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Tellurium in organic synthesis: the enantioselective synthesis of the pheromone blend components of *Mayetiola destructor*, *Drosophila mulleri* and *Contarinia pisi*

Renan S. Ferrarini, João V. Comasseto, Alcindo A. Dos Santos *

Instituto de Química, Universidade de São Paulo, CP 26077, CEP 05508-900, São Paulo—SP, Brazil

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A B S T R A C T

The components of the pheromone blend of *Mayetiola destructor*, *Drosophila mulleri,* and *Contarinia pisi* were synthesized in high enantiomeric excess (99% ee) from a common enantiopure dianion prepared from an enantiopure hydroxytelluride.

1. Introduction

Several insect pheromones have a medium to long oxygenated hydrocarbon chain, often with alkyl branching, and with specific or strongly dominating chirality and/or double bond configuration. Normally these compounds are not structurally complex, but their specific and/or double bond geometric purity display a pivotal role in their bioactivity.

The pea midge, *Contarinia pisi* (Diptera: Cecidomyiidae), is a serious pest of commercial peas in northern Europe.[1] Its female pheromone blend consists of a mixture of (2*S*,11*S*)-diacetoxytridecane **1**, (2*S*,12*S*)-diacetoxytricane **2,** and 2-acetoxytridecane **3**.[2] Laboratory and field experiments showed a strong dependence on the quantitative ratio and enantiomeric purity of these compounds in male attractancy.[3] The (*S*)-enantiomer of acetates **3** is also an aggregation pheromone component of the fruit fly *Drosophila mulleri*.[4] The C10–C11 unsaturated acetate **4** was identified by Foster et al. in 1991 as the sex pheromone of *Mayetiola destructor*,[5] one of the most damaging pests of wheat in the US and North Africa.[6] However, in wind tunnel and field experiments, this compound alone was significantly less attractive than the female extract.[7] Recently, Hillbur et al. identified other minor constituents of the pheromone blend of *M. destructor*, and a formulation of the synthetic samples of these compounds (*S*)-**3**, (*S*)-**4**, (*S*)-**5**, (*S*)-**6,** and (*S*)-**7** was as attractive as the female extract[8] (Fig. 1).

In recent years, we have devoted attention to the preparation and utilization of organometallics by tellurium/lithium[9] and tellurium/copper exchange reactions.[10] Our interest in this branch of chemistry is centered on the fact that these are some of the most rapid and clean heteroatom/metal exchange reactions, allowing the preparation of different organometallics, including vinyl, alkyl, and aryl intermediates of variable structure, complexity, and functionality.

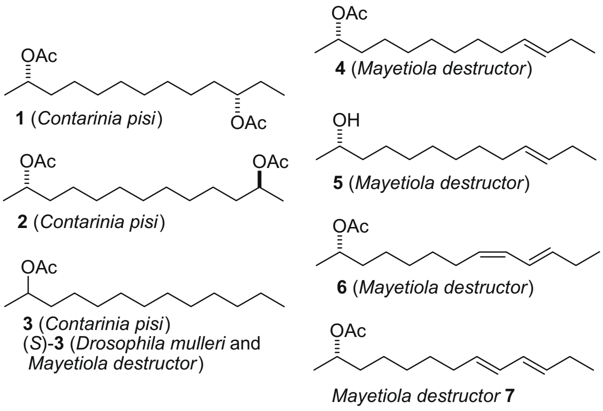

Figure 1. Components of the pheromone blend of *C. pisi*, *D. mulleri,* and *M. destructor*.

2. Results and discussion

Considering the structural similarity of compounds **1**–**7**, we envisioned a synthetic route based on a common key enantiopure hydroxytelluride, a precursor of a 1,4-C,O-dianion, which could introduce the (*S*)-2-hydroxybutyl moiety in an alkylation reaction with an appropriate electrophile. Herein, we report a straightforward enantioselective synthesis of compounds **2**, **3** (racemic and enantiopure), **4,** and **5** from the common precursor (*S*)-**8** based on this concept, as presented in the retrosynthetic analysis in Scheme 1.

