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Pd(0) catalyzed intramolecular alkylation: stereoselective synthesis of furan and isoxazoline-2-oxide analogs

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Abstract—New optically pure isoxazoline-2-oxide and furan analogs have been synthesized using Pd(0) catalyzed intramolecular cyclizations. Starting from a *meso*-diol, optically pure compounds were prepared without utilizing chiral ligands at any stage of the synthesis. The stereochemical outcome of the product (>99% ee) was influenced by desymmetrization catalyzed by *Pseudomonas cepacia* lipase and the stereoselective nature of the palladium catalyzed transformations.

1. Introduction

The use of palladium catalysts in carbon–carbon and carbon–heteroatom bond forming reactions has been of great synthetic utility.[1,2] For example, Hayashi, et al.[3] reported that palladium(0) catalyzed reaction of dimethyl (*Z*)-2-butenylene dicarbonate with dimethyl malonate led to formation of the (*R*)-dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**1**); though in low enantiomeric excess (67%). Also reported was the reaction of methyl acetyl acetate or acetylacetone with 2-butenylene dicarbonate, which led to formation of a trisubstituted furan derivative (**2**) (Scheme 1). The formation of compounds **1** and **2** has been rationalized through a nucleophilic attack of the enolate carbon leading to the C–C bond formation in **1** and the enolate oxygen leading to the formation of the C–O bond in compound **2**.[3] In another example of the carbon heteroatom bond formation, Mori[4] and co-workers reported the formation of compounds **3** and **4** (Scheme 1) through the Pd(0) mediated alkylation. Trost et al.[5] have reported the formation of isoxazoline-2-oxide **5** upon reaction of lithium[(phenylsulfonyl)methylene]nitronate with *cis*-1,4-diacetoxycyclopent-2-ene in the presence of Pd(0) catalysts (Scheme 1). The authors noted that ambivalent nature of the nitro-stabilized anions permitted both C and O alkylations.

The involvement of the heteroatom in the alkylation leading to the substituted furan, lactams, isoxazoline, and other ring systems provides opportunities for exploiting the palladium catalyzed reaction in synthesis of these and other important heterocyclic systems. Furan and isoxazoline derivatives belong to important classes of pharmacophores found in large number of natural products and are present in many therapeutic agents.[6] Furan derivatives have been used as a building block for a large number of heterocyclic substructures and also as synthons in natural product synthesis.[6k] Isoxazoline derivatives also have great biological importance, for example, many GPII/IIIa inhibitors and human leukocyte elastase (HLE) inhibitors also have isoxazoline skeleton.[7] Isoxazoline derivatives have also been incorporated in fullerenes rendering special properties as nanoscale connectors in molecular electronic devices.[8] However, there is a lack of convenient methods for the preparation of these isoxazoline derivatives. The general strategy for synthesis of these five-membered nitronates (isoxazoline-2-oxides) involves cyclization of γ-functionalized nitro compounds,[9a,b] which themselves require tedious preparation. An alternative approach to their synthesis involves [3+2] cycloaddition of nitrile oxides with olefins,[9c] which however suffers from another limitation of nitrile oxides undergoing rapid dimerization to furoxan *N*-oxide.[9d]

In this paper we explore the versatility of Pd catalyzed cyclizations and report stereoselective synthesis of several new furan and isoxazoline derivatives under mild reaction conditions. During preparation of this manuscript a report by Tanimori et al.[10] appeared that describes synthesis of the substituted hydrofuran systems by Pd(0) catalyzed transformations.

2. Results and discussion

The syntheses of furan and isoxazoline-2-oxide analogs (Scheme 2) were achieved by an intramolecular Pd(0) catalyzed cyclization and also involves enzymatic

Keywords: Isoxazoline-2-oxide; Furan; Palladium(0); Lipase.
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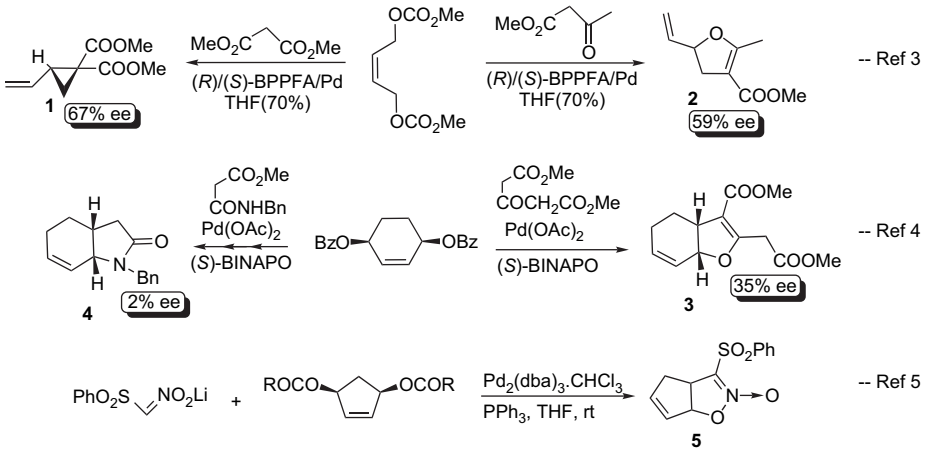
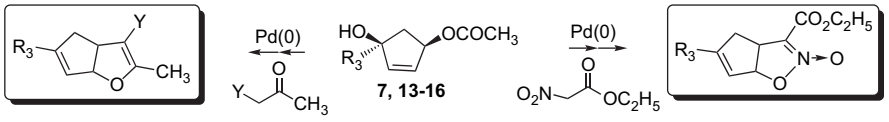


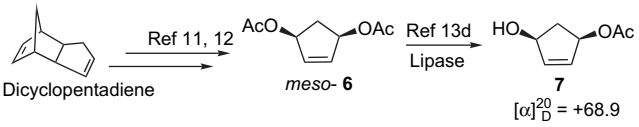
Scheme 1. Synthesis of furans and isoxazoline-2-oxides via Pd catalyzed cyclization.



Scheme 2. Isoxazoline-2-oxides and furan analogs via Pd catalyzed cyclization.

desymmetrization of *meso* starting materials. The synthetic approach described in this work brings the best of both (chemical and enzymatic) approaches in organic synthesis.

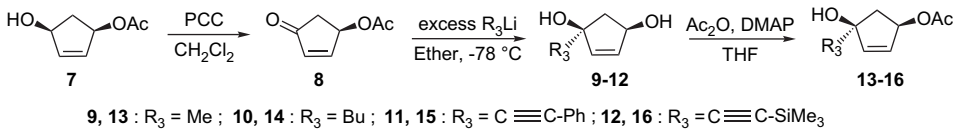
Commercially available dicyclopentadiene was heated to 170 °C to obtain the monomer cyclopentadiene, which was oxidized using peracetic acid to its monoepoxide.[11] The monoepoxide was subsequently treated with acetic anhydride in the presence of $Pd(PPh_3)_4$ to obtain the *meso*-3,5-diacetoxycyclopentene (**6**). The desymmetrization of the *meso*-diacetate (**6**) with lipase to give the (+)-monoacetate (**7**) is the pivotal stereo-differentiation reaction (Scheme 3). The desymmetrization of the *meso*-diacetate, unlike resolution of a racemic substrate in which the yield per enantiomer is limited to 50%, allowed conversion of higher than 97% to the enantiomerically pure single enantiomer.[12] A simple protection/deprotection strategy would enable access to the other enantiomer.



Scheme 3. Formation of enantiopure (+)-monoacetate (**7**).

