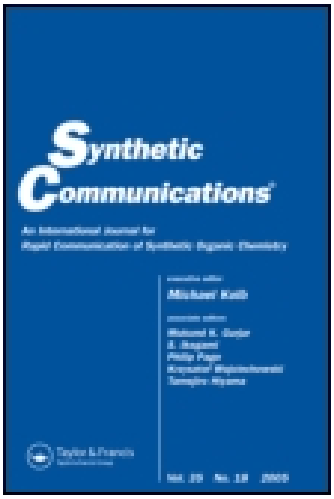


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis of cis-Fused Bicyclic Systems by Radical Cyclization Approach: Formal Synthesis of Ethisolide and iso-Avenaciolide

Gangavaram V. M. Sharma [a] & Devoju Harinada Chary [a]
[a] Organic and Biomolecular Chemistry Division , CSIR Indian Institute of Chemical Technology , Hyderabad , India
Published online: 14 May 2014.

To cite this article: Gangavaram V. M. Sharma & Devoju Harinada Chary (2014) Synthesis of cis-Fused Bicyclic Systems by Radical Cyclization Approach: Formal Synthesis of Ethisolide and iso-Avenaciolide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 44:12, 1771-1779, DOI: 10.1080/00397911.2013.871562

To link to this article: http://dx.doi.org/10.1080/00397911.2013.871562

Synthetic Communications®, 44: 1771–1779, 2014

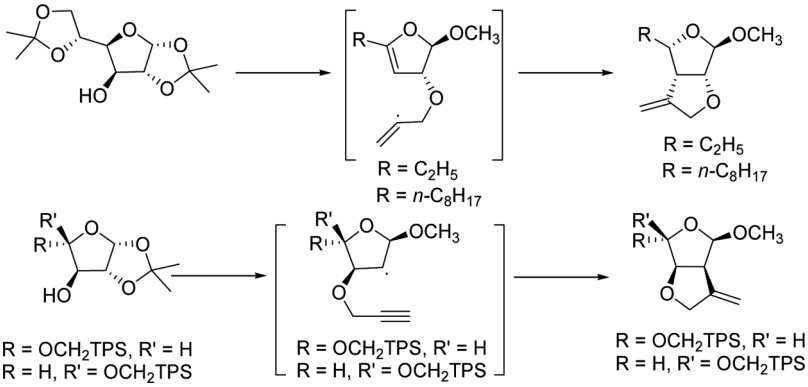
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2013.871562

Taylor & Francis
Taylor & Francis Group

SYNTHESIS OF *CIS*-FUSED BICYCLIC SYSTEMS BY RADICAL CYCLIZATION APPROACH: FORMAL SYNTHESIS OF ETHISOLIDE AND *ISO*-AVENACIOLIDE

Gangavaram V. M. Sharma and Devoju Harinada Chary
Organic and Biomolecular Chemistry Division, CSIR Indian Institute of Chemical Technology, Hyderabad, India

GRAPHICAL ABSTRACT



Abstract *Formal synthesis of ethisolide and* iso-*avenaciolide was achieved using furanoid glycal-vinyl radical intermediates. The vinyl radical cyclization by 5-*exo-*dig mode gave the* cis-*fused bicyclic systems with an efficient introduction of the* exo-*methylene group, besides helping in the inversion of the adjacent stereocentre. Further, the study describes the synthesis of* cis-*fused bicyclic systems from L-arabinose and D-xylose for the creation of diverse natural and synthetic products of this class.*

Keywords Carbohydrates; 5-*exo*-dig; *exo*-methylene; furanoid glycal; radical cyclization

INTRODUCTION

Modern carbohydrate chemistry is a diverse discipline strongly connected with organic and medicinal chemistry.[1] Nature uses diversity-oriented synthesis[2] (DOS), whereby it designs molecules of skeletal, structural, stereochemical, and functional diversity. Nature's DOS is reflected by the presence of a variety of α-methylene

Received October 16, 2013.
Address correspondence to Gangavaram V. M. Sharma, Organic and Biomolecular Chemistry Division, CSIR Indian Institute of Chemical Technology, Hyderabad, 500 007, India. E-mail: esmvee@iict.res.in