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* Corresponding author. Tel.: +55 11 3091 1180; fax: +55 11 3815 5579.
E-mail address: alcindo@iq.usp.br (A.A. Dos Santos).

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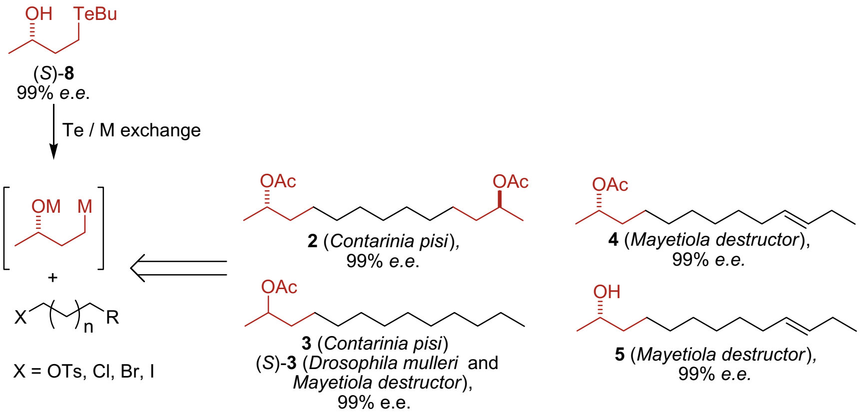
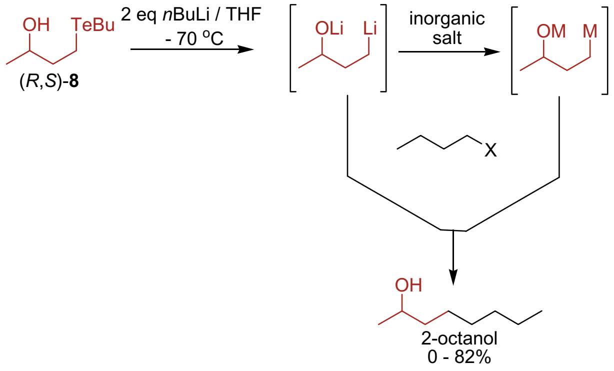


Scheme 1.

Initially, racemic **8**, which was prepared in a one-pot two-step procedure by hydrotelluration of methyl vinyl ketone (MVK) followed by reduction of the carbonyl group,[9b] was converted into the corresponding 1,4-C,O-dianion by treatment with 2 equiv of *n*-BuLi.[9b,d] Next, the di-lithium salt and other organometallics, obtained by transmetallation with the appropriate inorganic salt, were submitted to reaction with butyl electrophiles (bromide, iodide, chloride, and tosylate) in order to determine the optimal alkylation conditions. Scheme 2 and Table 1 summarize the results of this study.



Scheme 2.

The reaction of the di-lithium salt with butyl tosylate (Table 1, entry 6) was unsuccessful. Only moderate to poor yields were achieved using halides as electrophiles in the reaction with cuprates of different nature and stoichiometries (Table 1, entries 1–5). It was observed that butyl-tosylate presented a significantly better reactivity with the higher order cyanocuprates, but the yields were only reasonable when the temperature of the reaction media was quickly raised to −10 °C (entries 8 and 9). On the other hand, when using 2 equiv of the higher order cyanocuprate in THF at −70 °C for 6 h, the desired product was isolated in 82% yield (entry 10). Increasing the amount of the cyanocuprate (3 equiv, entry 11) or lowering the temperature (entry 12) did not improve the yield of the product.

