EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201400021

Domino Recombinant γ-Isomerization and Reverse Wacker Oxidation of γ-Vinyl-γ-butyrolactone: Synthesis of (+)-*trans*-, (–)- and (+)-Disparlures

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Keywords: Synthetic methods / Asymmetric synthesis / Cross-metathesis / Palladium / Oxidation / Pheromones

A domino palladium-catalyzed recombinant γ-isomerization and reverse Wacker oxidation of γ-vinyl-γ-butyrolactone has been explored. The strategy has been used in the stereoselective synthesis of (+)-*trans*-, (–)- and (+)-disparlures. The synthesis was achieved in seven to eight steps from D-glucono-δ-lactone with overall yields of 19.3, 20.7 and 22.6 %, respectively.

Introduction

The regioselective transformation of terminal olefins to carbonyl compounds has drawn considerable synthetic interest during the past few decades. The palladium-catalyzed Wacker process is a common choice to prepare methyl ketones from the corresponding olefins.[1] This process has been widely used in industry and synthetic research. The aldehyde-selective Wacker process has been a major challenge and considerable efforts have been made to address this important issue.[2] The overall outcome of the Wacker reaction mainly depends on regioselective hydration of the olefin followed by oxidation. The Markovnikov and anti-Markovnikov hydration of terminal olefins lead to the formation of methyl ketones and aldehydes, respectively. In particular, selective aldehyde formation was observed in the presence of chelating neighboring functionalities (oxygen, nitrogen or π complexation),[3] or by using various palladium and iron catalysts.[2] The heteroatom-directed reverse Wacker oxidation has been employed in natural product synthesis.[4] However, this process was rarely studied for γ-vinyl-γ-butyrolactone to corresponding aldehydes without effecting the lactone chiral center.[5] In continuation to our interest in the application of γ-vinyl-γ-butyrolactone in the synthesis of natural products,[6] recently we studied the recombinant inversion of γ-vinyl-γ-butyrolactone by palladium catalysis.[7] Here, we report an efficient domino recombinant γ-isomerization and reverse Wacker oxidation of γ-vinyl-γ-butyrolactone. The developed method was successfully used for the synthesis of (+)-*trans*-, (–)- and (+)-disparlures (Figure 1).

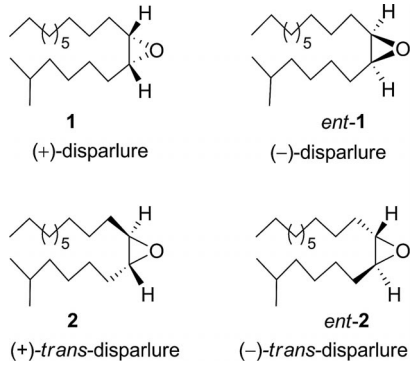

Figure 1. Structures of disparlures.

In 1970, Bierl identified disparlure as a sex-attractant pheromone, from the female gypsy moth, *Lymantria Dispar* L.[8] This moth is a harmful pest causing serious forest losses during outbreaks in Europe, Asia and North America. Iwaki et al.[9] proved the absolute stereochemistry of disparlure through the synthesis of both enantiomers. A recent study showed that (+)-disparlure (**1**) and *ent*-**1** have different binding affinity towards the two pheromone-binding proteins (PBP1 and PBP2).[10] Disparlure and its stereoisomers have been interesting synthetic targets for a long time.[11]

Results and Discussion

Our investigation began by wanting to generalize the applications of *syn*-lactone **4a** in various reactions.[12] *Syn*-lactone **4a** can now be prepared easily from D-glucono-δ-lactone by following a reliable one-pot process.[6] We subjected *syn*-lactone **4a** to the hetero-atom directed reverse Wacker oxidation[4] with $PdCl_2$ (10 mol-%) and CuCl (1.5 equiv.) in dimethylformamide (DMF)/H_2O (7:1) under O_2 gas to give aldehyde **5**. This compound after Wittig olefination with (isopentyl)triphenylphosphonium bromide (**6**)

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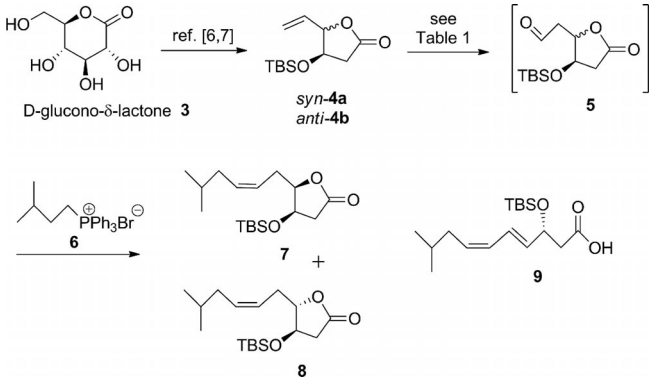
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201400021.