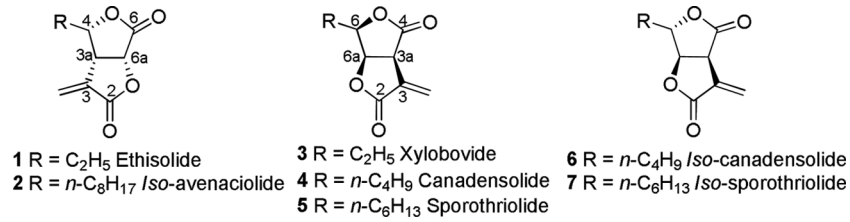


Figure 1. Natural and synthetic products containing α-methylene-*bis*-butyrolactone skeletons.

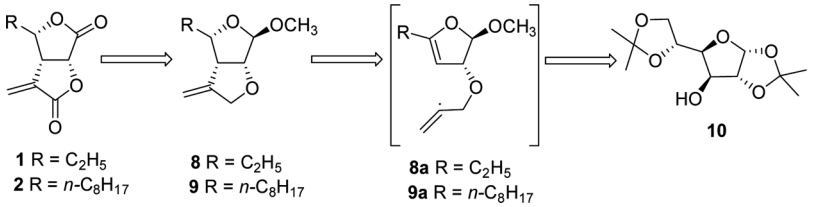
bis-butyrolactones[3,4] **15** (Fig. 1), besides a variety of other natural products. These natural products differ in the lengths of their side chains and the arrangements of the bicyclic systems to result in diversely fused furo-furan systems.

In our earlier studies, a 5-*exo*-dig[5] radical cyclization approach was efficiently utilized for the synthesis of this class of natural products[4] from diacetone glucose (DAG). In these studies, the radical cyclization[6] was found to be very successful in giving *cis*-fused bicyclic systems along with the concomitant introduction of *exo*-methylene group.

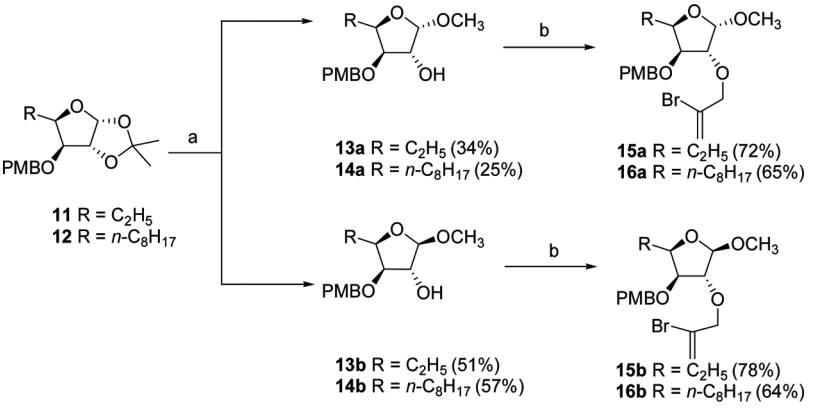
Ethisolide **1**[7] and *iso*-avenaciolide **2**[8] are two *bis*-lactone class of secondary metabolites isolated from the broths of *Aspergillus avenaceus* and *Penicillium* species respectively. Both these compounds have been shown to inhibit fungal growth and antibacterial activity.[9] The α-methylene-γ-butyrolactone system was found to impart biological activity to the natural products of this group. Structurally, **1** and **2** are similar, except for the length of their side chains.[10] In continuation of our studies[11] on radical cyclization reactions en route to the *bis*-butyrolactone class of natural products, herein we report our efforts on the synthesis of **1** and **2** (Fig. 1) with suitably substituted 5-vinyl radical,[12] which undergoes ring closure by a 5-*exo*-dig mode preferentially.

RESULTS AND DISCUSSION

The retrosynthetic strategy for **1** and **2**, as depicted in Scheme 1, revealed that bicyclic systems **8** and **9** are the late-stage intermediates, which could be realized from the glycal-vinyl radical intermediates **8a** and **9a** respectively. Such systems can be generated from DAG **10**. Thus, the main synthetic strategy is (a) to generate C-3/C-4 glycal and (b) to utilize a vinyl radical for the radical cyclization to invert the C-4 stereocenter, while creating the *cis*-fused bicyclic system.