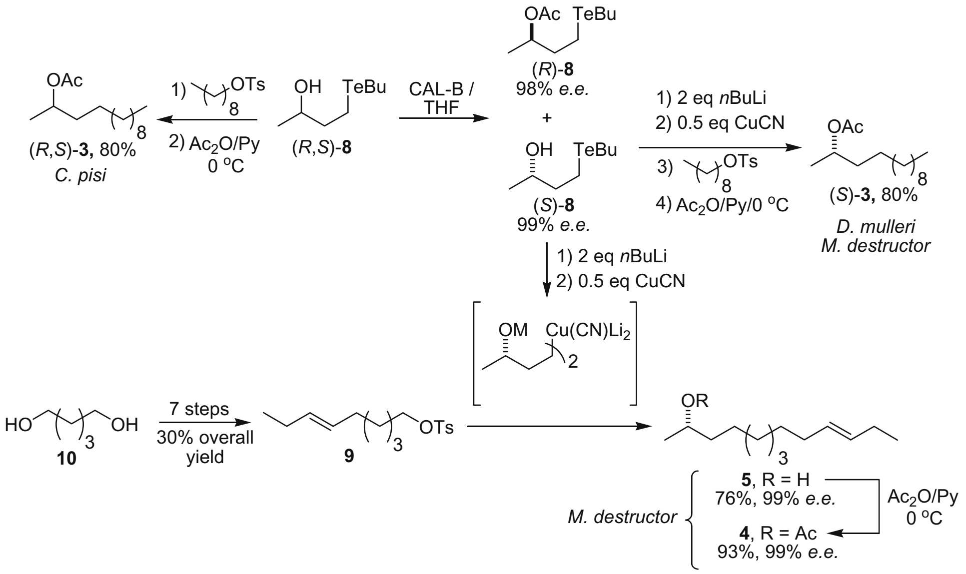
Complementary to these results and based on our previous studies on the tellurium/copper exchange reaction,[10] hydroxytelluride **8** was reacted with $Bu_2Cu(CN)Li_2$, aiming at direct conversion of the hydroxytelluride into the corresponding higher order cyanocuprate, thereby circumventing the tellurium/lithium exchange step. Contrary to the Te–C(sp^2)-bonded tellurides that were successfully converted into the corresponding Cu–C(sp^2) cyanocuprates, telluride **8** was totally inert toward this cuprate, even at high temperature and in the presence of a large excess of the cyanocuprate. This result is in agreement with that of the previous studies of our group where Te–C(sp^3)-bonded tellurides were submitted to the same reaction with this and other cuprate compositions and the tellurium/copper exchange failed.

Recently, we described the preparation of enantiopure hydroxytellurides by enzymatic kinetic resolution.[11] Using this protocol, hydroxytelluride (*S*)-**8** was obtained in 36% isolated yield and 99% ee. Utilizing the optimal reaction conditions (Table 1, entry 15), enantiopure (*S*)-**8** was converted into the corresponding higher order cyanocuprate by treatment with 2 equiv of *n*-BuLi followed by CuCN. The resulting O-functionalized cyanocuprate was reacted with tosylate **9**, prepared in 30% overall yield from diol

Table 1
Reaction of the dianion with butyl electrophiles

	X	Organometallic	Solvent	Conditions	Y (%)
1	Br	$R_2Cu(CN)Li_2$	THF/Et_2O	−70 to −10 °C, 7 h, 3 equiv	30
2	Br	$R_2CuBr{\cdot}DMS$	THF/Et_2O	−70 °C rt, 10 h, 3 equiv	20
3	Br	$R_2Cu(CN)Li_2$	THF	−70 °C, 4 h, 2 equiv	41
4	I	$R_2Cu(CN)Li_2$	THF	−70 to −10 °C, 5 h, 3 equiv	19
5	I	$R_2Cu(CN)Li_2$	THF	−70 °C, 3 h, 3 equiv	19
6	OTs	RLi	THF	−70 °C, 1 h, 2 equiv	Trace[a]
7	OTs	RCu(2-Th)(CN)Li_2	THF	−70 °C, 3 h, 2 equiv	50
8	OTs	$R_2Cu(CN)Li_2$	THF	−70 to −10 °C, 2 h, 3 equiv	43
9	OTs	$R_2Cu(CN)Li_2$	THF/Et_2O	−70 to −10 °C, 2 h, 4.5 equiv	56
10	OTs	$R_2Cu(CN)Li_2$	THF	−70 °C, 6 h, 2 equiv	82
11	OTs	$R_2Cu(CN)Li_2$	THF	−70 °C, 6 h, 3 equiv	80
12	OTs	$R_2Cu(CN)Li_2$	THF	−105 °C, 6 h, 3 equiv	65

[a] Determined by GC analysis.