and lithium bis(trimethylsilyl)amide (LiHMDS) gave two separable diastereomeric lactones **7** and **8** isolated in 39 and 6% yields, respectively (Table 1, Entry 1). The latter resulted through Pd-catalyzed domino recombinant γ-isomerization and reverse Wacker oxidation. The reaction with 20 mol-% of $PdCl_2$ afforded *syn*-lactone **7** with an improved yield of 60% along with isomerized product **8** in 9% yield (Table 1, Entry 2). Lowary and co-workers[5a] earlier reported a similar reaction to give exclusive *syn*-aldehyde product and did not isolate any γ-isomerization product. Slow isomerization of an aldehyde, such as **5** [with no *tert*-butyldimethylsilyl ether (β-OTBDMS) group], is known without involvement of Pd.[13] However, Pd is required for the Wacker process. We became interested in exploring this de novo domino recombinant γ-isomerization and reverse Wacker oxidation. We believed that an interplay of reaction conditions could lead predominantly to either compound **7**, through reverse Wacker oxidation as the major product, or to **8**, by a domino recombinant γ-isomerization followed by reverse Wacker oxidation. To maximize the γ-isomerization, we planned to premix **4a** with the palladium catalyst and CuCl under a nitrogen atmosphere. To this end, pre-mixed *syn*-lactone **4a** with palladium catalyst (10 mol-%) was stirred for 20 min before bubbling O_2 gas. The isolated aldehyde was subjected to Wittig reaction to give *anti*-lactone **8** as the major product (32%) along with *syn*-lactone **7** in 13% yield (Table 1, Entry 3). This indicates that because O_2 gas was not bubbled, it suppressed the Wacker oxidation but promoted Pd-catalyzed recombinant γ-isomerization. The reaction was further optimized with $PdCl_2$ (20 mol-%) to give *anti*-lactone **8** in 51% and **7** in 21% yield, respectively (Table 1, Entry 4). A one-pot β-epimerization followed by Wacker oxidation was attempted with $Pd(OAc)_2$ (20 mol-%; Table 1, Entry 5).[14] However, though β-epimerization was observed by formation of a mixture of **4a** and **4b** by TLC, no aldehyde formation was observed even after a prolonged reaction time. Consequently, the Wittig reaction was not attempted. Further attempts to improve the yield of the Wittig reaction by using *t*BuOK (2.5 equiv.), cleanly gave compound **9** (70%; Table 1, Entry 6) obtained through opening of the lactone. Later, we planned to analyze the reliability of our method by performing the Wacker oxidation on *anti*-lactone **4b**. *Anti*-lactone **4b** can be obtained from **4a** by a recombinant inversion method developed by us.[7] A reverse Wacker oxidation by using premixed *anti*-lactone **4b** with $PdCl_2$ (10 mol-%) and CuCl followed by Wittig reaction delivered **8** (48%) and **7** (11%; Table 1, Entry 7). The reaction yield of **8** was further improved to 64% by increasing the palladium catalyst loading from 10 to 20 mol-% (Table 1, Entry 8). This reaction indi-

Table 1. Domino recombinant γ-isomerization and reverse Wacker oxidation of lactones **4a** or **4b** and subsequent Wittig olefination.

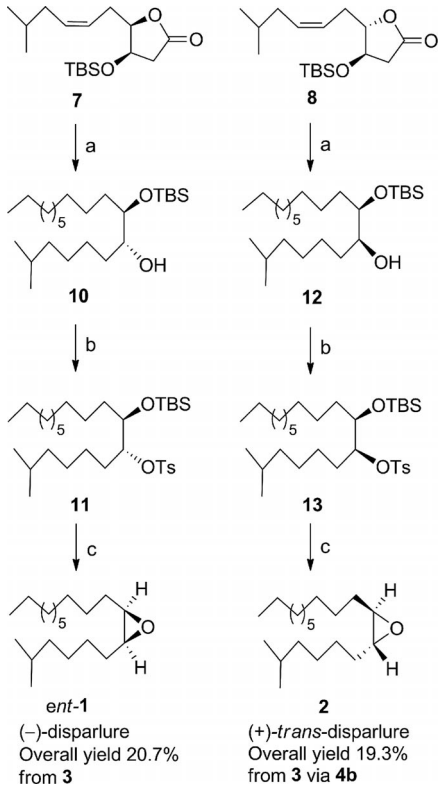


Entry	Reaction conditions	Isolated yields
1	(i) $PdCl_2$ (10 mol-%), CuCl (1.5 equiv.), DMF/H_2O (7:1), room temp., 20 min, then **4a**, O_2, 10 h; (ii) **6**, LiHMDS, THF, 0 °C, 45 min, then **5**, –20 °C, 8 h.	*syn*-**7** (39%) *anti*-**8** (6%)
2	(i) $PdCl_2$ (20 mol-%), CuCl (1.5 equiv.), DMF/H_2O (7:1), room temp., 20 min, then **4a**, O_2, 8 h; (ii) **6**, LiHMDS, THF, 0 °C, 45 min, then **5**, –20 °C, 8 h.	*syn*-**7** (60%) *anti*-**8** (9%)
3	(i) **4a**, $PdCl_2$ (10 mol-%), CuCl (1.5 equiv.), DMF/H_2O (7:1), room temp., 20 min, then O_2, room temp., 10 h; (ii) **6**, LiHMDS, THF, 0 °C, 45 min, then **5**, –20 °C, 8 h.	*syn*-**7** (13%) *anti*-**8** (32%)
4	(i) **4a**, $PdCl_2$ (20 mol-%), CuCl (1.5 equiv.), DMF/H_2O (7:1), room temp., 20 min, then O_2, room temp., 8 h; (ii) **6**, LiHMDS, THF, 0 °C, 45 min, then **5**, –20 °C, 8 h.	*syn*-**7** (21%) *anti*-**8** (51%)
5	(i) **4a**, $Pd(OAc)_2$ (20 mol-%), PPh_3 (80 mol-%), pyridine (0.5 equiv.), THF, 50 °C, 36 h; (ii) CuCl (1.5 equiv.), THF/DMF:H_2O (3.5:3.5:1), O_2, room temp., 12 h.	–[a]
6	(i) $PdCl_2$ (20 mol-%), CuCl (1.5 equiv.), DMF/H_2O (7:1), room temp., 20 min, then **4a**, O_2, 8 h; (ii) **6**, *t*BuOK (2.5 equiv.), THF, 0 °C, 45 min, then **5**, –20 °C, 3 h.	**9** (70%)
7	(i) **4b**, CuCl (1.5 equiv.), DMF/H_2O (7:1), O_2, room temp., 20 min, then $PdCl_2$ (10 mol-%), 8 h; (ii) **6**, LiHMDS, THF, 0 °C, 45 min, then **5**, –20 °C, 8 h.	*syn*-**7** (11%) *anti*-**8** (48%)
8	(i) **4b**, CuCl (1.5 equiv.), DMF/H_2O (7:1), O_2, room temp., 20 min, then $PdCl_2$ (20 mol-%), 6 h; (ii) **6**, LiHMDS, THF, 0 °C, 45 min, then **5**, –20 °C, 8 h.	*syn*-**7** (16%) *anti*-**8** (64%)

[a] No Wacker oxidation occurred. Only epimerization products were detected by TLC. Therefore the Wittig reaction was not attempted. THF = tetrahydrofuran.