Scheme 1. Retrosynthetic analysis of **1** and **2**.

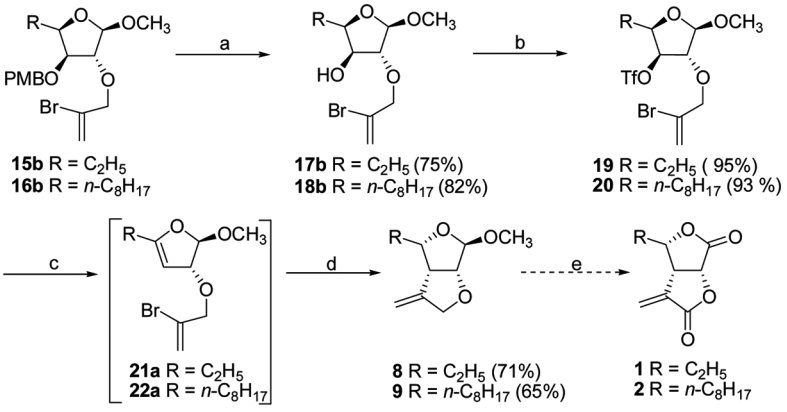


Reagents and conditions: (a) MeOH, H^+, 0 °C-rt, 7 h; (b) NaH, 2,3-Dibromopropene, THF, 0 °C-rt, 3 h.

Scheme 2. *S*ynthesis of intermediates **15** and **16**.

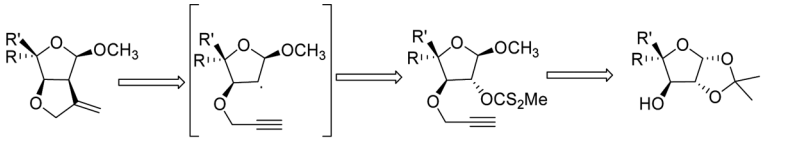
Accordingly, known[4a,4b] furanosides **11** and **12** on methanolysis with two to three drops of concentrated HCl in methanol at temperatures ranging from 0 °C to room temperature gave diastereomeric mixtures of methyl glycosides **13** (1:1.5) and **14** (1:2.3) respectively as α-anomers **13a** (34%)/**14a** (25%) and β-anomers **13b** (51%)/**14b** (57%). Reactions of **13a/13b** and **14a/14b** independently with 2,3-dibromopropene in the presence of NaH in dry tetrahydrofuran (THF) furnished the bromo derivatives **15a** (72%)/**15b** (78%) and **16a** (65%)/**16b** (64%) respectively (Scheme 2).

The β-anomers **15b** and **16b** were independently subjected to oxidative deprotection of the *p*-methoxybenzyl (PMB) group with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in aqueous CH_2Cl_2 to give the respective alcohols **17b** (75%) and **18b** (82%),



Reagents and conditions: (a) DDQ, CH_2Cl_2:H_2O (19:1), rt, 2 h; (b) Tf_2O, Pyridine, dry CH_2Cl_2, -20 °C, 30 min; (c) DBU, dry DMSO, 0 °C-rt, 12 h; (d) *n*-Bu_3SnH, AIBN, dry benzene, 80 °C, 12 h; (e) Ref. 7e.

Scheme 3. Synthesis of compounds **1** and **2**.



Scheme 4. Retrosynthetic analysis of **23** and **24**.

which on reaction with Tf_2O and pyridine in dry CH_2Cl_2 at $-20\,^{\circ}C$ for 30 min gave respective triflates **19** (95%) and **20** (93%) respectively (Scheme 3).

Treatment of **19** and **20** with DBU in dry dimethylsulfoxide (DMSO) at $0\,^{\circ}C$ to room temperature for 12 h afforded furanoid glycals **21a** and **22a** respectively, which, on reaction[7d,12] with *n*-Bu_3SnH in the presence of catalytic amount of azobisisobutyronitrile (AIBN) in dry benzene at reflux for 12 h, afforded *cis*-fused bicyclic systems **8** (71%) and **9** (65%) respectively. Further conversion of **8** and **9** to **1** and **2** has been reported in the literature,[7e] and the synthesis of **8** and **9** constitutes the formal synthesis of **1** and **2** (Scheme 3).