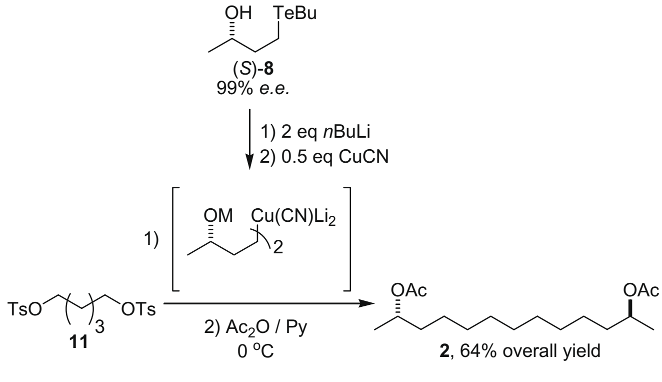


Scheme 3.

10, according to known well-established procedures,[12] leading to **5**, a component of the pheromone blend of *M. destructor*, in 76% isolated yield. Acetylation yielded **4**, another component of the pheromone blend of the same insect, in 93% yield (Scheme 3).

Acetates **3**, in racemic and optically active forms, were prepared in 80% isolated yield by reacting, respectively, the racemic and enantiopure higher order cyanocuprate with nonyl-tosylate followed by conventional acetylation, as presented in Scheme 3.

Diacetate **2** was prepared through a one-pot di-alkylation by reacting the optically active higher order cyanocuprate (4 equiv) with di-tosylate **11**. The resulting optically active diol was acetylated without purification to provide **2**, the major component of the pheromone blend of *C. pisi*, in 64% isolated yield (Scheme 4).



Scheme 4.

The preparation of all of the acetates presented in this work can be performed in a one-pot two-step procedure by quenching the alkylation reaction with acetic anhydride.

The enantiomeric excess of all of the compounds was estimated to be higher than 99% considering the enantiomeric purity of the starting material (*S*)-**8**, which was analyzed by chiral GC and by comparison of the specific rotations of the known products with the literature data.

3. Conclusion

In conclusion, four enantiopure pheromone blend components of *M. destructor*, *C. pisi*, and *D. mulleri* were synthesized in good yields in a one-pot operation using starting electrophiles that can be obtained from commercial sources (e.g., **11**) or through typical synthetic protocols. The conversion of an enantiopure hydroxytelluride into an equally enantiopure reactive dianionic organometallic (lithium and copper) allows the introduction of a chiral oxygenated functionality without the classic undesirable protection/deprotection sequences. The by-product dibutyltelluride (produced in the Te/Li exchange reaction) is fully compatible with all other subsequent reactions, including the acetic anhydride quench.

4. Experimental

4.1. Materials

All reagents and solvents used were previously purified and dried according to the literature.[13] THF was distilled from sodium/benzophenone under nitrogen immediately before use. *n*-Butyllithium was titrated using 1,10-phenanthroline as an indicator prior to use.[14] Nitrogen gas used in the reactions was deoxygenated and dried. All operations were carried out in flame-dried glassware. Column chromatography separations were performed with Vetec Silica Gel 60 (0.063–0.200 mm, 70–230 mesh) or Acros Organics silica gel (0.035–0.075 mm, pore diameter ca. 6 nm). Tellurium metal of 200 mesh was dried overnight in an oven at 100 °C. The following reagents were prepared by usual literature procedures: 2-(non-6-ynyloxy)tetrahydro-2*H*-pyran [39639-25-3][12c]; (*E*)-non-6-enyl 4-methylbenzenesulfonate [86548-29-0]; and 6-tosylhexyl 4-methylbenzenesulfonate [24293-28-5]. The remaining chemicals were obtained from commercial sources.