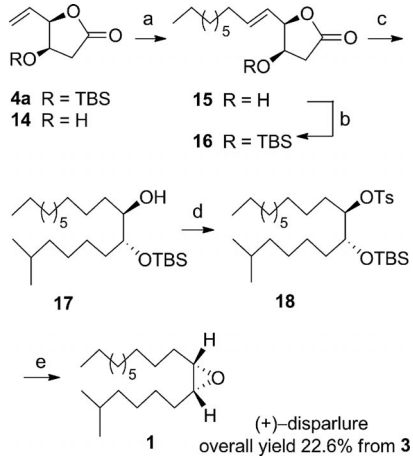
cates a probable equilibration between the *anti*- and *syn*-lactone through the formation of an intermediate π-allyl species.

With the synthesized lactones **7**, **8** and **4a**, we aimed to use them in the synthesis of (–)-disparlure (*ent*-**1**), (+)-*trans*-disparlure (**2**) and (+)-disparlure (**1**), respectively. Our synthetic approach for (–)-disparlure (*ent*-**1**) and (+)-*trans*-disparlure (**2**) is shown in Scheme 1. *syn*-Lactone **7** was reduced with diisobutylaluminium hydride (DIBAL-H) to the lactol and subsequent Wittig olefination with (*n*-octyl)triphenylphosphonium bromide and with *n*BuLi as base, provided the diene that was immediately hydrogenated to produce **10** in 86% yield (over three steps). Similarly, compound **8** led to **12** in 83% yield. Alcohol **10** on tosylation to **11** (quantitative), followed by treatment with tetra-*n*-butylammonium fluoride (TBAF) afforded (–)-disparlure (*ent*-**1**) in 91% yield, $[\alpha]_D^{25}$ = –1.6 (*c* = 1.2, CCl_4), ref.[11m] $[\alpha]_D$ = –1.0 (*c* = 1.7, CCl_4). Similarly, alcohol **12** on tosylation provided **13** in 94% yield. The latter on TBAF treatment then led to (+)-*trans*-disparlure (**2**) in 88% yield, $[\alpha]_D^{25}$ = +25.6 (*c* = 0.4, CCl_4), ref.[9] $[\alpha]_D^{25}$ = +27.5 (*c* = 0.5, CCl_4). The spectroscopic and analytical data of *ent*-**1** and **2** were in good agreement with reported data.[9]



Scheme 1. Synthesis of (–)-disparlure and (+)-*trans*-disparlure. Reagents and conditions: (a) (i) DIBAL-H (1.5 equiv.), Et_2O, –78 °C, 1 h; (ii) $Ph_3P^+CH_2(CH_2)_6CH_3Br^-$ (2.0 equiv.), THF, *n*BuLi (2.0 equiv.), 0 °C, 1 h, lactol, 0 °C to room temp., 8 h; (iii) H_2, $Pd(OH)_2$/C, *i*PrOH, room temp., 3 h, **10** (86%, over 3 steps), **12** (83%); (b) 4-Dimethylaminopyridine (DMAP; 4.0 equiv.) TsCl (3.0 equiv.), CH_2Cl_2, 0 °C to room temp., 24 h, **11** (quant), **13** (94%); (c) TBAF (3.4 equiv.), THF, 0 °C to room temp., 5 h, *ent*-**1** (91%), **2** (88%).

For (+)-disparlure (**1**) synthesis, the cross-metathesis[15] of lactone **4a** with 1-decene and Grubbs' second-generation (G-II) catalyst gave **16** in low yield (20%). The use of Grubbs–Hoveyda second-generation (GH-II) catalyst, furnished **16** in 45% yield. The cross-metathesis reaction of unprotected lactone **14** and 1-decene with G-II catalyst afforded **15** in excellent yield of 90% with calcd. <10% of *Z*-olefin isomer formed. Initial efforts for free hydroxy group silylation as the *tert*-butyldimethylsilyl (TBS) ether with TBSCl and imidazole were low yielding. Later a suitable condition was identified with TBSOTf and 2,6-lutidine to give **16** in 86% yield (Scheme 2). Low-temperature DIBAL-H reduction of the lactone to lactol and subsequent Wittig reaction with (isopentyl)triphenylphosphonium bromide (**6**) gave the diene, which was immediately hydrogenated by using $Pd(OH)_2$/C in *i*PrOH to produce saturated alcohol **17** in 70% yield (over three steps). Conversion of hydroxy group to tosylate (**18**, 91%) and further in situ TBAF-mediated OTBS deprotection resulted in spontaneous displacement of the tosyl group to give (+)-disparlure (**1**) in 90% yield, $[\alpha]_D^{25}$ = +1.6 (*c* = 1.1, CCl_4), ref.[11m] $[\alpha]_D$ = +1.0 (*c* = 1.5, CCl_4). The analytical and spectroscopic data of **1** were in excellent agreement with earlier reports.[11]



Scheme 2. Synthesis of (+)-disparlure. Reagents and conditions: (a) **14**, 1-decene (1.5 equiv.), G-II catalyst (2.0 mol-%), CH_2Cl_2, reflux, 72 h, **15** (90%) or **4a**, 1-decene (2.0 equiv.), GH-II catalyst (2.0 mol-%), reflux, 72 h, **16** (45%); (b) 2,6-lutidine (2.0 equiv.), TBDMSOTf (1.5 equiv.), CH_2Cl_2, 0 °C to room temp., 2 h, **16** (86%); (c) (i) DIBAL-H (1.5 equiv.), Et_2O, –78 °C, 1 h; (ii) $Br^-Ph_3P^+CH_2CH_2CH(CH_3)_2$ (4.0 equiv.), *n*BuLi (4.0 equiv.), toluene, 0 °C, 30 min, lactol, 0 °C to room temp., 3 h; (iii) H_2, $Pd(OH)_2$/C, *i*PrOH, room temp., 6 h, 70% (over 3 steps); (d) DMAP (2.5 equiv.) *p*TsCl (2.0 equiv.), CH_2Cl_2, 0 °C, 1 h, room temp., 5 h, 91%; (e) TBAF (3.4 equiv.), THF, 0 °C to room temp., 5 h, 90%.