Enzymatic asymmetric induction is a powerful tool in developing elegant synthetic methodologies for natural products.[13] We have recently reported chemoenzymatic approach to enantioselective synthesis of both (*R* and *S*) enantiomers of imperanene, a platelet aggregation inhibitor.[14] Desymmetrization of *meso* compounds is an extremely important reaction and involves elimination of one or more symmetry elements in the substrate. A large number of compounds including alcohols, esters, anhydrides, and nitriles have been subjected to enzymatic desymmetrizations.[13c] Hydrolases are the enzymes, which have shown immense potential in carrying out these desymmetrizations. Out of all the hydrolases, lipases have been extensively used.[13e] *meso*-2-Cycloalken-1,4-diols and diacetates have been subjected to enzymatic desymmetrizations utilizing lipase B from *Candida antarctica* (Novo SP-435) in organic and aqueous media.[13e] Of a number of different available lipases, the lipase from *Pseudomonas cepacia* (PS-30) was used to carry out hydrolytic desymmetrization of the diacetate.[13d] PS-30 catalyzed reaction of *meso*-diacetate **6** produced monoacetate **7** in high enantiopurity (>97%) and 60% yield. Higher conversion could not be achieved even with extended reaction time. So, the recovered diacetate was again subjected to hydrolysis with the recovered enzyme to obtain enantiopure monoacetate **7** ($[\alpha]_D^{20}$ +68.9 ($CHCl_3$); lit.[12] $[\alpha]_D^{20}$ +69.6 ($CHCl_3$)) in total yield of 90%. The absolute stereochemistry of the monoacetate was established upon its comparison with the literature data[12,13e] as (+)-(1*S*,4*R*)-4-acetoxylcylcopent-2-en-1-ol. The enantiopurity of monoacetate **7** was confirmed by GC analyses upon injecting racemic and enzymatically prepared monoacetate through a cylcodexB (30 m×0.25 mm, J&W scientific) chiral capillary column.

Monoacetate **7** was converted to ketone **8** using PCC (pyridinium chlorochromate) in the presence of sodium acetate in CH_2Cl_2 (Scheme 4).[15] Ketone **8** was treated with alkyl lithium to generate the *cis*-diols, **9**–**12** as the major products (>98%). Spectral data for compounds **10**–**12** were in complete agreement with the structures and for the known compound **9**, ^1H and ^{13}C spectral data were identical to that reported in the literature.[16] Importantly, compound **11** produced colorless orthorhombic crystals and single crystal X-ray diffraction experiment confirmed that the two hydroxyl groups are on the same side of the cyclopentene ring thus confirming the cis relationship. The ORTEP drawing is included in the Supplementary data. The absolute stereochemistry of the molecule was also established as



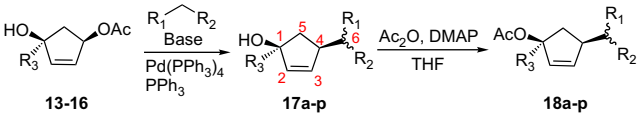
Scheme 4. Syntheses of **13**–**16**.

(1*S*,4*R*). Although diols **9**, **10**, and **12**, did not crystallize but all had the (+)-sign of optical rotation similar to that of **11**. Their absolute stereochemistry was therefore deduced as 1*S*,4*R*, identical to that of **11**.

The diols thus obtained were treated with 1 mol of acetic anhydride and catalytic amount of DMAP to obtain the corresponding monoacetates (**13**–**16**) (Scheme 4). The monoacetates were then coupled to the soft nucleophiles generated from the active methylene compounds (Table 1) via Pd catalyzed alkylation to give compounds **17a**–**p** (Scheme 5).

Table 1. Pd(0) catalyzed alkylation to obtain compounds **17a**–**p**

Compound	R_1	R_2	R_3	Diastereomeric ratio	Yield
17a	NO_2	CO_2Et	H	1.07:1	62
17b	NO_2	CO_2Et	Me	1.12:1	70
17c	NO_2	CO_2Et	Bu	1.11:1	72
17d	NO_2	CO_2Et	C≡C–Ph	1.13:1	60
17e	NO_2	CO_2Et	C≡C–$SiMe_3$	1.15:1	68
17f	COMe	CO_2Et	H	1.04:1	68
17g	COMe	CO_2Et	Me	1.28:1	65
17h	COMe	CO_2Et	Bu	1.19:1	70
17i	COPh	SO_2Ph	H	1.07:1	68
17j	COPh	SO_2Ph	Me	1.15:1	71
17k	COPh	SO_2Ph	Bu	1.13:1	73
17l	COPh	SO_2Ph	C≡C–Ph	1.06:1	61
17m	COPh	SO_2Ph	C≡C–$SiMe_3$	1.10:1	69
17n	CN	COOEt	H	1.05:1	60
17o	CN	$PhSO_2$	H	1.23:1	68
17p	CO_2Me	CO_2Me	H	—	73



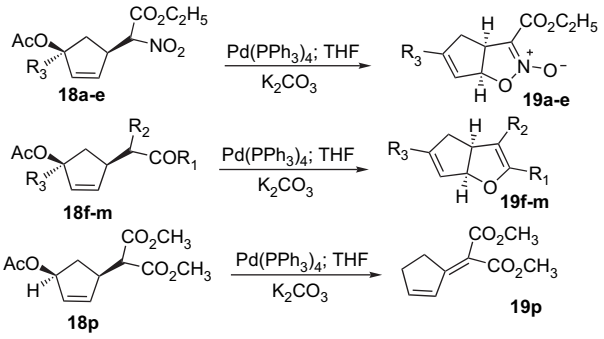
Scheme 5. Syntheses of compounds **17a**–**p** via Pd(0) catalysis.

Pd catalyzed alkylation could result in the formation of a 1,2- or 1,4-adduct,[17] but under the conditions studied the reaction proceeds with high regio- and stereo-selectivity to give the 1,4 adducts, **17a**–**p**. The stereochemistry of the Pd catalyzed allylation has been studied extensively and is known to proceed with retention of configuration via double inversion.[17]

As evident from the mechanism for these alkylations (Scheme 5) compounds **17a**–**o** would be a mixture of a pair of diastereomers at the site of the carbon–carbon bond formation (C–6). The diastereomeric ratio of **17a**–**o** determined from integral value of the H-6, H-2, and H-3 resonances in their ^1H spectra was calculated to be ~1:1 (Table 1). These pairs of diastereomers were inseparable on a chromatographic column and appeared as a single spot on a TLC plate. As the diastereotopic center (C-6) is prone to racemization (because of its proximity to the electron withdrawing groups) and is involved in generation of a carbanion in the following steps, no efforts were devoted to its resolution and the mixture was taken for further steps without separation.

Acetates **18a**–**p** were prepared by treating **17a**–**p** with acetic anhydride in the presence of excess triethylamine and catalytic amount of DMAP. Most tertiary acetates but **18b** and **18d** were unstable and not amenable to purification on chromatographic columns and hence, were subjected to palladium catalyzed alkylation without any further purification.

Isoxazoline-2-oxides **19a**–**e** were obtained in good to excellent yield and in optically pure form upon treating the acetates **18a**–**e**, in presence of K_2CO_3 and palladium tetrakistriphenylphosphine (Scheme 6, Table 2). Similar reaction with the acetates **18f**–**m** led to the formation of the substituted dihydrofurans **19f**–**m** in optically pure form (Scheme 6, Table 2).

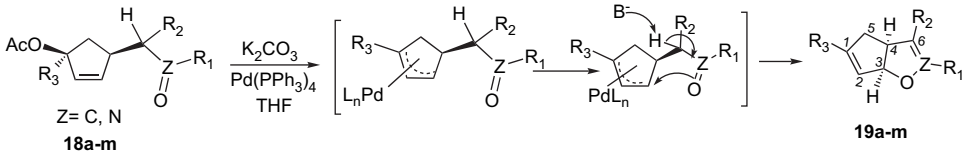


Scheme 6. Pd catalyzed intramolecular cyclization.