4.2. Analysis

^{1}H and ^{13}C NMR spectra were obtained on Bruker AC-200 (200 MHz, ^{1}H; 50 MHz, ^{13}C), DRX-500 (500 MHz, ^{1}H; 125 MHz, ^{13}C), or Varian INOVA 300 (300 MHz, ^{1}H; 75 MHz, ^{13}C) spectrometers. All spectra were taken in $CDCl_3$, and the chemical shifts are given in ppm with respect to tetramethylsilane (TMS) used as an internal standard. ^{125}Te NMR spectra were obtained on a Bruker DRX-500 (157 MHz, ^{125}Te) spectrometer using $CDCl_3$ as the solvent. The chemical shifts refer to diphenyl ditelluride $(PhTe)_2$ in $CDCl_3$ (1 mol L^{-1}) (δ 420 ppm at 25 °C) as an external standard.

Low resolution mass spectra were obtained on a Shimadzu CG 17A/CG/MS-QP5050A instrument. Near IR spectra were obtained on a Bomen MB-100 spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of the Institute of Chemistry, Universidade de São Paulo. IUPAC names were obtained using the software ChemDraw, version 8.0.

4.3. Typical procedures

4.3.1. Preparation of higher order cyanocuprate from hydroxytelluride (*S*)-8 and its reaction with tosylates

To a 25 mL two-necked round-bottomed flask equipped with magnetic stirring under a nitrogen atmosphere containing a THF (8 mL) solution of hydroxytelluride (*S*)-**8** (1.03 g, 4 mmol) at −70 °C was slowly added *n*-butyllithium (2 equiv, 1.9 mol L^{-1}, 4.2 mL, 8 mmol, solution in hexane). The resulting clear solution was stirred for 40 min. To a second two-necked round-bottomed flask equipped with magnetic stirring under a nitrogen atmosphere were added CuCN (179 mg, 2 mmol) and THF (6 mL). The light yellow solution of the first flask was transferred via a cannula to the second flask, and the temperature was maintained at −70 °C for 20 min. To the resulting clear yellow solution was added a THF (1 mL) solution of the appropriate tosylate (1 mmol). The reaction was monitored by TLC until total consumption of the tosylate was observed (about 6 h). The reaction media was warmed to room temperature and quenched with an ammonium chloride/ammonium hydroxide solution (3:1, 4 mL) and vigorously stirred. The aqueous and organic phases were separated and the aqueous phase was washed with ethyl acetate (3 × 10 mL). The organic phases were combined and washed with brine (1 × 5 mL), dried over magnesium sulfate, and filtered. Evaporation of the solvents gave the crude product, which was purified by silica gel flash chromatography eluting with hexane/ethyl acetate. Acetates **3**, (*S*)-**3**, (*S*)-**4,** and (*S*,*S*)-**2** were obtained directly by quenching the reaction media with acetic anhydride or by diluting the crude extracted product in pyridine (4 mL) at 0 °C followed by the addition of acetic anhydride (2.5 mmol for acetates **3**, (*S*)-**3**, (*S*)-**4,** and 5 mmol for diacetate (*S*,*S*)-**2**.

(2S,12S)-Tridecane-2,12-diyl diacetate (S,S)-**2**: (yield 64%); colorless oil: δ_H (500 MHz, $CDCl_3$) 1.20 (d, *J* = 6.5 Hz, 6H); 1.26–1.34 (m, 14H); 1.43–1.48 (m, 2H); 1.54–1.61 (m, 2H); 2.02 (s, 6H); 4.88 (sext, *J* = 6.5 Hz, 2H); δ_C (125 MHz, $CDCl_3$) 19.9; 21.4; 25.4; 29.4; 29.5; 29.6; 35.9; 71.1; 170.8; MS *m/z* (rel int.) 300 (M^+, <1); 257 (3); 197 (1); 180 (5); 138 (5); 110 (2); 96 (15); 87 (10); 68 (2); 55 (4); 43 (100); IR cm^{-1} (neat) 2930; 2857; 1738; 1372; 1244; 1127; 1023; lit.[15] $[\alpha]_D^{23} = +1.8$ (*c* 1,21 $CHCl_3$), found $[\alpha]_D^{20} = +2.0$ (*c* 1.20 $CHCl_3$);