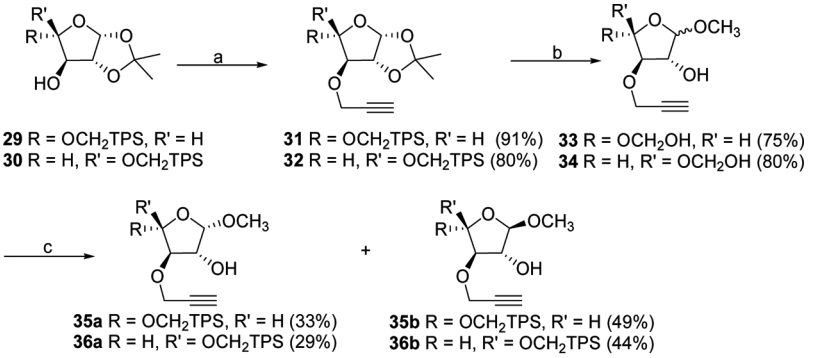
Synthesis of Bicyclic Systems 23 and 24

Earlier, the synthesis of natural products such as xylobovide **3**,[4e] canadensolide **4**,[4d] and sporothriolide **5**,[4b] besides synthetic products *iso*-canadensolide **6**[13] (Fig. 1) have been reported. In all our earlier approaches, the side chain was introduced before the construction of *cis*-fused bicyclic systems. Hence, to create diverse molecules, it was proposed to undertake the synthesis of *cis*-fused bicyclic systems by 5-*exo*-dig radical cyclization from the precursors derived from L-arabinose and D-xylose, so that the requisite side chains can be introduced appropriately on these bicyclic systems for the synthesis of related natural and synthetic products.

According to the retrosynthetic strategy, the bicyclic systems **23** and **24** could be made from the xanthates **27** and **28**, through the radical precursors **25** and **26**, whereas the xanthate derivatives **27** and **28** in turn could be realized from L-arabinose and D-xylose derivatives **29** and **30** respectively (Scheme 4).

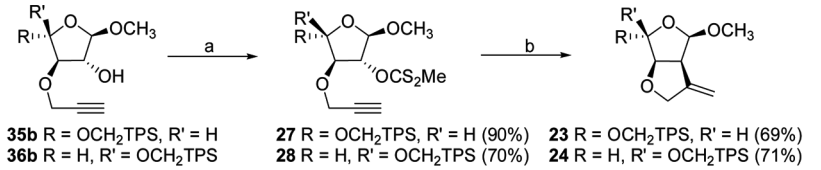
Accordingly, known silyl ethers **29**[14] and **30**[15] on alkylation with propargyl bromide in the presence of NaH in THF at room temperature for 4 h furnished the propargyl ethers **31** (91%) and **32** (80%). Methanolysis of **31** and **32** with concentrated HCl (catalyst) in MeOH at $0\,^{\circ}C$ to room temperature for 6 h gave the α- and β-methyl glycosides **33** (75%) and **34** (80%), with concomitant hydrolysis of *tert*-butyldiphenylsilyl (TBDPS) group. The anomeric mixtures **33** and **34** on reaction with TBDPSCl and imidazole in dry CH_2Cl_2 at $0\,^{\circ}C$ to room temperature for 2 h afforded the α-anomers **35a** (33%)/**36a** (29%) and β-anomers **35b** (49%)/**36b** (44%) (Scheme 5).

The β-anomers **35b** and **36b** on reaction with NaH, CS_2, and MeI in THF at $0\,^{\circ}C$ to room temperature for 2 h furnished xanthates **27** (90%)/**28** (70%), which on radical cyclization independently under standard reaction conditions using *n*-Bu_3SnH and AIBN (catalyst) in dry benzene at reflux for 12 h afforded **23** (69%)/**24** (71%) (Scheme 6).



Reagents and conditions: (a) Propargyl bromide, NaH, THF, 0 °C-rt, 4 h; (b) MeOH, H^+, 0 °C-rt, 6 h; (c) TBDPSCl, imidazole, dry CH_2Cl_2, 0 °C-rt, 2 h.

Scheme 5. Synthesis of intermediates of **35** and **36**.



Reagents and conditions: (a) CS_2, MeI, NaH, THF, 0 °C-rt, 2 h; (b) *n*-Bu_3SnH, AIBN, dry benzene, 80 °C, 12 h.