Conclusions

In summary, we have developed de novo an efficient domino recombinant γ-isomerization and reverse Wacker oxidation of γ-vinyl-γ-butyrolactone. The developed method was then used in the stereoselective synthesis of (+)- and (–)-disparlures and (+)-*trans*-disparlure. Further

studies to extend this strategy on larger-ring-size lactones to give useful building blocks for natural products synthesis are in progress and will be reported in due course.

Experimental Section

General Information: Flasks were oven or flame dried and cooled in a desiccator. Dry reactions were carried out under an atmosphere of Ar or N_2. Solvents and reagents were purified by standard methods. Thin-layer chromatography was performed with EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or under UV lamp. ^1H and ^{13}C NMR spectra were recorded with a Bruker, AVANCE III 400 spectrometer and the chemical shifts are calculated relative to the tetramethylsilane peak at δ = 0.00 pm for ^1H NMR spectra, and relative to the $CDCl_3$ peak at δ = 77.00 ppm (t) for ^{13}C NMR spectra. IR spectra were obtained with a Perkin–Elmer Spectrum One FT–IR spectrometer and samples were prepared by evaporation from $CHCl_3$ on CsBr plates. Optical rotations were measured with a Jasco P-2000 digital polarimeter. High-resolution mass spectra (HRMS) were obtained by using positive electrospray ionization and by TOF method.

(4*R*,5*R*)-4-(*tert*-Butyldimethylsilyloxy)-5-(*Z*)-(5-methylhex-2-enyl)dihydrofuran-2(3*H*)-one (7) and (4*R*,5*S*)-4-(*tert*-Butyldimethylsilyloxy)-5-(*Z*)-(5-methylhex-2-enyl)dihydrofuran-2(3*H*)-one (8): Reaction conditions were as stated in Table 1, Entry 2: A mixture of $PdCl_2$ (30.7 mg, 0.173 mmol, 20 mol-%) and CuCl (129 mg, 1.3 mmol, 1.5 equiv.) in DMF (5 mL) and H_2O (1 mL) was stirred for 20 min at room temperature. To this mixture was added compound **4a** (210 mg, 0.866 mmol) in DMF (2 mL) and oxygen gas was bubbled through the solution for 8 h. It was then filtered through a small pad of silica gel and washed with EtOAc. The filtrate was washed with water (3 × 50 mL), brine, dried (Na_2SO_4) and concentrated to give crude aldehyde **5** (200 mg) as a colorless oil, which was used directly in the next reaction.

To a stirred suspension of (isopentyl)triphenylphosphonium bromide (**6**; 430 mg, 1.04 mmol, 1.2 equiv.) in dry THF (15 mL) was added LiHMDS (1.2 M solution in THF, 0.9 mL, 1.04 mmol, 1.2 equiv.) at 0 °C and stirred for 45 min. It was then cooled to –20 °C and a solution of aldehyde **5** (200 mg) in THF (5 mL) was added. The reaction mixture was stirred for 8 h and then quenched with saturated aq. NH_4Cl solution. The mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (19:1) as an eluent to afford **8** (24.4 mg, 9%) as a colorless oil. Further elution gave **7** (162.5 mg, 60%) as a colorless oil.

Data for 7: $[a]_D^{25}$ = +6.1 (*c* = 0.75, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3020, 2957, 2931, 2860, 1779, 1465, 1364, 1259, 1160, 1102, 1085, 1030, 951, 897, 840, 668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 5.61–5.54 (m, 1 H), 5.49–5.43 (m, 1 H), 4.47–4.44 (m, 1 H), 4.35–4.31 (m, 1 H), 2.72 (dd, *J* = 17.2, 5.3 Hz, 1 H), 2.65–2.58 (m, 1 H), 2.45 (dd, *J* = 17.2, 1.5 Hz, 1 H), 2.42–2.37 (m, 1 H), 1.95 (t, *J* = 7.1 Hz, 2 H), 1.67–1.62 (m, 1 H), 0.91–0.89 (m, 15 H), 0.09 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.3, 132.1, 123.9, 84.8, 69.3, 39.6, 36.5, 28.5, 26.9, 25.6, 22.3, 22.2, 17.9, –4.6, –5.2 ppm. HRMS: calcd. for $[C_{17}H_{32}O_3Si + Na]^+$ 335.2013; found 335.2012.

Data for 8: $[a]_D^{25}$ = –13.5 (*c* = 1.5, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3026, 2955, 2931, 2859, 1788, 1603, 1496, 1464, 1384, 1362, 1258, 1197, 1167, 1134, 1086, 1005, 922, 838, 779, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 5.64–5.59 (m, 1 H), 5.45–5.38 (m, 1 H), 4.31 (td, *J* = 6.5, 3.1 Hz, 1 H), 4.22–4.19 (m, 1 H), 2.74 (dd, *J* = 17.7, 6.6 Hz, 1 H), 2.42 (dd, *J* = 17.6, 4.0 Hz, 1 H), 2.38 (t, *J* = 6.8 Hz, 2 H), 1.95 (td, *J* = 7.1, 1.3 Hz, 2 H), 1.67–1.62 (m, 1 H), 0.90–0.86 (m, 15 H), 0.071 (s, 3 H), 0.061 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.9, 133.0, 122.8, 87.5, 71.3, 38.1, 36.5, 30.5, 28.5, 25.5, 22.3, 17.8, –4.8, –4.9 ppm. HRMS: calcd. for $[C_{17}H_{32}O_3Si + Na]^+$ 335.2013; found 335.2012.

(4*R*,5*R*)-4-(*tert*-Butyldimethylsilyloxy)-5-(*Z*)-(5-methylhex-2-enyl)dihydrofuran-2(3*H*)-one (7) and (4*R*,5*S*)-4-(*tert*-Butyldimethylsilyloxy)-5-(*Z*)-(5-methylhex-2-enyl)dihydrofuran-2(3*H*)-one (8): Reaction conditions were as stated in Table 1, Entry 4: To a stirred solution of compound **4a** (120 mg, 0.495 mmol) in DMF (3.5 mL) and water (0.5 mL) were added $PdCl_2$ (17.6 mg, 0.099 mmol, 20 mol-%) and CuCl (73.6 mg, 0.743 mmol, 1.5 equiv.) and the mixture stirred for 20 min. Then oxygen gas was bubbled through the solution for 8 h at room temperature. It was then filtered through a small pad of silica gel and washed with EtOAc. The filtrate was washed with water (3 × 50 mL), brine, dried (Na_2SO_4) and concentrated to give aldehyde **5** (120 mg) as a colorless oil, which was used directly in the next reaction.