(2S)-Tridec-2-yl acetate (S)-**3**: (yield 80%); colorless oil: δ_H (300 MHz, $CDCl_3$) 0,88 (t, *J* = 6.3 Hz, 3H); 1.19 (d, *J* = 6.3 Hz, 3H); 1.26–1.60 (m, 20H); 2.02 (s, 3H); 4.88 (sext, *J* = 6.3 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 14.1; 19.9; 21.3; 22.7; 25.4; 29.3; 29.4; 29.5; 29.55; 29.6; 31.9; 35.9; 71.0; 170.7; MS *m/z* (rel int.) 207 (1); 182 (8); 111 (8); 97 (16); 87 (21); 83 (15); 71 (10); 69 (20); 57 (20); 43 (100); IR cm^{-1} (neat) 2926; 2855; 1734; 1464; 1372; 1244; 1022; lit.[5] $[\alpha]_D^{31} = +0.8$ (*c* 0.8 $CHCl_3$); lit.[16] $[\alpha]_D^{23} = +4.3$ (*c* = 0.95 hexane; reported *e.e.* 93.5%); lit.[17] $[\alpha]_D^{18} = +4.5$ (*c* 0.98 hexane; reported *e.e.* 98%); lit.[18] $[\alpha]_D^{21} = +2.1$ (*c* 0.25 hexane); lit.[19] $[\alpha]_D^{23} = +3.4$ (*c* 0.94 hexane; reported *e.e.* 90%); found $[\alpha]_D^{20} = +4.5$ (*c* 1.00 hexane). The analytical data of racemic **3** are identical to those of (*S*)-**3**.

(S,E)-Tridec-10-en-2-yl acetate (S)-**4**: (yield 93%); colorless oil: δ_H (200 MHz, $CDCl_3$) 0.96 (t, *J* = 7.46 Hz, 3H); 1.19 (d, *J* = 6.6 Hz, 3H); 1.27–1.42 (m, 12H); 1.92–1.98 (m, 4 H); 2.02 (s, 3H); 4.88 (sext, *J* = 6.1 Hz, 1H); 5.29–5.51 (m, 2H); δ_H (50 MHz, $CDCl_3$) 13.9; 19.9; 21.4; 25.4; 25.6; 29.0; 29.4; 29.6; 29.7; 32.5; 35.9; 71.1; 129.3; 131.9; 170.8; lit.[20] $[\alpha]_D^{25} = +4.3$ (*c* 2.42 pentane; reported *e.e.* 100%); lit.[21] $[\alpha]_D^{21} = +0.9$ (*c* 2.04 $CHCl_3$; reported *e.e.* 95.5%); found $[\alpha]_D^{22} = +0.95$ (*c* 1.02, $CHCl_3$, 99% *e.e.*).

(S,E)-Tridec-10-en-2-ol **5**: (yield 76%); colorless oil: δ_H (500 MHz, $CDCl_3$) 0.96 (t, *J* = 7.5 Hz, 3H); 1.19 (d, *J* = 6.0 Hz, 3H); 1.29–1.47 (m, 12H); 1.95–2.02 (m, 4 H); 3.79 (sext, *J* = 6.0 Hz, 1H); 5.37–5.47 (m, 2H); δ_C (125 MHz, $CDCl_3$) 13.9; 23.5; 25.6; 25.8; 29.1; 29.5; 29.6; 29.7; 32.5; 39.4; 68.2; 129.3; 131.9; MS *m/z* (rel int.) 198 (M^+, 2); 180 (4) 151 (2); 138 (6); 109 (16); 95 (42); 82 (78); 68 (100); 55 (70); 41 (92); IR cm^{-1} (neat) 3361; 2963; 2927; 2854; 1461; 1374; 965; lit.[21] $[\alpha]_D^{22} = +6.4$ (*c* 8.89 $CHCl_3$; reported *e.e.* 95.5%); found $[\alpha]_D^{20} = +6.8$ (*c* 1.00 $CHCl_3$).