Scheme 6. Synthesis of **23** and **24**.

EXPERIMENTAL

Solvents were dried over standard drying agents and freshly distilled prior to use. All commercially available chemicals were used without further purification. All reactions were performed under nitrogen. ^{1}H NMR and ^{13}C NMR spectra were measured with Varian Gemini FT 200-MHz, Bruker Avance 300-MHz, Unity 400-MHz, and Inova 500-MHz spectrometers with Tetramethylsilane (TMS) as internal standard for solutions in $CDCl_3$. *J* values are given in hertz. Chemical shifts were reported in parts per million (ppm) relative to solvent signal. All column chromatographic separations were performed using silica gel (Acme's, 60–120 mesh). Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40 °C in vacuo. IR spectra were recorded on at Perkin-Elmer IR-683 spectrophotometer with NaCl optics. Optical rotations were measured with JASCO DIP 300 digital polarimeter at 25 °C. Mass spectra were recorded on CEC-21-11013 or Finnigan Mat 1210 double focusing mass spectrometers operating at a direct inlet system or LC/MSD Trap SL (Agilent Technologies).

(3a*R*,4*S*,6*R*,6a*R*)-4-Ethyl-hexahydro-6-methoxy-3-methylenefuro [3,4-*b*]furan (8)

Tf_2O (0.49 mL, 3.00 mmol) was added to a solution of **17b** (0.70 g, 2.50 mmol) and pyridine (0.40 mL, 5.00 mmol) in CH_2Cl_2 (4 mL) at −20 °C and stirred for

30 min. It was decanted, dissolved in aqueous $NaHCO_3$ solution (6 mL), and extracted with CH_2Cl_2 (2×10 mL). Combined organic layers were washed with aqueous $NaHCO_3$ solution (5 mL), water (5 mL), 2 N aqueous HCl (5 mL), and brine (5 mL). The organic layer was dried (Na_2SO_4) and evaporated to give **19** (0.98 g, 95%) as a yellow syrup, which was used as such for the next reaction.

DBU (0.70 mL, 4.61 mmol) was added to a stirred solution of **19** (0.95 g, 2.30 mmol) in dry DMSO (5 mL) at 0 °C and stirred for 12 h. Reaction mixture was extracted with EtOAc (2×10 mL) and washed with water (5 mL) and brine (5 mL). It was dried (Na_2SO_4) and evaporated to afford **21a** as a light yellow liquid, which was used as such for the next reaction.

n-Bu_3SnH (0.51 mL, 1.91 mmol) and AIBN (cat.) were added to a solution of **21a** (0.25 g, 0.95 mmol) in dry benzene (25 mL) under N_2 atmosphere at reflux and heated at reflux for 12 h. The reaction mixture was cooled to room temperature, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (60–120 silica gel, ethyl acetate–petroleum ether, 0.9:9.1) to give **8** (0.13 g, 71%) as a colorless liquid; $[\alpha]_D^{25} = -49.2$ (*c* 0.23, $CHCl_3$); IR (neat): 3437, 2926, 2856, 1737, 1219, 1051, 769 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (t, 3H, $J = 7.3$ Hz, CH_3), 1.49 (m, 2H, CH_2), 3.19 (t, 1H, $J = 7.1$ Hz, H-3a), 3.29 (s, 3H, OCH_3), 3.94 (m, 1H, H-4), 4.16 (m, 2H, OCH_2), 4.53 (d, 1H, $J = 6.4$ Hz, H-6a), 4.81 (s, 1H, H-6), 4.92 (d, 1H, $J = 1.7$ Hz, olefinic) 5.06 (d, 1H, $J = 1.5$ Hz, olefinic);^{13}C NMR (75 MHz, $CDCl_3$): δ 147.1, 107.7, 96.2, 88.5, 80.9, 72.6, 54.1, 50.0, 24.3, 11.4. HRMS (EI): *m/z* calculated for $C_{10}H_{17}O_3(M^+ + H)$ 185.1177; found 185.1170.