Table 2. Compounds **19a**–**m** via Pd catalyzed cyclization

Compound	R_1	R_2	R_3	Yield[a]	$[\alpha]_D^{20}$ (CH_2Cl_2)
19a	—	—	H	85	−95.2
19b	—	—	Me	64	−90.4
19c	—	—	Bu	70	−88.3
19d	—	—	C≡C–Ph	63	−182.3
19e	—	—	C≡C–$SiMe_3$	67	−177.2
19f	Me	CO_2Et	H	85	−77.8
19g	Me	CO_2Et	Me	57	−146.1
19h	Me	CO_2Et	Bu	55	−258.8
19i	Ph	SO_2Ph	H	>98	−20.0
19j	Ph	SO_2Ph	Me	59	−16.7
19k	Ph	SO_2Ph	Bu	62	−10.0
19l	Ph	SO_2Ph	C≡C–Ph	65	−15.0
19m	Ph	SO_2Ph	C≡C–$SiMe_3$	64	−20.1
19n	CN	COOEt	H	—[b]	—
19o	CN	SO_2Ph	H	—[b]	—

[a] Product isolated after column chromatography.
[b] Starting material was recovered.



Scheme 7. Mechanism for the formation of isoxazoline-2-oxide and furan systems.

It is noteworthy to mention that starting from a *meso*-diol, optically pure compounds were prepared without utilizing chiral ligands at any stage of the reaction. The stereochemical outcome of the product is solely influenced by the *P. cepacia* lipase and the stereoselective nature of the palladium catalyzed transformations. Literature reports on the synthesis of the furan derivatives have been catalyzed by palladium(0) in presence of chiral ligands leading to, at best, modest enantioenrichments.[3,4,10] The cyclization reactions were also evaluated in presence of various bases, i.e., NaH, K_2CO_3, and KO^{t}Bu (Scheme 6) in THF using catalytic amount of Pd(0) catalysts. The yield of the reaction was independent of the base used. For all reactions recorded in Table 2 $K_2CO_3$was used as the base. $Pd(PPh_3)_4$ and $Pd_2(dba)_3$ were the two Pd(0) catalysts evaluated in this reaction and identical results were obtained. Pd(II) catalysts like $PdCl_2$ did not catalyze the cyclization. The cyclizations were also attempted in absence of base or catalyst and such variations did not give the desired product indicating that both base and the catalyst are vital for this cyclization.

Mechanism for formation of compounds **19a**–**m** is shown in Scheme 7, where the base deprotonates the methine proton between the two electron-withdrawing groups. The carbanion thus generated results in the formation of **19a**–**m** via electron-flow through NO_2 group (for isoxazoline-2-oxides) or enolate oxygen (for furan) (Scheme 7). The stereochemical outcome of the reaction is the result of two sequential steps. First is the formation of the Pd π-allyl complex formed on the opposite side of the OAc leaving group because of steric control. In the second step, the attack of the nucleophile proceed in an *anti* fashion with respect to metal resulting in a highly stereoselective reaction.[18] One of the isoxazoline-2-oxide **19d** produced colorless orthorhombic crystals. The single crystal X-ray diffraction experiment confirmed its structure (Supplementary data). Unfortunately, the X-ray data could not establish the absolute stereochemistry of **19d** but it is deduced from the stereochemistry of the monoacetate **7**, as (1*S*,5*S*)-3-aza-4-(ethoxycarbonyl)-7-phenylethynyl-2-oxabicyclo[3.3.0]oct-3,7-diene-3-oxide.

Compounds **18n** and **18o**, containing a –CN group, did not give the desired bicyclic system; starting material was always recovered and confirmed by ^{1}H NMR. In order to obtain the ee, compound **19a** was treated with chiral shift-reagent, europium tris[3-(hepta-fluoropropylhydroxymethylene)-(+)-camphorate] and ^{1}H NMR indicated enantiomeric excesses for compound **19a** to be >97%.

Figure 1 shows ^{1}H NMR comparison of racemic and enantioenriched **19a** in presence (+)-Eu(hfc)$_3$. The H-3 signals were used for calculation of % ee. The absence of doublet at 5.9 ppm in enantioenriched **19a** indicates a >97% ee. Interestingly, compound **18p** led to an unusual product **19p**, which most probably results from an interconversion between the two π-allyl complexes **I** and **II** (Scheme 8).[19]

In summary, we have studied Pd catalyzed cyclization to obtain optically pure furan and isoxazoline-2-oxide analogs that is practical, and utilizes mild reaction conditions. The method involves tandem use of the enzymatic and chemical catalysis. The key step is the desymmetrization of the *meso*-

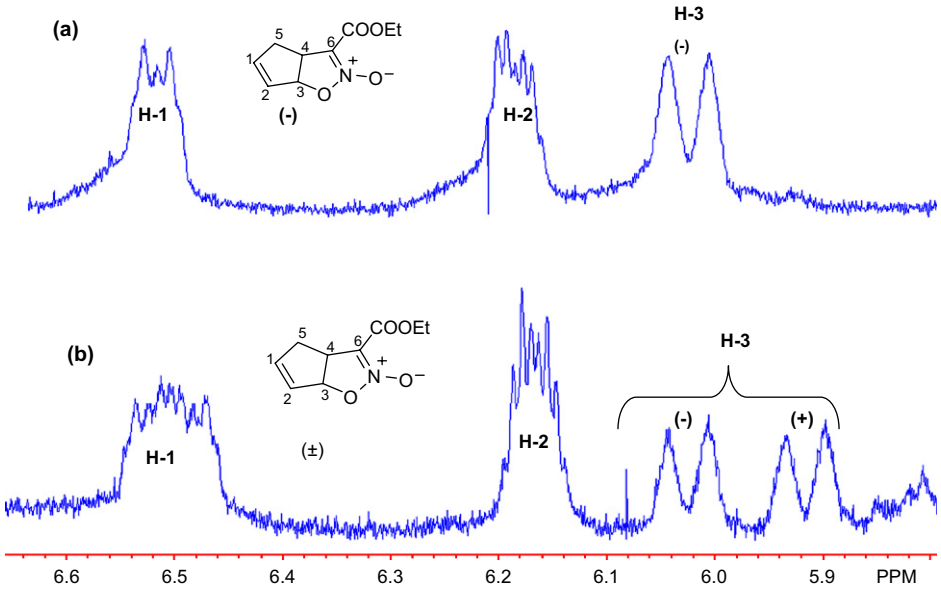
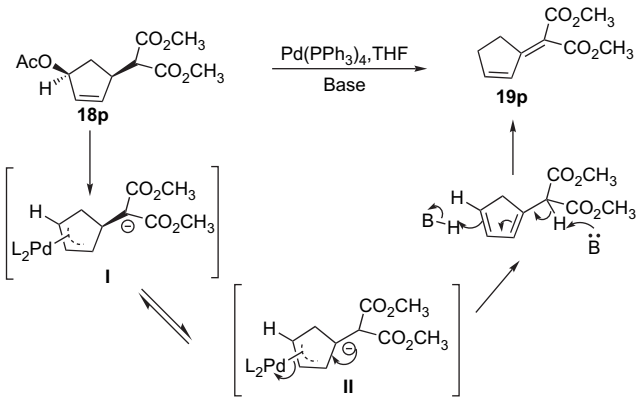


Figure 1. ^{1}H NMR of compound **19a**: (a) enantioriched and (b) racemic in the presence of (+)-Eu(hfc)$_3$.



Scheme 8. Plausible mechanism for the formation of compound **19p**.

diacetate (**6**) using commercially available *P. cepacia* lipase (PS-30), in high ee. We have also demonstrated the compatibility of this Pd(0) catalyzed cyclization with wide spectrum of functional groups like NO_2, COOR, COR, and SO_2R. This work provides a new pathway to obtain optically pure furan and isoxazoline-2-oxide analogs, which are rather difficult to obtain via previous strategies.

3. Experimental

3.1. General

Lipase PS-30 was a generous gift from Amano Enzyme. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 250 MHz spectrometer and Varian 400, 500 MHz in $CDCl_3$ and acetone-d_6 with TMS as the standard. Chemical shifts are reported in parts per million, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), h (sextet), m (multiplet) and br s (broad singlet). Optical rotations were measured with a Rudolph Research Analytical AutoPol IV Automatic polarimeter. Thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thickness of silica gel. All solvents were dried and distilled prior to use and organic solvent extracts dried over Na_2SO_4. Mass calculations were carried out on an ESI LC MS system (Agilent Technologies). GC studies were carried out on Shimadzu gas chromatogram (Model 17A). A cyclodextrin column (30 m×0.25 mm) from J&W Scientific was used for determining the ee of the monoacetate **7**.