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References

1. (a) Wall, C.; Pickett, J. A.; Garthwaite, D. G.; Morris, N. *Entomol. Appl.* **1985**, *39*, 11–14; (b) Pillon, O.; Thieuleux, J. *Med. Fac. Landbouww. Univ. Gent.* **1995**, *60*, 645–650.
2. Hillbur, Y.; Anderson, P.; Arn, H.; Bengtsson, M.; Löfqvist, J.; Biddle, A. J.; Smitt, O.; Högberg, H.-E.; Plass, E.; Franke, S.; Francke, W. *Naturwissenschaften* **1999**, *86*, 292–294.
3. Hillbur, Y.; El-Sayed, A.; Bengtsson, M.; Lögqvist, J.; Biddle, A.; Plass, E.; Francke, W. *J. Chem. Ecol.* **2000**, *26*, 1941–1952.
4. Bartelt, R. J.; Schaner, A. M.; Jackson, L. L. *J. Chem. Ecol.* **1989**, *15*, 399–411.
5. Millar, J. G.; Foster, S. P.; Harris, M. O. *J. Chem. Ecol.* **1991**, *17*, 2437–2447.
6. (a) Gagné, R. J. *The Plant-feeding Gall Midges of North America*; Cornell University Press: Ithaca, 1989; (b) El Bouhssini, M.; Nsarellah, M. N.; Nachit, M. M.; Bentika, A.; Benlahbib, O.; Lhaloui, S. *Genet. Resour. Crop Evol.* **1999**, *46*, 107–109; (c) Berzonsky, W. A.; Ding, H.; Haley, S. D.; Harris, M. O.; Lamb, R. J.; McKenzie, r. I. H.; Ohm, H. W.; Patterson, F. L.; Peairs, F. B.; Porter, D. R.; Ratcliffe, R. H.; Shanower, T. G. *Plant Breed Rev.* **2003**, *22*, 221–296; (d) Harris, M. O.; Stuart, J. J.; Mohan, M.; Nair, S.; Lamb, R. J.; Rohfritsch, O. *Annu. Rev. Entomol.* **2003**, *48*, 549–577.
7. (a) Harris, M. O.; Foster, S. P. *J. Chem. Ecol.* **1991**, *17*, 2421–2435; (b) Harris, M. O., Foster, S. P.; Gall midges. In *Pheromones of Non-Lepidopteran Insects Associated with Agricultural Plants*, Hardie, J., Minks, A. K., Eds.; CAB International: Oxford, UK, 1999; pp 27–49.
8. Anderson, M. N.; Haftmann, J.; Stuart, J. J.; Cambron, S. E.; Harris, M. O.; Foster, S. P.; Franke, S.; Francke, W.; Hillbur, Y. *J. Chem. Ecol.* **2009**, *35*, 81–95.
9. (a) Comasseto, J. V.; Barrientos-Astigarraga, R. E. *Aldrichim. Acta* **2000**, *33*, 66–78; (b) Princival, J. L.; Barros, S. M. G.; Comasseto, J. V.; Dos Santos, A. A. *Tetrahedron Lett.* **2005**, *46*, 4423–4425; (c) Dos Santos, A. A.; Comasseto, J. V. *J. Braz. Chem. Soc.* **2005**, *16*, 511–513; (d) Dos Santos, A. A.; Ferrarini, R. S.; Princival, J. L.; Comasseto, J. V. *Tetrahedron Lett.* **2006**, *47*, 8933–8935; (e) Dos Santos, A. A.; Princival, J. L.; Comasseto, J. V.; Barros, S. M. G.; Brainer Neto, J. E. *Tetrahedron* **2007**, *63*, 5167–5172; (f) Bassora, B. K.; Da Costa, C. E.; Gariani, R. A.; Comasseto, J. V.; Dos Santos, a. A. *Tetrahedron Lett.* **2007**, *48*, 1485–1487; (g) Ferrarini, R. S.; Princival, J. L.; Comasseto, J. V.; Dos Santos, A. A. *J. Braz. Chem. Soc.* **2008**, *19*, 811–812; (h) Comasseto, J. V.; Dos Santos, A. A. *Phosphorus, Sulfur Silicon* **2008**, *183*, 939–947; (i) Wendler, E. P.; Dos Santos, A. A. *Synlett* **2009**, 1034–1040.