(3a*R*,4*S*,6*R*,6a*S*)-Hexahydro-6-methoxy-3-methylene-4-octylfuro[3,4-*b*]furan (9)

To a solution of **18b** (0.80 g, 2.19 mmol) and pyridine (0.35 mL, 4.38 mmol) in CH_2Cl_2 (10 mL) at −20 °C, Tf_2O (0.40 g, 2.63 mmol) was added and stirred for 30 min. Workup as described for **19** gave **20** (1.01 g, 93%) as a yellow syrup, which was used as such for the next reaction.

DBU (0.49 mL, 3.21 mm) was added to a stirred solution of **20** (0.80 g, 1.60 mmol) in DMSO (5 mL) at 0 °C and stirred for 12 h. Workup as described for **21a** afforded **22a** as a light yellow liquid, which was used as such for the next reaction.

n-Bu_3SnH (0.93 mL, 3.47 mmol) and AIBN (cat.) were added to a solution of **22a** (0.60 g, 1.73 mmol) in dry benzene (25 mL) under N_2 atmosphere at reflux and heated at reflux for 12 h. Workup as described for **8** and purification of the residue by column chromatography (60–120 silica gel, ethyl acetate–petroleum ether, 0.9:9.1) gave **9** (0.30 g, 65%) as a colorless liquid; $[\alpha]_D^{25} = -192.8$ (*c* 0.14, $CHCl_3$); IR (neat): 3412, 2891, 2797, 1764, 1176, 1083, 804 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, $J = 6.1$ Hz, CH_3), 1.27 (m, 14H, $7 \times CH_2$), 3.17 (t, 1H, $J = 6.8$ Hz, H-3a), 3.29 (s, 3H, OCH_3), 4.02 (m, 1H, H-4), 4.17 (s, 2H, OCH_2), 4.50 (d, 1H, $J = 6.4$ Hz, H-6a), 4.81 (s, 1H, H-6), 4.92 (s, 1H, olefinic), 5.06 (s, 1H, olefinic); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.3, 111.7, 105.1, 82.5, 79.9, 71.6, 61.0, 55.2, 31.9, 29.7, 26.8, 26.3, 22.6, 14.1. HRMS (ESI): *m/z* calculated for $C_{16}H_{29}O_3(M^+ + H)$ 269.2038; found 269.2072.

(((3a*S*,4*R*,6*S*,6a*R*)-Hexahydro-4-methoxy-3-methylenefuro[3,4-*b*] furan-6-yl)methoxy)(*tert*-butyl)diphenylsilane (23)

A solution of **27** (0.80 g, 1.45 mmol) in dry benzene (25 mL) under N_2 atmosphere was treated with *n*-Bu_3SnH (0.78 mL, 2.91 mmol) at room temperature and heated at reflux for 30 min. After 30 min, catalytic amount of AIBN was added at reflux and stirred for 12 h. Workup as described for **8** and purification of the residue by column chromatography (60–120 silica gel, ethyl acetate–petroleum ether, 1.2:8.8) afforded **23** (0.43 g, 69%) as a colorless liquid; $[\alpha]_D^{25} = -45.7$ (*c* 0.1, $CHCl_3$); IR (neat): 2864, 1756, 1612, 1387, 1234, 1113, 768 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 9H, $C(CH_3)_3$), 3.40 (s, 4H, H-3a and OCH_3), 3.77 (d, 2H, $J = 3.3$ Hz, OCH_2), 4.25–4.38 (m, 2H, allylic-CH_2), 4.49–4.54 (m, 1H, H-6), 4.68 (dd, 1H, $J = 2.2$, 6.7 Hz, H-6a), 5.05 (br.s, 2H, olefinic), 5.12 (d, 1H, $J = 6.0$ Hz, H-4), 7.34–7.42 (m, 6H, Ar-H), 7.64–7.70 (m, 4H, Ar-H);^{13}C NMR (75 MHz, $CDCl_3$): δ 146.2, 135.5 (4C), 129.67 (2C), 127.6 (4C), 106.7, 105.9, 85.9, 84.1, 73.4, 64.5, 55.6, 54.9, 26.7, 19.2. HRMS (ESI): *m/z* calculated for $C_{25}H_{32}O_4NaSi$ ($M^+ + Na$) 447.19621; found 447.19692.