3.2. X-ray crystallography

Single-crystal X-ray diffraction data for the compounds **11** and **19d** were collected on a Bruker SMART-APEX CCD Diffractometer with Kyroflex Low Temperature System using Mo Kα radiation (λ=0.71073 Å), operating in the Ω and φ scan mode. Diffracted data were corrected for absorption using the SADABS program. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 622489 and 622490. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

3.2.1. (+)-(1*S*,4*R*)-4-Acetoxylcylcopent-2-en-1-ol (7).[11,12,13d]

meso-Diacetate **6**,[13d] (10 g, 0.054 mol) was taken in a mixture of phosphate buffer (pH 7.0; 75 ml) and acetone (5 ml) in a round bottom flask. Lipase PS-30 (500 mg) was added while maintaining the pH of the reaction mixture at 7.0 using 1 N NaOH solution. The reaction was stopped when no change in the pH of the reaction medium occurred. The conversion at this point was estimated to be ~60% by TLC. The reaction mixture was extracted with ethyl acetate (3×200 mL). The organic layer was dried over Na_2SO_4 and concentrated by rotoevaporation. The crude product was subjected to column chromatography over silica gel using ethyl acetate/hexane (1:3) to isolate the monoacetate **7** as a white solid, mp 40–42 °C; $[\alpha]_D^{20}$ +68.9 ($CHCl_3$); lit.[12] $[\alpha]_D^{20}$ +69.6 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.60 (dt, 1H, J=14.8, 4.0 Hz), 2.01 (s, 3H), 2.76 (p, 1H, J=7.2 Hz), 4.6 (m, 1H), 5.4 (m, 1H), 5.94 (d, 1H, J=4.0 Hz), 6.06 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.5, 40.4, 74.6, 77.2, 132.3, 139.1, 171.3 ppm.

3.2.2. (*R*)-4-Acetoxy-2-cyclopenten-1-one (8).[15]

Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.03 (s, 3H), 2.22 (dt, 1H, J=18.7, 2.2 Hz), 2.73 (dt, 1H, J=19.0, 6.75 Hz), 5.78 (m, 1H), 6.26 (d, 1H, J=5.7 Hz), 7.5 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 20.8, 40.9, 71.9, 136.9, 158.9, 170.4, 204.8 ppm.

3.3. General procedure for preparation of compounds 9–12

To a solution of (*R*)-4-acetoxy-2-cyclopenten-1-one **8** (200 mg, 1.428 mmol) in freshly distilled ether (15 ml) at −78 °C was added 1.6 M solution of methyl lithium in ether (3.57 ml, 5.712 mmol) under a nitrogen atmosphere. The reaction was allowed to stir for 1 h and was quenched using NH_4Cl solution. The product was purified by column chromatography using ethyl acetate/hexane (2:1) to afford **9** (150 mg, yield=92%) as a viscous liquid.

3.3.1. (1*S*,4*R*)-1-Methylcyclopent-2-ene-1,4-diol (9). Viscous liquid; $[\alpha]_D^{20}$ +55.2 (c 0.02, acetone); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.27 (s, 3H, CH_3), 1.71 (dd, 1H, J=14.5, 2.7 Hz), 2.29 (dd, 1H, J=14.5, 7.2 Hz), 3.9 (br s, 2H), 4.58 (d, 1H, J=6.2 Hz), 5.79 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 27.5, 49.5, 75.2, 81.2, 134.0, 141.0 ppm. HRESIMS calcd for $C_6H_{11}O_2$ ($[M+H]^+$): 115.0759; found: 115.0758.

3.3.2. (1*S*,4*R*)-1-Butyl-cyclopent-2-ene-1,4-diol (10). Viscous liquid; $[\alpha]_D^{20}$ +50.2 (c 0.03, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.81 (t, 3H, CH_3, J=6.7 Hz), 1.24 (m, 2H), 1.55 (m, 5H, H-4+OH), 1.60 (dd, 1H, J=5.5, 3.2 Hz), 2.03 (s, 1H, OH), 2.31 (dd, 1H, J=14.2, 7.0 Hz), 4.60 (d, 1H, J=5.5 Hz), 5.83 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.0, 23.0, 26.5, 40.1, 48.2, 75.4, 84.1, 135.0, 140.0 ppm. HRESIMS calcd for $C_9H_{17}O_2$ ($[M+H]^+$): 157.1229; found: 157.1221.

3.3.3. (1*S*,4*R*)-1-Phenylethynyl-cyclopent-4-ene-1,4-diol (11). White solid: mp=114–116 °C; $[\alpha]_D^{20}$ +330.5 (c 0.11, acetone); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.97 (s, 1H, OH), 2.00 (s, 1H, OH), 2.04 (dd, 1H, J=14.0, 3.2 Hz), 2.82 (dd, 1H, J=14.0, 6.7 Hz), 4.78 (dd, 1H, J=6.7, 3.2 Hz), 6.01 (s,

2H), 7.26–7.32 (m, 5H) ppm; ^{13}C NMR ($(CD_3)_2CO$, 62.5 MHz): δ 52.4, 75.0, 76.2, 83.3, 93.3, 123.9, 129.1, 129.3, 132.2, 136.9, 137.7 ppm. HRESIMS calcd for $C_{13}H_{13}O_2$ ([M+H]$^+$): 201.0916; found: 201.0921.

3.3.4. X-ray crystallographic data for (11). In the crystal of (1*S*,4*R*)-1-phenylethynyl-cyclopent-4-ene-1,4-diol, four molecules were found in each unit cell. The compound crystallized in an orthorhombic space group *P*2 (1), with cell dimensions a=5.3082(10) Å, b=8.4869(16) Å, c=17.005(3) Å. A total of 5642 unique reflection data were obtained to give a final R index [$I>2\sigma(I)$] of $R1$=0.0337, $wR2$=0.0894 and R indices (all data) $R1$=0.0365, $wR2$=0.0918.

3.3.5. (1*S*,4*R*)-1-Trimethylsilanylethynyl-cyclopent-4-ene-1,4-diol (12). Viscous liquid; $[\alpha]_D^{20}$ +278.2 (c 0.03, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.23 (s, 9H), 1.90 (br s, 1H, OH), 1.94 (dd, 1H, J=14.2, 3.5 Hz), 2.47 (s, 1H, OH), 2.72 (dd, 1H, J=14.2, 7.0 Hz), 4.72 (m, 1H), 5.91 (d, 1H, J=5.5 Hz), 5.97 (dd, 1H, J=5.5, 2.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ −0.5, 50.6, 75.0, 75.6, 85.3, 105.8, 136.5, 137.4 ppm. HRESIMS calcd for $C_{10}H_{17}O_2Si$ ([M+H]$^+$): 197.0998; found: 197.0995.

3.4. General procedure for preparation of compounds 13–16

To a solution of **9** (100 mg, 0.877 mmol) in dry THF (10 ml) at room temperature was added acetic anhydride (89 mg, 0.877 mmol), and catalytic amount of DMAP. The reaction was allowed to stir for 3 h and then concentrated. The residue was taken in ethyl acetate (40 ml) and was treated twice with saturated sodium bicarbonate solution (20 ml), followed by brine (10 ml). The organic layer was dried over sodium sulfate and the resulting product **13** was purified by column chromatography using ethyl acetate/hexane (1:2) (80.25 mg, yield=58.77%).

3.4.1. (1*R*,4*S*)-4-Hydroxy-4-methyl-2-cyclopenten-1-yl acetate (13). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.32 (s, 3H), 1.80 (dd, 1H, J=14.5, 3.5 Hz), 1.97 (s, 3H), 2.2 (br s, 1H), 2.36 (dd, 1H, J=14.5, 7.5 Hz), 5.46 (m, 1H), 5.76 (d, 1H, J=5.5 Hz), 5.92 (d, 1H, J=5.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 21.2, 27.3, 46.7, 77.6, 80.9, 130.2, 143.2, 170.8 ppm. HRESIMS calcd for $C_8H_{13}O_3$ ([M+H]$^+$): 157.0865; found: 157.0871.