10. (a) Dos Santos, A. A.; Da Costa, C. E.; Princival, J. L.; Comasseto, J. V. *Tetrahedron: Asymmetry* **2006**, *17*, 2252–2259; (b) Comasseto, J. V.; Berriel, J. N. *Synth. Commnun.* **1990**, *20*, 1681–1685; (c) Tucci, F. C.; Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 5721–5724; (d) Tucci, F. C.; Chieffi, A.; Comasseto, J. V. *J. Org. Chem.* **1996**, *61*, 4975–4989; (e) Barrientos-Astigarraga, R. E.; Ellensohn, R. M.; Comasseto, J. V. *Tetrahedron Lett.* **1999**, *40*, 5115–5118; (f) Moraes, D. N.; Barrientos-Astigarraga, R. E.; Castelani, P.; Comasseto, J. V. *Tetrahedron* **2000**, *56*, 3327–3337; (g) Castelani, P.; Comasseto, J. V. *Organometallics* **2003**, *22*, 2108–2111; (h) Castelani, P.; Luque, S.; Comasseto, J. V. *Tetrahedron Lett.* **2004**, *45*, 4473–4475; (i) Castelani, P.; Comasseto, J. V. *Tetrahedron* **2005**, *61*, 2319–2326; (j) Diego, D. G.; Cunha, R. L. O. R.; Comasseto, J. V. *Tetrahedron Lett.* **2006**, *47*, 7147–7148.
11. (a) Comasseto, J. V.; Gariani, R. A. *Tetrahedron* **2009**, doi:10.1016/j.tet.2009.06.121.; (b) Dos Santos, A. A.; Da Costa, C. E.; Princival, J. L.; Comasseto, J. V. *Tetrahedron: Asymmetry* **2006**, *17*, 2252–2259.
12. (a) Chong, J. M.; Heuft, M. A.; Rabbat, P. *J. Org. Chem.* **2000**, *65*, 5837–5838; (b) Bestmann, H. J.; Gunawardena, N. E. *Synthesis* **1992**, *12*, 1239–1241; (c) Buck, M.; Chong, J. M. *Tetrahedron Lett.* **2001**, *42*, 5825–5827; (d) Warthen, J. D., Jr.; Jacobson, M. *Synthesis* **1973**, *10*, 616.
13. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1980.
14. Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1976**, *9*, 165–168.
15. Chow, S.; Kitching, W. *Tetrahedron: Asymmetry.* **2002**, *13*, 779–793.
16. Enders, D.; Plant, A. *Liebigs Ann. Chem.* **1991**, 1241–1243.

17. Hintze, F.; Hoppe, D. *Synthesis* **1992**, 1216–1218.
18. Ishmuratov, G. Y.; Kharisov, R. Y.; Botsman, O. V.; Zorin, V. V.; Tolstikov, G. A. *Russ. Chem. Bull. Int. Ed.* **2000**, *49*, 1899–1901.
19. Hamada, T.; Daikai, K.; Irie, R.; Katsuki, T. *Tetrahedron: Asymmetry* **1995**, *6*, 2441–2451.
20. Kamekawa, M.; Tachibana, H.; Ohtani, T.; Naoshima, Y. *Biosci. Biotechnol. Biochem.* **1993**, *57*, 1962–1963.
21. Takeuchi, Y.; Mori, K. *Biosci. Biotechnol. Biochem.* **1993**, *57*, 1967–1968. and references cited therein.