(((3a*S*,4*R*,6*R*,6a*R*)-Hexahydro-4-methoxy-3-methylenefuro[3,4-*b*]furan-6-yl)methoxy)(*tert*-butyl)diphenylsilane (24)

A solution of **28** (0.12 g, 0.22 mmol) in dry benzene (25 mL) under N_2 atmosphere was treated with *n*-Bu_3SnH (0.17 mL, 0.43 mmol) at room temperature and heated at reflux for 30 min. After 30 min, a catalytic amount of AIBN was added at reflux and stirred for 12 h. Workup as described for **8** and purification of the residue by column chromatography (60–120 silica gel, ethyl acetate–petroleum ether, 1.2:8.8) afforded **24** (0.07 g, 71%) as a colorless liquid; $[\alpha]_D^{25} = -32.7$ (*c* 0.31, $CHCl_3$); IR (neat): 2934, 2889, 1744, 1674, 1426, 1218, 1165, 767 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.05 [s, 9H, $C(CH_3)_3$], 3.32 (s, 1H, H-6), 3.39 (s, 3H, OCH_3), 3.83 (d, 2H, $J = 4.1$ Hz, OCH_2), 4.25 (m, 2H, allylic-CH_2), 4.61–4.68 (m, 2H, H-6a and H-3a), 4.96 (d, 1H, $J = 6.0$ Hz, H-4), 5.02 (br.s, 2H, olefinic), 7.34–7.42 (m, 6H, Ar-H), 7.70–7.72 (m, 4H, Ar-H);^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9, 135.6 (2C), 133.2 (2C), 129.6 (2C), 127.6 (4C), 106.9, 105.1, 85.1, 76.9, 73.6, 63.4, 55.2, 54.5, 26.7, 19.1. HRMS (ESI): *m/z* calculated for $C_{25}H_{32}O_4NaSi$ ($M^+ + Na$) 447.19621; found 447.19538.

CONCLUSION

The *cis*-fused bicyclic systems were successfully synthesized by 5-*exo*-dig radical cyclization from appropriate vinyl radical intermediates en route to the formal synthesis of ethisolide and *iso*-avenaciolide. The concomitant introduction of *exo*-methylene group and inversion of adjacent sterocenter took place while creating *cis*-fused bicyclic systems. For the creation of diversity of bicyclic systems with different side chains and different substitutions in furonoside ring at C-4 position, two *cis*-fused bicyclic systems were synthesized by 5-*exo*-dig cyclization from D-xylose and L-arabinose. The yields of the products in the present study are comparable to the earlier reports.

FUNDING

H. C. acknowledges the financial support in the form of a research fellowship from the Council of Scientific and Industrial Research (CSIR), New Delhi, India. Both authors thank CSIR for financial support.

SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher's website.

