.* **2001**, *66*, 2146–2148; carbenoids: (j) Jones, G. B.; Wright, J. M.; Plourde, G. W., II; Hynd, G.; Huber, R. S.; Mathews, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 1937–1944; (k) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2002**, *124*, 2584–2594.
8. Hopf, H.; Theurig, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1099–1100.
9. Nuss, J. M.; Murphy, M. M. *Tetrahedron Lett.* **1994**, *35*, 37–40.
10. (a) Pitsch, W.; Klein, M.; Zabel, M.; König, B. *J. Org. Chem.* **2002**, *67*, 6805–6807; (b) Orita, A.; Hasegawa, D.; Nakano, T.; Otera, J. *Chem. Eur. J.* **2002**, *8*, 2000–2004; (c) Cao, X.; Yang, Y.; Wang, X. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2485–2489; (d) Chaffins, S.; Brettreich, M.; Wudl, F. *Synthesis* **2002**, 1191–1194; (e) Wandel, H.; Wiest, O. *J. Org. Chem.* **2002**, *67*, 388–393; (f) Plourde, G. W., II; Warner, P. M.; Parrish, D. A.; Jones, G. B. *J. Org. Chem.* **2002**, *67*, 5369–5374.
11. (a) Fritsch, P. *Liebigs Ann. Chem.* **1894**, *279*, 319–323; (b) Buttenberg, W. P. *Liebigs Ann. Chem.* **1894**, *279*, 324–337; (c) Wiechell, H. *Liebigs Ann. Chem.* **1894**, *279*, 337–344.
12. (a) Recent reviews: Knorr, R. *Chem. Rev.* **2004**, *104*, 3795–3849; (b) Eymery, F.; Iorga, B.; Savignac, P. *Synthesis* **2000**, 185–213; (c) Braun, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 430–450; (d) Kirmse, W. *Angew. Chem., Int. Ed.* **1997**, *36*, 1164–1170.
13. Selected recent reports on experimental studies: (a) Marchand, A. P.; Namboothiri, I. N. N.; Ganguly, B.; Bott, S. G. *J. Am. Chem. Soc.* **1998**, *120*, 6871–6876; (b) Harada, T.; Iwazaki, K.; Otani, T.; Oku, A. *J. Org. Chem.* **1998**, *63*, 9007–9012; (c) Gilbert, J. C.; Hou, D.-R. *Tetrahedron* **2004**, *60*, 469–474; (d) Marchand, A. P.; Alihodzic, S.; Bott, S. G.; Watson, W. H.; Bodige, S. G.; Gilardi, R. *Tetrahedron* **1998**, *54*, 13427–13434.
14. Selected reports on theoretical studies: (a) Johnson, R. P.; Daoust, K. J. *J. Am. Chem. Soc.* **1995**, *117*, 362–367; (b) Tseng, J.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 5474–5477; (c) Bachrach, S. M.; Gilbert, J. C.; Laird, D. W. *J. Am. Chem. Soc.* **2001**, *123*, 6706–6707; (d) Hayes, R. L.; Fattal, E.; Govind, N.; Carter, E. A. *J. Am. Chem. Soc.* **2001**, *123*, 641–657.
15. (a) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 27–44; (b) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296–1320; (c) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081–1119; (d) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539–556; (e) Ye, F.; Orita, A.; Doumoto, A.; Otera, J. *Tetrahedron* **2003**, *59*, 5635–5643.
16. Selected recent articles: (a) Rezaei, H.; Yamanoi, S.; Chemla, F.; Normant, J. F. *Org. Lett.* **2000**, *2*, 419–421; (b) Gibtner, T.; Hampel, F.; Gisselbrecht, J.-P.; Hirsch, A. *Chem. Eur. J.* **2002**, *8*, 408–431; (c) Shun, A. L. K. S.; Tykwinski, R. R. *J. Org. Chem.* **2003**, *68*, 6810–6813; (d) Tobe, Y.; Iwasa, N.; Umeda, R.; Sonoda, M. *Tetrahedron Lett.* **2001**, *42*, 5485–5488; (e) Eisler, S.; Chahal, N.; McDonald, R.; Tykwinski, R. R. *Chem. Eur. J.* **2003**, *9*, 2542–2550; (f) Shun, A. L. K. S.; Chernick, E. T.; Eisler, S.; Tykwinski, R. R. *J. Org. Chem.* **2003**, *68*, 1339–1347; (g) Tsuboya, N.; Hamasaki, R.; Ito, M.; Mitsuishi, M.; Miyashita, T.; Yamamoto, Y. *J. Mater. Chem.* **2003**, *13*, 511–513; (h) Yanagisawa, H.; Miura, K.; Kitamura, M.; Narasaka, K.; Kaori, A. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2009–2026; (i) Kaafarani, B. R.; Wex, B.; Wang, F.; Catanescu, O.; Chien, L. C.; Neckers, D. C. *J. Org. Chem.* **2003**, *68*, 5377–5380.
17. Thermal rearrangement of acetylenes **3** to vinylidenecarbenes **2** under Flash Vacuum Pyrolysis (FVP) conditions has also been described: (a) Brown, R. F. C. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 655–661, and the references cited therein; (b) Mabry, J.; Johnson, R. P. *J. Am. Chem. Soc.* **2002**, *124*, 6497–6501.