3.4.2. (1*R*,4*S*)-4-Hydroxy-4-butyl-2-cyclopenten-1-yl acetate (14). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.84 (t, 3H, J=6.7 Hz), 1.26 (m, 4H), 1.54 (m, 2H), 1.72 (m, 2H, 1H+OH), 1.97 (s, 3H), 2.40 (dd, 1H, J=14.7, 7.5 Hz), 5.43 (m, 1H), 5.80 (dd, 1H, J=5.5, 2.2 Hz), 5.91 (dd, 1H, J=4.7, 0.7 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.0, 21.2, 23.1, 26.4, 40.0, 45.0, 77.5, 83.8, 131.0, 142.0, 170.9 ppm. HRESIMS calcd for $C_{11}H_{19}O_3$ ([M+H]$^+$): 199.1334; found: 199.1333.

3.4.3. (1*R*,4*S*)-4-Hydroxy-4-phenylethynyl-2-cyclopenten-1-yl acetate (15). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.98 (s, 3H), 2.09 (dd, 1H, J=14.5, 3.7 Hz), 2.82 (s, 1H), 2.91 (dd, 1H, J=14.5, 7.2 Hz), 5.6 (m, 1H), 5.92 (dd, 1H, J=5.5, 2.2 Hz), 6.07 (d, 1H, J=5.5 Hz), 7.20–7.35 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 21.2, 47.8, 76.0, 77.1, 84.5, 90.2, 122.2, 128.3, 128.6, 131.6, 132.0, 139.7, 170.9 ppm. HRESIMS calcd for $C_{15}H_{15}O_3$ ([M+H]$^+$): 243.1021; found: 243.1018.

3.4.4. (1*R*,4*S*)-4-Hydroxy-4-trimethylsilanylethynyl-2-cyclopenten-1-yl acetate (16). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.20 (s, 9H), 1.99 (s, 3H), 2.02 (dd, 1H, J=14.5, 3.7 Hz), 2.50 (s, 1H, OH), 2.84 (dd, 1H, J=14.5, 7.5 Hz), 5.54 (m, 1H), 5.93 (dd, 1H, J=5.2, 2.0 Hz), 6.00 (d, 1H, J=5.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ −0.3, 21.1, 47.5, 75.4, 76.8, 85.0, 105.9, 132.6, 139.9, 170.7 ppm. HRESIMS calcd for $C_{12}H_{19}O_3Si$ ([M+H]$^+$): 239.1104; found: 239.1101.

3.5. General procedure for preparation of compounds 17a–p (Scheme 5)

To a solution of ethyl nitroacetate (100 mg, 0.752 mmol) in dry THF (10 ml) at room temperature was added potassium carbonate (110 mg, 0.800 mmol) under a nitrogen atmosphere. The reaction was allowed to stir for 20 min and $Pd(PPh_3)_4$ (43.4 mg, 0.037 mmol), PPh_3 (197 mg, 0.752 mmol), and monoacetate **7** (106 mg, 0.752 mmol) dissolved in 5 ml THF was added to it. The reaction was allowed to stir at 40 °C for 12 h and then vacuum filtered through Celite with subsequent concentration of the filtrate. The product was purified by column chromatography using ethyl acetate/hexane (1:2) to afford **17a** (120 mg, yield=62%) as a yellow viscous liquid.

3.5.1. Ethyl (2*R/S*,1′*R*,4′*S*)-2-(4′-hydroxy-2′-cyclopenten-1′-yl)-2-nitroacetate (17a). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25 (t, 3H, J=7.2 Hz), 1.57 (m, 1H), 1.92 (br s, 1H), 2.50 (m, 1H), 3.46 (t, 1H, J=2.4 Hz), 4.23 (q, 2H, J=6.8 Hz), 4.79 (br s, 1H), 5.06 (t, 1H, J=8.0 Hz), 5.74–5.83 (dd, 1H, J=6.0, 4.8 Hz), 5.95–5.97 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0, 36.2, 36.8, 45.4, 45.1, 63.3, 76.0, 76.3, 91.0, 91.4, 131.6, 132.0, 137.7, 137.9, 163.8, 163.9 ppm. HRESIMS calcd for $C_9H_{14}NO_5$ ([M+H]$^+$): 216.0872; found: 216.0875.

3.5.2. Ethyl (2*R/S*,1′*R*,4′*S*)-2-(4′-hydroxy-4-methyl-2′-cyclopenten-1′-yl)-2-nitroacetate (17b). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.21 (t, 3H, J=7.5 Hz), 1.34 (s, 3H), 1.79 (dt, 1H, J=14.2, 5.0 Hz), 1.95 (br s, 1H), 2.19 (dd, 1H, J=14.2, 8.2 Hz), 3.50 (m, 1H), 4.19 (q, 2H, J=7.5 Hz), 5.03 (t, 1H, J=8.2 Hz), 5.59 (2dd, 1H, J=5.5, 2.0 Hz), 5.82 (dt, 1H, J=5.5, 2.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.9, 27.5, 27.6, 42.2, 42.8, 45.1, 45.5, 63.1, 82.1, 82.4, 90.6, 91.0, 129.1, 129.6, 141.8, 142.1, 163.7 ppm. HRESIMS calcd for $C_{10}H_{16}NO_5$ ([M+H]$^+$): 230.1029; found: 230.1034.

3.5.3. Ethyl (2*R/S*,1′*R*,4′*S*)-2-(4′-hydroxy-4-butyl-2′-cyclopenten-1′-yl)-2-nitroacetate (17c). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.90 (t, 3H, J=7.0 Hz), 1.2–1.4 (m, 7H, $2CH_2$+CH_3), 1.61 (t, 2H, J=7.0 Hz), 1.75 (dt, 1H, J=14.2, 4.5 Hz), 1.89 (s, OH), 2.30 (dd, 1H, J=14.2, 8.2 Hz), 3.53 (m, 1H), 4.26 (q, 2H, J=7.2 Hz), 5.15 (dd, 1H, J=8.2, 6.5 Hz), 5.70 (dd, 0.5H, J=5.7, 2.0 Hz), 5.77 (dd, 0.5H, J=5.7, 2.2 Hz), 5.88 (dt, 1H, J=5.5, 2.2 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz):

δ 13.9, 14.0, 23.0, 26.3, 40.4, 41.0, 45.2, 45.4, 63.1, 85.1, 91.1, 129.8, 130.2, 140.7, 140.9, 161.5 ppm. HRESIMS calcd for $C_{13}H_{22}NO_5$ ([M+H]$^+$): 272.1498; found: 272.1493.

3.5.4. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-4-phenylethynyl-2′-cyclopenten-1′-yl)-2-nitroacetate (17d). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.24 (dt, 3H, J=6.7, 1.0 Hz), 2.1 (m, 1H), 2.53 (d, 1H, J=2.7 Hz, OH), 2.74 (m, 1H), 3.65 (m, 1H), 4.19 (q, 2H, J=6.7 Hz), 5.06 (dd, 1H, J=9.0, 1.0 Hz), 5.79, 5.87 (2dd, 1H, J=5.5, 2.0 Hz), 6.00 (dt, 1H, J=5.5, 1.7 Hz), 7.22–7.36 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.9, 43.7, 44.4, 44.9, 45.2, 63.21, 63.26, 76.5, 77.5, 85.2, 89.8, 90.6, 90.8, 122.1, 128.3, 128.7, 131.5, 131.6, 132.0, 138.8, 138.9, 163.5 ppm. HRESIMS calcd for $C_{17}H_{18}NO_5$ ([M+H]$^+$): 316.1185; found: 316.1180.