To a stirred suspension of (isopentyl)triphenylphosphonium bromide (**6**; 307 mg, 0.743 mmol, 1.5 equiv.) in dry THF (10 mL) was added LiHMDS (1.2 M solution in THF, 0.62 mL, 0.743 mmol, 1.5 equiv.) at 0 °C and stirred for 45 min. It was then cooled to –20 °C and a solution of aldehyde **5** (120 mg) in THF (5 mL) was added. The reaction mixture was stirred for 8 h and then quenched with saturated aq. NH_4Cl solution. The mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (9:1) as an eluent to afford **8** (78.9 mg, 51%) as a colorless oil. Further elution gave **7** (32.5 mg, 21%) as a colorless oil. The analytical and spectroscopic data for **7** and **8** were the same as before.

(3*R*,4*E*,6*Z*)-3-(*tert*-Butyldimethylsilyloxy)-9-methyldeca-4,6-dienoic Acid (9): Reaction conditions were as stated in Table 1, Entry 6: A mixture of $PdCl_2$ (29.3 mg, 0.165 mmol, 20 mol-%) and CuCl (122.7 mg, 1.24 mmol, 1.5 equiv.) in DMF (5 mL) and H_2O (1 mL) was stirred for 20 min at room temperature. To this mixture was then added compound **4a** (0.2 g, 0.825 mmol) in DMF (2 mL) and oxygen gas was bubbled through the solution for 8 h. The mixture was then filtered through a small pad of silica gel and washed with EtOAc. The filtrate was washed with water (3 × 50 mL), brine, dried (Na_2SO_4) and concentrated to give crude aldehyde **5** (200 mg) as a colorless oil, which was used directly in the next reaction.

To a stirred suspension of (isopentyl)triphenylphosphonium bromide (**6**; 0.852 g, 2.062 mmol, 2.5 equiv.) in dry THF (15 mL) was added *t*BuOK (0.231 g, 2.062 mmol, 2.5 equiv.) at 0 °C and stirred for 45 min. It was then cooled to –20 °C and a solution of aldehyde **5** (200 mg) in THF (5 mL) was added. The reaction mixture was stirred for 3 h and then quenched with saturated aq. NH_4Cl solution. The mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (1:1) as eluent to afford **9** (0.181 g, 70%) as a colorless oil. $[a]_D^{25}$ = +4.5 (*c* = 1.5, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3475, 3020, 2959, 2928, 2872, 1772, 1719, 1635, 1467, 1405, 1366, 1168, 1050, 975, 908, 668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 6.51 (dd, *J* = 15.1, 11.1 Hz, 1 H), 6.00 (t, *J* = 11.0 Hz, 1 H), 5.63 (dd, *J* = 15.1, 6.5 Hz, 1 H), 5.50 (dt, *J* = 10.8, 7.9 Hz, 1 H), 4.64 (q, *J* = 6.0 Hz, 1 H), 2.57 (d, *J* =

6.0 Hz, 2 H), 2.05 (dd, J = 15.1, 11.1 Hz, 2 H), 1.68–1.61 (m, 1 H), 0.91–0.89 (m, 15 H), 0.09 (s, 3 H), 0.08 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.4, 134.0, 132.0, 128.2, 125.9, 70.1, 43.6, 36.8, 28.7, 25.7, 22.3, 22.27, 18.1, –4.4, –5.1 ppm. HRMS: calcd. for $[C_{17}H_{32}O_3Si + Na]^+$ 335.2013; found 335.2019.

(4*R*,5*R*)-4-(*tert*-Butyldimethylsilyloxy)-5-(*Z*)-(5-methylhex-2-enyl)dihydrofuran-2(3*H*)-one (7) and (4*R*,5*S*)-4-(*tert*-Butyldimethylsilyloxy)-5-(*Z*)-(5-methylhex-2-enyl)dihydrofuran-2(3*H*)-one (8): Reaction conditions were as stated in Table 1, Entry 8: Compounds **7** and **8** were obtained from **4b** (150 mg, 0.619 mmol) by a similar procedure as described in Table 1, Entry 2. This delivered **7** (30.9 mg, 16%) and **8** (123.8 mg, 64%) as colorless oils.

(7*R*,8*R*)-8-(*tert*-Butyldimethylsilyloxy)-2-methyloctadecan-7-ol (10): To a stirred solution of **7** (114 mg, 0.365 mmol) in dry Et_2O (10 mL) at –78 °C was added DIBAL-H (1.75 M solution in toluene, 0.31 mL, 0.547 mmol, 1.5 equiv.) dropwise under a N_2 atmosphere. The reaction mixture was stirred for 1 h and then quenched with saturated aq. Rochelle's salt solution (3 mL) and stirred vigorously at room temperature for 1 h. The aqueous layer was separated and extracted with CH_2Cl_2 (3× 10 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated to give the corresponding lactol (114 mg), which was used directly in the next reaction.

To a stirred suspension of (*n*-octyl)triphenylphosphonium bromide (333 mg, 0.73 mmol, 2.0 equiv.) in dry THF (10 mL) was added *n*BuLi (1.6 M solution in hexane, 0.46 mL, 0.73 mmol, 2.0 equiv.) at 0 °C. The mixture was stirred for 1 h and a solution of the above lactol (114 mg, 0.362 mmol) in THF (3 mL) was added. It was warmed to room temperature and stirred for 8 h and then quenched with saturated aq. NH_4Cl solution. The mixture was extracted with EtOAc (3× 10 mL) and the combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (49:1) as an eluent to afford the diene (143 mg) as a colorless oil. The diene was immediately used in the hydrogenation reaction.