REFERENCES

1. Gruner, S. A. W.; Locardi, E.; Lohof, E.; Kessler, H. *Chem. Rev.* **2002**, *102*, 491–514.
2. For other reviews of diversity-oriented synthesis, see (a) Burke, M. D.; Schreiber, S. L. *Angew. Chem. Int. Ed.* **2004**, *43*, 46–58; (b) Tan, D. S. *Nat. Chem. Biol.* **2005**, *1*, 74–84; (c) Spring, D. R. *Org. Biomol. Chem.* **2003**, *1*, 3867–3870; (d) Spandl, R. J.; Bender, A.; Spring, D. R. *Org. Biomol. Chem.* **2008**, *6*, 1149–1158.
3. (a) Al-Tel, T. H.; Al-Qawasmeh, R. A.; Sabri, S. S.; Voelter, W. *J. Org. Chem.* **2009**, *7*, 4690–4696; (b) Santos, D.; Ariza, X.; Garcia, J.; Lloyd-Williams, P.; Martínez-Laporta, A.; Sánchez, C. *J. Org. Chem.* **2013**, *78*, 1519–1524; (c) Mondal, S.; Ghosh, S. *Tetrahedron* **2008**, *64*, 2359–2368; (d) Hon, Y.-S.; Chen, H.-F. *Tetrehedron Lett.* **2007**, *48*, 8611–8614.
4. (a) Sharma, G. V. M.; Vepachedu, S. R. *Tetrahedron Lett.* **1990**, *31*, 4931–4932; (b) Sharma, G. V. M.; Krishnudu, K. *Tetrahedron Lett.* **1995**, *36*, 2661–2664; (c) Sharma, G. V. M.; Krishnudu, K. *Tetrahedron: Asymmetry* **1999**, *10*, 869–875; (d) Sharma, G. V. M.; Vepachedu, S. R. *Tetrahedron* **1991**, *47*, 519–524; (e) Sharma, G. V. M.; Gopinath, T. *Tetrahedron Lett.* **2005**, *46*, 1307–1309.
5. (a) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482–483; (b) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736; (c) Srikrishna, A. *J. Chem. Soc., Chem. Commun.* **1987**, 587–588.
6. (a) Giese, B.; Kopping, B.; Gobel, T.; Dickhaut, J.; Thoma, G.; Kulicke, K. J.; Trach, F. In *Organic Reactions*; L. A. Paquette (Ed.); Wiley: New York, 1996; vol. 48, pp. 301–856; (b) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon Carbon Bonds*; Pergamon: Oxford, 1986; (c) Renaud, P.; Sibi, M. P. *Radicals in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2001; vols. 1 and 2; (d) *Org. Biomol. Chem.* **2011**, *15* (special issue).
7. Racemic: (a) Burke, S. D.; Pacofsky, G. J. *Tetrahedron Lett.* **1986**, *27*, 445–448; (b) Blot, V.; Reboul, V.; Metzner, P. *Eur. J. Org. Chem.* **2006**, 1934–1939; (c) Tsuboi, S.; Sakamoto, J.-I.; Yamashita, H.; Sakai, T.; Utaka, M. *J. Org. Chem.* **1998**, *63*, 1102–1108; (d) Wee, A. G. H. *Terahedron* **1990**, *46*, 5065–5076; (e) Cossy, J.; Ranaivosata, J.-L.; Bellosta, V. *Tetrahedron* **1996**, *52*, 629–638; (f) Cossy, J.; Ranaivosata, J.-L.; Bellosta, V. *Tetrahedron Lett.* **1994**, *35*, 1205–1208.
8. Racemic: (a) Damon, R. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1975**, *16*, 4551–4554; (b) Yamada, K.; Kato, M.; Iyoda, M.; Hirata, Y. *J. Chem. Soc., Chem. Commun.* **1973**, 499–500; (c) Labeeuw, O.; Blanc, D.; Phansavath, P.; Ratovelomanana-Vidal, V.; Genêt, J.-P. *Eur. J. Org. Chem.* **2004**, 2352–2358; (d) Chen, M.-J.; Narkunan, K.; Liu, R.-S. *J. Org. Chem.* **1999**, *64*, 8311–8318; (e) Rodríguez, C. M.; Martín, T.; Martín, V. S. *J. Org. Chem.* **1996**, *61*, 8448–8452.
9. Arjona, O.; Gomez, A. M.; Lopez, J. C.; Plumet, J. *J. Chem. Rev.* **2007**, *107*, 1919–2036.
10. Burke, S. D.; Pacofsky, G. J.; Piscopio, A. D. *J. Org. Chem.* **1992**, *57*, 2228–2235.

11. Sharma, G. V. M.; Chary, D. H.; Mouli, N. C.; Achrainer, F.; Sateesh, P.; Zipse, H. *Org. Biomol. Chem.* **2011**, *9*, 4079–4084.
12. (a) Maiti, S.; Takasu, K.; Katsumata, A.; Kuroyanagi, J.-I.; Ihara, M. *Arkivoc* **2002**, *7*, 197–211; (b) Denes, F.; Beaufils, F.; Renaud, P. *Synlett* **2008**, *16*, 2389–2399.
13. Kato, M.; Kageyama, M.; Tanaka, R.; Kuwahara, K.; Yoshikoshi, A. *J. Org. Chem.* **1975**, *40*, 1932–1941.
14. (a) Rauter, A. P.; Ramoa-Ribeiro, F.; Fernandes, A. C.; Figueiredo, J. A. *Tetrahedron* **1995**, *51*, 6529–6540; (b) Sharma, G. V. M.; Mouli, C. C. *Tetrahedron Lett.* **2002**, *43*, 9159–9161.
15. Radha Krishna, P.; Kannan, V.; Ilangovan, A.; Sharma, G. V. M. *Tetrahedron: Asymmetry* **2001**, *12*, 829–837.