18. For a sequential (three-step) transformation of arene-1,2-dialdehyde monoacetal to arene-1,2-diyne via dibromomethylenation and treatment with LDA: Tovar, J. D.; Jux, N.; Jarrosson, T.; Khan, S. I.; Rubin, Y. *J. Org. Chem.* **1997**, *62*, 3432–3433.
19. Satoh, T.; Sakamoto, T.; Watanabe, M. *Tetrahedron Lett.* **2002**, *43*, 2043–2046.
20. Gilbert, J. C.; Giamalva, D. H. *J. Org. Chem.* **1992**, *57*, 4185–4188.
21. Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769–3772.

22. For recent examples of the Corey–Fuchs dibromomethylenation of aldehydes, see: (a) Dolhem, F.; Lievre, C.; Demailly, G. *Tetrahedron Lett.* **2002**, *43*, 1847–1849; (b) Hwang, G. T.; Son, H. S.; Ku, J. K.; Kim, B. H. *J. Am. Chem. Soc.* **2003**, *125*, 11241–11248.
23. For other dihaloolefination methods for aldehydes, see: (a) Korotchenko, V. N.; Shastin, A. V.; Nenajdenko, V. G.; Balenkova, E. S. *Org. Biomol. Chem.* **2003**, *1*, 1906–1908; (b) Savignac, P.; Petrova, J.; Dreux, M.; Coutrot, P. *Synthesis* **1975**, 535–537; (c) Villieras, J.; Perriot, P.; Normant, J. F. *Synthesis* **1975**, 458–461.
24. (a) Korotchenko, V. N.; Shastin, A. V.; Nenajdenko, V. G.; Balenkova, E. S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 883–887; (b) Takeda, T.; Endo, Y.; Reddy, A. C. S.; Sasaki, R.; Fujiwara, T. *Tetrahedron* **1999**, *55*, 2475–2486; (c) Rezaei, H.; Normant, J. F. *Synthesis* **2000**, 109–112; (d) Burton, G.; Elder, J. S.; Fell, S. C. M.; Stachulski, A. V. *Tetrahedron Lett.* **1988**, *29*, 3003–3006; (e) Savignac, P.; Coutrot, P. *Synthesis* **1976**, 197–199; (f) Michel, P.; Gennet, D.; Rassat, A. *Tetrahedron Lett.* **1999**, *40*, 8575–8578; (g) Neidlein, R.; Winter, M. *Synthesis* **1998**, *9*, 1362–1366; (h) Olah, G. A.; Wu, A. *Synthesis* **1990**, 885–886.
25. (a) **8b**: Farooq, O. *Synthesis* **1994**, 1035–1036; (b) **8c**: (i) Bhattacharjee, D.; Popp, F. D. *J. Heterocycl. Chem.* **1980**, *17*, 315–320; (ii)Meziane, M. A. A.; Royer, S.; Bazureau, J. P. *Tetrahedron Lett.* **2001**, *42*, 1017–1020; (c) **8d**: Mallouli, A.; Lepage, Y. *Synthesis* **1980**, *9*, 689; (d) **8e**: Ref. 25b; (ii) (e) **8f**: Shafiee, A. *J. Heterocycl. Chem.* **1975**, *12*, 177–179.
26. (a) **10a**: (i) Huynh, C.; Linstrumelle, G. *Tetrahedron* **1988**, *44*, 6337–6344; (ii) Matzger, A. J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1998**, *39*, 6791–6794; (iii) Torii, S.; Hase, T.; Kuroboshi, M.; Amatore, C.; Jutand, A.; Kawafuchi, H. *Tetrahedron Lett.* **1997**, *38*, 7391–7394; (iv) Refs. 3, 4b and 4d; (b) **10b**: (i) Grissom, J. W.; Gunawardena, G. U. *Tetrahedron Lett.* **1995**, *36*, 4951–4954; (ii) Chakraborty, M.; McConville, D. B.; Saito, T.; Meng, H.; Rinaldi, P. L.; Tessier, C. A.; Youngs, W. J. *Tetrahedron Lett.* **1998**, *39*, 8237–8240; (c) **10c**: (i) Ref. 26b (i); (ii) Lu, M.; Pan, Y.; Peng, Z. *Tetrahedron Lett.* **2002**, *43*, 7903–7906; (d) **10d**: Kaneko, T.; Takahashi, M.; Hirama, M. *Tetrahedron Lett.* **1999**, *40*, 2015–2018; (e) Ref. 4b; (f) **10g**: Sugihara, Y.; Miyatake, R.; Yagi, T. *Chem. Lett.* **1993**, 933–936, see Ref. 4e; (g) **10h**: (i) Müller, E.; Sauerbier, M.; Streichfuss, D.; Thomas, R.; Winter, W.; Zountsas, G.; Heiss, J. *Liebigs Ann. Chem.* **1971**, *750*, 63–75; (ii) Bleckmann, W.; Hanack, M. *Chem. Ber.* **1984**, *117*, 3021–3033; (iii) Miljanic, O. S.; Vollhardt, K. P. C.; Whitener, G. D. *Synlett* **2003**, 29–30.