3.5.5. Ethyl(2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-4-trimethylsilanylethynyl-2′-cyclopenten-1′-yl)-2-nitroacetate (17e). Viscous yellow liquid, ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.19 (s, 9H), 1.21 (t, 3H, J=7.0 Hz, CH_3), 1.93 (m, 1H), 2.50 (s, 1H, OH), 2.74 (m, 1H), 3.62 (m, 1H), 4.20 (q, 2H, J=6.7 Hz, CH_2), 5.03 (dd, 1H, J=9.0, 1.0 Hz), 5.75–5.81 (2dd, 1H, J=5.5, 2.0 Hz), 6.01 (dt, 1H, J=5.5, 1.7 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ −0.2, 14.0, 42.7, 44.2, 60.5, 72.3, 75.4, 85.2, 90.8, 132.6, 148.1, 167.3 ppm. HRESIMS calcd for $C_{14}H_{22}NO_5Si$ ([M+H]$^+$): 312.1267; found: 312.1264.

3.5.6. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-2′-cyclopenten-1′-yl)-3-oxobutanoate (17f). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.18 (t, 3H, J=7.2 Hz), 1.28 (t, 1H, J=7.0 Hz), 2.18 (s, 3H), 2.37 (p, 1H, J=7.2 Hz), 3.19 (m, 1H), 3.45 (m, 1H), 4.14 (q, 2H, J=7.2 Hz), 4.6 (m, 1H), 5.67–5.83 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.2, 29.7, 29.9, 37.2, 37.8, 43.1, 43.2, 61.0, 64.7, 65.1, 76.22, 76.28, 134.2, 134.6, 135.2, 135.5, 168.7, 169.0, 202.61, 202.66 ppm. HRESIMS calcd for $C_{11}H_{17}O_4$ ([M+H]$^+$): 213.1127; found: 213.1134.

3.5.7. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-4-methyl-2′-cyclopenten-1′-yl)-3-oxobutanoate (17g). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.20 (t, 3H, J=7.0 Hz), 1.29 (s, 3H), 1.50–1.71 (2dd, 1H, J=14.0, 5.2 Hz), 2.16 (m, CH_3+H-5), 2.55 (br s, 1H, OH), 3.24 (m, 1H), 3.47 (dd, 1H, J=8.7, 3.0 Hz), 4.13 (q, 2H, J=7.0 Hz), 5.52–5.62 (2dd, 1H, J=5.2, 2.5 Hz), 5.7 (dd, 1H, J=5.5, 2.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.0, 27.5, 29.6, 30.0, 43.3, 43.5, 43.6, 44.2, 61.4, 64.1, 64.2, 82.2, 82.3, 131.8, 132.3, 139.7, 140.0, 168.8, 169.1, 202.3 ppm. HRESIMS calcd for $C_{12}H_{19}O_4$ ([M+H]$^+$): 227.1283; found: 227.1280.

3.5.8. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-4-butyl-2′-cyclopenten-1′-yl)-3-oxobutanoate (17h). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.83 (t, 3H, J=7.0 Hz), 1.21 (m, 7H, CH_3+2CH_2), 1.50 (m, 4H, 1H+CH_2+OH), 2.17 (m, 4H, CH_3+1H), 3.21 (m, 1H), 3.45 (dd, 1H, J=5.2, 3.0 Hz), 4.11 (q, 2H, J=7.0 Hz), 5.67 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.0, 13.1, 22.1, 25.4, 25.6, 28.6, 29.0, 39.45, 39.47, 41.2, 41.4, 42.3, 42.5, 60.5, 63.3, 63.4, 84.1, 84.4, 132.1, 133.4, 137.1, 137.4, 167.8, 201.4 ppm. HRESIMS calcd for $C_{15}H_{25}O_4$ ([M+H]$^+$): 269.1753; found: 269.1756.

3.5.9. 2-Phenylsulfonyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-2′-cyclopenten-1′-yl)-1-phenyl-ethanone (17i). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.26–2.2 (dt, 1H, J=14.0, 4.5 Hz), 2.52 (m, 2H), 3.32 (m, 1H), 4.67–4.80 (m, 1H), 5.05 (dd, 1H, J=21.2, 9.5 Hz), 5.45–5.49 (ddd, 1H, J=5.7, 2.5, 1.0 Hz), 5.8–5.9 (dt, 1H, J=5.7, 2.5 Hz), 7.3–7.7 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 38.2, 38.4, 43.5, 44.0, 74.0, 74.3, 75.7, 128.7, 128.8, 128.9, 129.7, 129.8, 133.7, 134.0, 134.2, 134.6, 136.2, 137.1, 137.17, 192.9, 193.3 ppm. HRESIMS calcd for $C_{19}H_{19}O_4S$ ([M+H]$^+$): 343.1094; found: 343.1097.

3.5.10. 2-Phenylsulfonyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-4-methyl-2′-cyclopenten-1′-yl)-1-phenyl-ethanone (17j). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.36 (s, 3H), 1.49 (dd, 1H, J=14.0, 5.0 Hz), 2.05 (m, 1H), 2.29 (s, 1H, OH), 3.16–3.39 (m, 1H), 5.14 (dd, 1H, J=9.7, 2.5 Hz), 5.53, 5.78 (from 2 diastereomers) (2dd, 1H, J=5.5, 2.5 Hz), 6.14 (dd, 1H, J=5.2, 1.7 Hz), 7.29–7.86 (m, 10H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 27.5, 29.6, 43.3, 43.5, 43.6, 44.2, 64.1, 64.2, 82.2, 82.3, 127.9, 128.4, 128.5, 128.74, 128.76, 130.1, 130.4, 131.8, 132.3, 132.6, 133.8, 180.9, 190.4 ppm. HRESIMS calcd for $C_{20}H_{21}O_4S$ ([M+H]$^+$): 357.1161; found: 357.1158.

3.5.11. 2-Phenylsulfonyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-4-butyl-2′-cyclopenten-1′-yl)-1-phenyl-ethanone (17k). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.79 (t, 3H), 1.18 (m, 4H, 2CH_2), 1.46 (m, 3H, CH_2+ 1H), 1.89 (s, 1H, OH), 2.01 (dd, 1H, J=13.7, 8.0 Hz), 3.40 (m, 1H), 5.15 (d, 1H, J=9.7 Hz), 5.35 (dd, 0.5H, J=5.5, 1.7 Hz), 5.68 (dd, 0.5H, J=5.5, 2.0 Hz), 5.78 (dd, 0.5H, J=5.5, 1.5 Hz), 6.23 (dd, 0.5H, J=5.7, 2.0 Hz), 7.29–7.86 (m, 10H, COPh+PhSO_2) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 12.8, 22.0, 25.3, 25.4, 39.3, 39.5, 41.5, 41.6, 42.6, 43.2, 72.9, 73.0, 83.4, 84.4, 127.73, 127.79, 127.8, 128.6, 128.7, 131.1, 132.0, 132.9, 133.1, 136.0, 136.2, 138.2, 191.9 ppm. HRESIMS calcd for $C_{23}H_{27}O_4S$ ([M+H]$^+$): 399.1630; found: 399.1634.

3.5.12. 2-Phenylsulfonyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-4-phenylethynyl-2′-cyclopenten-1′-yl)-1-phenyl-ethanone (17l). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.72 (dd, 0.5H, J=14.2, 4.0 Hz), 2.47 (dd, 0.5H, J=14.2, 7.2 Hz), 2.73 (m, 2H), 3.47 (m, 1H), 5.15 (dd, 0.5H, J=15.0, 10.0 Hz), 5.49 (dd, 0.5H, J=5.2, 2.0 Hz), 5.84 (dd, 1H, J=5.2, 1.5 Hz), 5.99 (dd, 0.5H, J=5.2, 1.0 Hz), 6.47 (dd, 0.5H, J=5.2, 2.2 Hz), 7.15–7.86 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 43.5, 44.1, 45.4, 45.7, 73.5, 73.9, 76.5, 77.4, 84.9, 85.0, 90.2, 90.4, 122.2, 122.3, 128.3, 128.3, 128.5, 128.8, 128.92, 128.97, 129.7, 129.8, 131.6, 131.7, 133.9, 134.1, 134.2, 135.1, 136.9, 137.04, 137.08, 137.2, 137.6, 192.8, 193.2 ppm. HRESIMS calcd for $C_{27}H_{23}O_4S$ ([M+H]$^+$): 443.1317; found: 443.1321.