To a stirred solution of diene (143 mg) in propane-2-ol (12 mL) was added 10% $Pd(OH)_2$ on charcoal (20 mg) and stirred under H_2 (balloon pressure) atmosphere at room temperature for 3 h. The mixture was filtered through a small pad of Celite and washed with EtOAc and the filtrate concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (97:3) as eluent to give alcohol **10** (130.1 mg, 86% overall) as a colorless oil. $[\alpha]_D^{25}$ = –1.9 (c = 1.0, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3470, 2928, 2857, 1464, 1385, 1366, 1255, 1086, 1006, 837, 775, 669 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 3.51–3.47 (m, 1 H), 3.45–3.41 (m, 1 H), 2.13 (d, J = 6.8 Hz, 1 H), 1.56–1.14 (m, 27 H), 0.91–0.85 (m, 18 H), 0.08 (s, 3 H), 0.07 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 75.1, 72.6, 39.0, 34.2, 33.9, 31.9, 29.9, 29.6, 29.57, 29.3, 27.9, 27.6, 27.4, 25.9, 25.2, 25.0, 22.7, 22.6, 18.1, 14.1, –4.1, –4.6 ppm. HRMS: calcd. for $[C_{25}H_{54}O_2Si + Na]^+$ 437.3785; found 437.3784.

(7*S*,8*R*)-8-(*tert*-Butyldimethylsilyloxy)-2-methyloctadecan-7-ol (12): This compound was prepared from **8** (70 mg, 0.223 mmol) by a similar procedure as described for **10**, to give **12** (77.1 mg, 83%) as a colorless oil. $[\alpha]_D^{25}$ = –1.1 (c = 0.8, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3470, 2954, 2928, 2857, 1465, 1384, 1365, 1258, 1086, 836, 805, 775, 669 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 3.62–3.56 (m, 2 H), 2.14 (d, J = 2.9 Hz, 1 H), 1.53–1.14 (m, 27 H), 0.92–0.84 (m, 18 H), 0.076 (s, 3 H), 0.072 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 75.3, 74.7, 39.0, 31.9, 31.8, 30.4, 29.8, 29.6, 29.3, 28.0, 27.6, 27.5, 26.4, 26.2, 26.0, 25.9, 25.8, 22.7, 22.6, 18.1, 14.1, –4.5 ppm. HRMS: calcd. for $[C_{25}H_{54}O_2Si + Na]^+$ 437.3785; found 437.3789.

(7*R*,8*R*)-8-(*tert*-Butyldimethylsilyloxy)-2-methyloctadecan-7-yl-4-methylbenzenesulfonate (11): To a stirred solution of **10** (80 mg, 0.193 mmol) in dry CH_2Cl_2 (5 mL), was added 4-(dimethylamino)-pyridine (DMAP; 94.3 mg, 0.772 mmol, 4.0 equiv.) and *p*-toluenesulfonyl chloride (110.6 mg, 0.58 mmol, 3.0 equiv.) at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. It was then quenched with water (5 mL) and the solution extracted with CH_2Cl_2 (3× 10 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (99:1) as eluent to give **11** (109.8 mg, quant.) as a colorless oil. $[\alpha]_D^{25}$ = +26.3 (c = 1.0, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2954, 2928, 2856, 1599, 1496, 1464, 1368, 1257, 1188, 1177, 1116, 1098, 936, 901, 837, 814, 776, 667 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.78 (d, J = 8.2 Hz, 2 H), 7.33 (d, J = 8.1 Hz, 2 H), 4.34–4.29 (m, 1 H), 3.75–3.71 (m, 1 H), 2.44 (s, 3 H), 1.66–1.02 (m, 27 H), 0.90–0.80 (m, 18 H), 0.049 (s, 3 H), 0.006 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 134.3, 129.7, 127.8, 84.9, 72.1, 38.9, 31.9, 30.3, 29.6, 29.5, 29.3, 29.1, 27.9, 27.3, 26.3, 25.7, 25.6, 25.5, 22.7, 22.5, 21.6, 17.9, 14.1, –4.46, –4.8 ppm. HRMS: calcd. for $[C_{32}H_{60}O_4SiS + Na]^+$ 591.3874; found 591.3873.

(7*S*,8*R*)-8-(*tert*-Butyldimethylsilyloxy)-2-methyloctadecan-7-yl-4-methylbenzenesulfonate (13): This compound was prepared from **12** (35 mg, 0.0844 mmol) by a similar procedure as described for **11**, to give **13** (45.2 mg, 94%) as a colorless oil. $[\alpha]_D^{25}$ = +2.3 (c = 0.8, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2955, 2927, 2856, 1717, 1599, 1466, 1366, 1257, 1188, 1177, 1097, 915, 836, 813, 777, 723, 666, 555 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.79 (d, J = 8.3 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 4.41 (dt, J = 2.5, 9.0 Hz, 1 H), 3.89–3.86 (m, 1 H), 2.43 (s, 3 H), 1.58–1.12 (m, 27 H), 0.91–0.81 (m, 18 H), 0.07 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 134.6, 129.6, 127.8, 88.7, 74.0, 38.8, 38.7, 34.3, 31.9, 29.6, 29.56, 29.5, 29.3, 27.9, 27.7, 27.0, 25.9, 25.7, 25.4, 22.7, 22.6, 21.6, 18.1, 14.1, –4.5, –4.8 ppm. HRMS: calcd. for $[C_{32}H_{60}O_4SiS + Na]^+$ 591.3874; found 591.3876.

***cis*-(7*S*,8*R*)-7,8-Epoxy-2-methyloctadecane, (–)-Disparlure (*ent*-1):** To a stirred solution of **11** (90 mg, 0.158 mmol) in dry THF (5 mL) was added TBAF (1.0 M solution in THF, 0.54 mL, 0.537 mmol, 3.4 equiv.) at 0 °C under an N_2 atmosphere. The reaction mixture was slowly warmed to room temperature and stirred for 5 h. It was then quenched with water and extracted with EtOAc (3× 15 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (99:1) as eluent to afford *ent*-**1** (40.6 mg, 91%) as a colorless oil. $[\alpha]_D^{25}$ = –1.6 (c = 1.2, CCl_4), ref.[11m] $[\alpha]_D$ = –1.0 (c = 1.5, CCl_4). IR ($CHCl_3$): $\tilde{\nu}$ = 2955, 2926, 2856, 1466, 1385, 1367, 1266, 1170, 1021, 839, 722 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 2.91–2.88 (m, 2 H), 1.55–1.16 (m, 27 H), 0.89–0.86 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.2, 38.9, 31.9, 29.6, 29.5, 29.3, 27.9, 27.8, 27.79, 27.3, 26.8, 26.6, 22.7, 22.6, 14.1 ppm. HRMS: calcd. for $[C_{19}H_{38}O + Na]^+$ 305.2815; found 305.2812.