3.5.13. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-4-trimethylsilanylethynyl-2′-cyclopenten-1′-yl)-1-phenyl-ethanone (17m). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.19 (s, 9H), 1.85 (dd, 1H, J=14.2, 4.0 Hz), 2.47 (s, 1H, OH), 2.73 (m, 1H), 3.49 (m, 1H), 5.14 (d, 1H, J=10.0 Hz), 5.45 (dd, 0.5H, J=5.2, 2.0 Hz), 5.79 (dd, 0.5H, J=5.2, 1.5 Hz), 5.97 (dd, 0.5H, J=5.2, 1.0 Hz), 6.37 (dd, 0.5H, J=5.2, 2.2 Hz), 7.15–7.86 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$,

62.5 MHz): δ −0.3, 43.52, 43.56, 45.4, 45.5, 73.71, 73.74, 75.23, 75.29, 87.9, 89.0, 106.1, 106.2, 122.3, 123.0, 128.4, 128.5, 129.01, 129.08, 130.4, 133.9, 135.1, 136.1, 137.8, 140.5, 140.6, 197.5, 197.6 ppm. HRESIMS calcd for $C_{24}H_{27}O_4SSi$ ([M+H]$^+$): 439.1399; found: 439.1395.

3.5.14. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-2′-cyclopenten-1′-yl)-2-cyanoacetate (17n). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.27 (t, 3H, *J*=7.7 Hz), 1.5 (tt, 1H, *J*=14.2, 4.0 Hz), 2.47 (s, 1H, OH), 2.56 (m, 1H), 3.23 (m, 1H), 3.53 (d, 1H, *J*=6.7 Hz), 4.2 (q, 2H, *J*=7.7 Hz), 4.76 (m, 1H), 5.73–5.83 (dt, 1H, *J*=5.5, 1.2 Hz), 5.99 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.9, 36.8, 43.0, 44.5, 44.8, 62.9, 76.0, 76.1, 116.1, 116.2, 132.0, 132.4, 137.6, 137.7, 165.3, 165.4 ppm. HRESIMS calcd for $C_{10}H_{14}NO_3$ ([M+H]$^+$): 196.0974; found: 196.0977.

3.5.15. Phenylsulfonyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-hydroxy-2′-cyclopenten-1′-yl)-2-acetonitrile (17o). Viscous yellow liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.6 (dq, 1H, *J*=14.0, 4.5 Hz), 2.2 (br s, 1H, OH), 2.58 (m, 1H), 3.43 (m, 1H), 3.99 (dd, 1H, *J*=27.2, 4.5 Hz), 4.76 (s, 1H), 5.76–6.02 (m, 2H), 7.55–7.71 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 37.1, 38.8, 41.6, 42.2, 61.9, 62.1, 75.8, 76.2, 113.5, 113.7, 129.4, 129.8, 131.71, 131.75, 135.43, 135.47, 136.2, 136.3, 138.32, 138.35 ppm. HRESIMS calcd for $C_{13}H_{14}NO_3S$ ([M+H]$^+$): 264.0694; found: 264.0688.

3.5.16. 2-(4-Hydroxy-cyclopent-2-enyl)-malonic acid dimethyl ester (17p). Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.33 (m, 1H, *J*=14.0, 4.5 Hz), 2.35 (p, 1H, *J*=7.6 Hz), 3.05 (m, 2H), 3.30 (t, 1H, *J*=7.6 Hz), 3.58 (s, 6H), 4.63 (s, 1H), 5.67 (d, 1H, *J*=5.2 Hz), 5.74 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.6, 43.8, 52.6, 56.4, 76.3, 134.1, 135.9, 169.0, 169.2 ppm. HRESIMS calcd for $C_{10}H_{15}O_5$ ([M+H]$^+$): 215.0919; found: 215.0922.

3.6. General procedure for preparation of compounds 18a–p

To a solution of **17a** (100 mg, 0.465 mmol) in dry THF (10 ml) at room temperature was added acetic anhydride (51 mg, 0.5 mmol) and catalytic amount of DMAP. The reaction was allowed to stir for 3 h and then concentrated. The residue was taken up in ethyl acetate (40 ml) and extracted twice with saturated sodium bicarbonate solution (20 ml), followed by brine (10 ml). The organic layer was dried over sodium sulfate and the resulting product **18a** (110 mg, yield=92%) was obtained as light yellow liquid.

3.6.1. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-acetoxy-2′-cyclopenten-1′-yl)-2-nitroacetate (18a). Viscous liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25 (t, 3H, *J*=7.2 Hz), 1.54–1.69 (m, 1H), 1.97 (s, 3H), 2.53–2.61 (m, 1H), 3.51 (br s, 1H), 4.25 (q, 2H, *J*=7.2 Hz), 4.96 (t, 1H, *J*=8.8 Hz), 5.58 (br s, 1H), 5.89–5.98 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0, 21.3, 33.2, 33.7, 44.7, 44.8, 63.3, 78.1, 78.4, 91.1, 91.3, 133.8, 134.0, 134.3, 134.7, 163.5, 170.8 ppm. HRESIMS calcd for $C_{11}H_{16}NO_6$ ([M+H]$^+$): 258.0977; found: 258.0978.

3.6.2. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-acetoxy-4-methyl-2′-cyclopenten-1′-yl)-2-nitroacetate (18b). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.21 (t, 3H, *J*=7.0 Hz), 1.5 (s, 3H), 1.91 (s, 3H), 2.02 (dt, 1H, *J*=14.2, 4.5 Hz), 2.21 (m, 1H), 3.52 (m, 1H), 4.2 (q, 2H, *J*=7.0 Hz), 4.99 (dd, 1H, *J*=9.2, 2.0 Hz), 5.71 (dd, 0.5H, *J*=5.5, 2.5 Hz), 5.76 (dd, 0.5H, *J*=5.7, 2.5 Hz), 6.13 (dt, 1H, *J*=5.5, 2.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.9, 22.0, 24.5, 24.6, 40.3, 41.0, 44.5, 45.0, 63.1, 90.1, 90.4, 90.8, 131.2, 131.6, 138.6, 138.8, 163.5, 170.4 ppm. HRESIMS calcd for $C_{12}H_{18}NO_6$ ([M+H]$^+$): 272.1134; found: 272.1131.

3.6.3. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-acetoxy-4-phenylethynyl-2′-cyclopenten-1′-yl)-2-nitroacetate (18d). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.14 (dt, 3H, *J*=7.2, 2.0 Hz), 1.98 (s, 3H), 2.24 (m, 1H), 2.83 (m, 1H), 3.68 (m, 1H), 4.18 (dq, 2H, *J*=7.0, 1.5 Hz), 4.97 (dd, 1H, *J*=9.2, 5.5 Hz), 5.9 (m, 1H), 6.27 (dt, 1H, *J*=5.5, 2.0 Hz), 7.19–7.35 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.9, 21.6, 41.9, 42.4, 44.4, 44.8, 63.2, 63.3, 81.9, 82.1, 86.3, 86.7, 90.5, 122.0, 128.2, 128.7, 131.8, 133.2, 133.7, 135.9, 136.2, 163.3, 169.1 ppm. HRESIMS calcd for $C_{19}H_{20}NO_6$ ([M+H]$^+$): 358.1291; found: 358.1294.