(+)-*trans*-(7*R*,8*R*)-Disparlure (2): This compound was prepared from **13** (30 mg, 0.053 mmol) by a similar procedure as described for *ent*-**1**, to afford **2** (13.1 mg, 88%) as a colorless oil. $[\alpha]_D^{25}$ = +25.6 (c = 0.4, $CHCl_3$), ref.[9] $[\alpha]_D^{25}$ = +27.5 (c = 0.5, CCl_4). IR ($CHCl_3$): $\tilde{\nu}$ = 2956, 2927, 2856, 1467, 1384, 1367, 1261, 1169, 1046, 900, 668 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 2.67–2.64 (m, 2 H), 1.57–1.14 (m, 27 H), 0.97–0.82 (m, 9 H) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 58.9, 38.9, 32.2, 32.1, 31.9, 29.6, 29.5, 29.4, 29.3, 27.9, 27.2, 26.3, 26.0, 22.7, 22.6, 14.1 ppm. HRMS: calcd. for $[C_{19}H_{38}O + K]^+$ 321.2554; found 321.2559.

(4*R*,5*R*)-5-[(*E*)-Hex-1-en-1-yl]-4-hydroxydihydrofuran-2(3*H*)-one (15): To a stirred and degassed solution of **14** (50 mg, 0.390 mmol) and 1-decene (83 mg, 0.585 mmol, 1.5 equiv.) in dry CH_2Cl_2 (5 mL) at room temperature was added Grubbs' second-generation catalyst (6.8 mg, 0.008 mmol, 2.0 mol-%) and the reaction mixture was heated to reflux for 72 h. It was then cooled and filtered through a small pad of silica gel and the filtrate concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (17:3) as eluent to give **15** (84.4 mg, 90%) as a colorless oil. $[\alpha]_D^{25}$ = +22.0 (*c* = 0.6, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3453, 3018, 2927, 2856, 1771, 1670, 1466, 1327, 1164, 1076, 1014, 967, 906, 845 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 6.02–5.94 (m, 1 H), 5.61–5.54 (m, 1 H), 4.87–4.84 (m, 1 H), 4.47–4.45 (m, 1 H), 2.77 (dd, *J* = 17.6, 5.4 Hz, 1 H), 2.61 (dd, *J* = 17.6, 1.0 Hz, 1 H), 2.15–2.10 (m, 2 H), 1.74 (br. s, 1 H), 1.35–1.26 (m, 12 H), 0.87 (t, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.4, 138.7, 121.5, 85.4, 69.6, 38.8, 32.3, 31.7, 29.2, 29.1, 29.0, 28.6, 22.5, 13.9 ppm. HRMS: calcd. for $[C_{14}H_{24}O_3 + Na]^+$ 263.1623; found 263.1623.

(4*R*,5*R*)-4-(*tert*-Butyldimethylsilyloxy)-5-[(*E*)-hex-1-en-1-yl]dihydrofuran-2(3*H*)-one (16) from (4a): This compound was prepared from **4a** (30 mg, 0.124 mmol) and 1-decene (34.8 mg, 0.248 mmol, 2.0 equiv.) by using Grubbs–Hoveyda's second-generation catalyst (1.6 mg, 0.0025 mmol, 2.0 mol-%) by a similar procedure as described for the preparation of **15**, to give **16** (19.8 mg, 45%) as a colorless oil. $[\alpha]_D^{25}$ = +19.6 (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3021, 2956, 2929, 2857, 1781, 1464, 1314, 1257, 1158, 1092, 1025, 971, 954, 904, 839 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 5.87–5.80 (m, 1 H), 5.66–5.60 (m, 1 H), 4.74 (dd, *J* = 17.0, 3.9 Hz, 1 H), 4.43–4.41 (m, 1 H), 2.71 (dd, *J* = 17.2, 5.3 Hz, 1 H), 2.45 (dd, *J* = 17.2, 1.5 Hz, 1 H), 2.11–2.06 (m, 2 H), 1.41–1.26 (m, 12 H), 0.89–0.86 (m, 12 H), 0.041 (s, 3 H), 0.036 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.5, 137.9, 123.3, 86.0, 71.0, 39.7, 32.4, 31.8, 29.4, 29.2, 28.7, 25.6, 22.6, 18.1, 14.1, –4.9, –5.0 ppm. HRMS: calcd. for $[C_{20}H_{38}O_3Si + Na]^+$ 377.2488; found 377.2481.

(4*R*,5*R*)-4-(*tert*-Butyldimethylsilyloxy)-5-[(*E*)-hex-1-en-1-yl]dihydrofuran-2(3*H*)-one (16) from (15): To a stirred solution of **15** (258 mg, 1.06 mmol) in dry CH_2Cl_2 (5 mL) was added 2,6-lutidine (227 mg, 2.12 mmol, 2.0 equiv.) and TBDMSOTf (423 mg, 1.60 mmol, 1.5 equiv.) at 0 °C. The reaction mixture was stirred at room temperature for 2 h. It was then diluted with CH_2Cl_2 (5 mL) and H_2O (5 mL). The solution was extracted with CH_2Cl_2 (3× 20 mL) and the combined organic phases were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (9:1) as eluent to afford **16** (323 mg, 86%) as a colorless oil. $[\alpha]_D^{25}$ = +19.4 (*c* = 0.8, $CHCl_3$). Other analytical data were same as before.

(7*R*,8*R*)-7-(*tert*-Butyldimethylsilyloxy)-2-methyloctadecan-8-ol (17): To a stirred solution of **16** (100 mg, 0.282 mmol) in dry Et_2O (10 mL) at –78 °C was added DIBAL-H (1.75 M solution in toluene, 0.24 mL, 0.423 mmol, 1.5 equiv.) dropwise under a N_2 atmosphere. The reaction mixture was stirred for 1 h and then quenched with saturated aq. Rochelle's salt solution (3 mL) and stirred vigorously at room temperature for 1 h. The aqueous layer was separated and extracted with CH_2Cl_2 (3× 10 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated to give the corresponding lactol (100 mg), which was used directly in the next reaction.

To a stirred suspension of (isopentyl)triphenylphosphonium bromide (**6**; 467 mg, 1.13 mmol, 4.0 equiv.) in dry toluene (10 mL) was added *n*BuLi (1.6 M solution in hexane, 0.70 mL, 1.13 mmol, 4.0 equiv.) at 0 °C. The mixture was stirred for 30 min and a solution of lactol (100 mg) in toluene (3 mL) was added. It was slowly warmed to room temperature, stirred for 3 h and then quenched with saturated aq. NH_4Cl solution. The solution was extracted with EtOAc (3× 10 mL) and the combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (19:1) as eluent to afford the diene (80 mg) as a colorless oil. The diene was immediately used in the hydrogenation reaction.

To the stirred solution of diene (80 mg) in propane-2-ol (12 mL) was added 10% $Pd(OH)_2$ on charcoal (13 mg) and stirred under H_2 (balloon pressure) atmosphere at room temperature for 6 h. The mixture was filtered through a small pad of Celite and washed with EtOAc and the filtrate concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (97:3) as eluent to give alcohol **17** (82 mg, 70% overall) as a colorless oil. $[\alpha]_D^{25}$ = –5.6 (*c* = 0.16, $CHCl_3$), ref.[11m] $[\alpha]_D^{25}$ = –3.8 (*c* = 3.2, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3460, 2951, 2929, 2857, 1465, 1383, 1366, 1257, 1086, 837, 667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 3.51–3.47 (m, 1 H), 3.45–3.39 (m, 1 H), 2.15 (d, *J* = 6.9 Hz, 1 H), 1.60–1.52 (m, 1 H), 1.50–1.39 (m, 4 H), 1.37–1.15 (m, 22 H), 0.92–0.85 (m, 18 H), 0.08 (s, 3 H), 0.07 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 75.1, 72.6, 38.9, 34.2, 33.9, 31.9, 29.7, 29.62, 29.6, 29.3, 27.9, 27.7, 27.4, 26.2, 26.0, 25.9, 25.2, 22.7, 22.6, 18.1, 14.1, –4.1, –4.6 ppm. HRMS: calcd. for $[C_{25}H_{54}O_2Si + Na]^+$ 437.3791; found 433.3794.

(11*R*,12*R*)-12-(*tert*-Butyldimethylsilyloxy)-17-methyloctadecan-11-yl-4-methylbenzenesulfonate (18): To a stirred solution of alcohol **17** (50 mg, 0.120 mmol) in dry CH_2Cl_2 (2 mL), was added DMAP (37 mg, 0.30 mmol, 2.5 equiv.) and *p*-toluenesulfonyl chloride (46 mg, 0.240 mmol, 2 equiv.) at 0 °C. The reaction mixture was slowly warmed to room temperature over 1 h and stirred for 5 h. It was then quenched with water (5 mL) and the solution extracted with CH_2Cl_2 (3× 10 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (97:3) as an eluent to give **18** (62.5 mg, 91%) as a colorless oil. $[\alpha]_D^{25}$ = +26.9 (*c* = 0.4, $CHCl_3$), ref.[11m] $[\alpha]_D^{25}$ = +24.8 (*c* = 1.2, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2953, 2928, 2857, 1599, 1464, 1368, 1258, 1188, 1177, 1097, 935, 897, 837, 814, 776, 667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.78 (d, *J* = 8.2 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 4.33–4.29 (m, 1 H), 3.75–3.71 (m, 1 H), 2.44 (s, 3 H), 1.68–1.11 (m, 27 H), 0.91–0.80 (m, 18 H), 0.049 (s, 3 H), 0.006 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 134.3, 129.7, 127.8, 84.9, 72.1, 38.9, 38.6, 31.9, 30.3, 29.6, 29.5, 29.3, 29.1, 27.7, 27.4, 27.3, 26.9, 26.3, 26.0, 25.7, 25.5, 22.7, 22.6, 22.5, 21.6, 17.9, 14.1, –4.5, –4.8 ppm. HRMS: calcd. for $[C_{32}H_{60}O_4SiS + H]^+$ 569.4060; found 569.4055.

***cis*-(7*R*,8*S*)-7,8-Epoxy-2-methyloctadecane, (+)-Disparlure (1):** This compound was prepared from **18** (50 mg, 0.088 mmol) by a similar procedure as described for *ent*-**1**, to afford **1** (22.3 mg, 90%) as a colorless oil. $[\alpha]_D^{25}$ = +1.6 (*c* = 1.1, CCl_4), ref.[11m] $[\alpha]_D$ = +1.0 (*c* = 1.5, CCl_4). IR ($CHCl_3$): $\tilde{\nu}$ = 2951, 2926, 2855, 1466, 1384, 1367, 1260, 1028, 918, 837, 721 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 2.93–2.89 (m, 2 H), 1.60–1.16 (m, 27 H), 0.92–0.82 (m, 9 H) ppm. ^{13}C NMR (100 MHz,$CDCl_3$): δ = 57.3, 38.9, 31.9, 29.5, 29.3, 27.9, 27.83, 27.8, 27.3, 26.8, 26.6, 22.7, 22.6, 14.1 ppm. HRMS: calcd. for $[C_{19}H_{38}O + H]^+$ 283.3001; found 283.3003.

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

Acknowledgments

The authors thank the Department of Science and Technology (DST), New Delhi (grant number SR/S1/OC-25/2008) and Department of Chemistry, IIT-Bombay for financial support. V. B. and P. K. thank the Council of Scientific and Industrial Research (CSIR), New Delhi for research fellowships.

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Received: January 6, 2014
Published Online: April 11, 2014