3.6.4. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-acetoxy-2′-cyclopenten-1′-yl)-3-oxobutanoate (18f). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.12 (t, 3H, *J*=7.2 Hz), 1.4 (t, 1H), 1.96 (s, 3H), 2.18 (s, 3H), 2.9 (p, 1H, *J*=7.5 Hz), 3.33 (m, 2H), 4.03 (q, 2H, *J*=7.2 Hz), 5.5 (m, 1H), 5.81–5.82 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.1, 21.2, 29.4, 29.7, 34.6, 34.7, 42.9, 43.0, 61.5, 61.6, 65.2, 65.3, 78.8, 78.9, 131.2, 131.3, 137.5, 137.6, 168.3, 170.7, 201.0, 201.9 ppm. HRESIMS calcd for $C_{13}H_{19}O_5$ ([M+H]$^+$): 255.1233; found: 255.1231.

3.6.5. 2-Phenylsulfonyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-acetoxy-2′-cyclopenten-1′-yl)-1-phenyl-ethanone (18i). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.85–1.97 (s, 3H), 2.2–2.6 (m, 2H), 3.2–3.4 (m, 1H), 4.50 (dd, 1H, *J*=27.2, 10.2 Hz), 5.4–5.6 (m, 1H), 5.7–5.9 (dt, 1H, *J*=5.5, 2.2 Hz), 6.5 (m, 1H), 7.34–7.78 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 21.1, 21.2, 34.8, 35.6, 43.1, 43.8, 60.4, 65.1, 74.0, 74.2, 76.6, 128.8, 128.83, 128.89, 128.97, 129.92, 132.5, 134.1, 134.3, 134.4, 135.9, 136.6, 136.9, 137.1, 137.6, 170.4, 170.6, 192.5, 192.9 ppm. HRESIMS calcd for $C_{21}H_{21}O_5S$ ([M+H]$^+$): 385.1100; found: 385.1103.

3.6.6. Ethyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-acetoxy-2′-cyclopenten-1′-yl)-2-cyanoacetate (18n). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.26 (t, 3H, *J*=7.0 Hz), 1.65 (m, 1H), 1.9 (s, 3H), 2.57 (p, 1H, *J*=6.5 Hz), 3.25 (m, 1H), 3.4–3.58 (2doublets, (0.5×2H), *J*=6.5 Hz), 4.23 (q, 2H, *J*=7.0 Hz), 5.59 (m, 1H), 5.89–5.99 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.0, 21.1, 33.8, 34.5, 42.7, 44.3, 62.9, 78.2, 78.3, 115.1, 133.5, 134.73, 165.1, 170.7, 170.8 ppm. HRESIMS calcd for $C_{12}H_{16}NO_4$ ([M+H]$^+$): 238.1079; found: 238.1080.

3.6.7. Phenylsulfonyl (2*R*/*S*,1′*R*,4′*S*)-2-(4′-acetoxy-2′-cyclopenten-1′-yl)-2-acetonitrile (18o). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.76–1.9 (m, 1H), 2.0 (s, 3H), 2.67 (m, 1H), 3.41 (m, 1H), 3.87–4.05 (2doublets, 1H, *J*=6.25, 5.0 Hz), 5.55 (m, 1H), 5.91–6.05 (m, 2H), 7.56–7.98 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 20.1, 32.8, 34.5, 40.5, 40.6, 60.5, 60.8, 76.9, 77.0,

111.8, 128.4, 128.5, 132.8, 133.0, 133.2, 133.5, 134.4, 134.9, 135.1, 169.7, 169.6 ppm. HRESIMS calcd for $C_{15}H_{16}NO_4S$ ($[M+H]^+$): 306.0800; found: 306.0814.

3.6.8. 2-(4-Acetoxy-cyclopent-2-enyl)-malonic acid dimethyl ester (18p). Viscous liquid; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.56 (dt, 1H, J=14.0, 4.5 Hz), 2.05 (s, 3H), 2.54 (dt, 1H, J=14.0, 8.0 Hz), 3.33 (m, 2H), 3.77 (s, 6H), 5.6 (m, 1H), 5.88 (dt, 1H, J=5.7, 2.0 Hz), 6.00 (dt, 1H, J=5.7, 2.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.0, 34.5, 43.4, 52.3, 52.4, 56.7, 78.7, 131.3, 137.2, 168.4 (splits into 2), 170.6 ppm. HRESIMS calcd for $C_{12}H_{17}O_6$ ($[M+H]^+$): 257.1025; found: 257.1029.

3.7. General procedure for preparation of compounds 19a–m and 19p

To a solution of **18a** (70 mg, 0.272 mmol) in dry THF (10 ml) at room temperature were added potassium carbonate (37.6 mg, 0.272 mmol) and $Pd(PPh_3)_4$ (15 mg, 0.013 mmol). The reaction was allowed to stir for 12 h at 60 °C and then vacuum filtered over Celite with subsequent concentration of the filtrate. The product was purified by wet column chromatography using ethyl acetate/hexane (1:2) to afford **19a** using column chromatography as a yellow viscous liquid (45 mg, yield=85%).

3.7.1. (1*S*,5*S*)-3-Aza-4-(ethoxycarbonyl)-2-oxabicyclo[3.3.0]oct-3,7-diene-3-oxide (19a). Viscous liquid; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.29 (t, 3H, J=5.8 Hz), 2.63–2.78 (m, 2H), 4.17–4.28 (m, 3H, CH_2+H-4), 5.56–5.62 (m, 1H), 5.75–5.78 (m, 1H), 6.09–6.12 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.0, 38.2, 44.6, 61.4, 84.2, 111.3, 127.7, 137.0, 158.9 ppm. HRESIMS calcd for $C_9H_{12}NO_4$ ($[M+H]^+$): 198.0766; found: 198.0762.

3.7.2. (1*S*,5*S*)-3-Aza-4-(ethoxycarbonyl)-7-methyl-2-oxabicyclo[3.3.0]oct-3,7-diene-3-oxide (19b). Viscous liquid; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.31 (t, 3H, J=6.8 Hz), 1.81 (s, 3H), 2.56 (d, 1H, J=17.6 Hz), 2.73 (dd, 1H, J=17.2, 8.0 Hz), 4.27 (m, 3H), 5.45 (s, 1H), 5.56 (d, 1H, J=8.8 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.4, 16.6, 42.6, 45.6, 61.8, 85.1, 112.1, 122.6, 148.5, 160.0 ppm. HRESIMS calcd for $C_{10}H_{14}NO_4$ ($[M+H]^+$): 212.0923; found: 212.0918.

3.7.3. (1*S*,5*S*)-3-Aza-7-butyl-4-(ethoxycarbonyl)-2-oxabicyclo[3.3.0]oct-3,7-diene-3-oxide (19c). Viscous liquid; ^1H NMR ($CDCl_3$, 250 MHz): δ 0.79 (t, 3H, J=7.0 Hz), 1.20 (m, 5H, CH_2+CH_3), 1.33 (m, 2H), 2.07 (t, 2H, J=7.5 Hz), 2.53 (d, 1H, J=17.5 Hz), 2.75 (dd, 1H, J=16.0, 7.7 Hz), 4.24 (m, 3H), 5.43 (d, 1H, J=1.0 Hz), 5.33 (d, 1H, J=8.7 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.9, 13.9, 22.4, 29.6, 30.6, 42.5, 45.8, 61.5, 84.8, 112.3, 120.8, 150.3, 160.8 ppm. HRESIMS calcd for $C_{13}H_{20}NO_4$ ($[M+H]^+$): 254.1392; found: 254.1394.

3.7.4. (1*S*,5*S*)-3-Aza-4-(ethoxycarbonyl)-7-phenylethynyl-2-oxabicyclo[3.3.0]oct-3,7-diene-3-oxide (19d). White solid: mp=72–74 °C; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.26 (t, 3H, J=7.0 Hz), 2.81–3.04 (m, 2H), 4.27 (m, 3H), 5.66 (d, 1H, J=9.0 Hz), 6.01 (d, 1H, J=2.0 Hz), 7.25–7.40 (m, 5H, Ph) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.2, 41.8, 45.0, 61.8, 83.7, 83.9, 95.5, 110.9, 122.1, 128.4, 129.0, 131.0, 131.4, 131.7, 159.0 ppm; MS(ESI) m/z= 298.1 $[M+H]^+$. HRESIMS calcd for $C_{17}H_{16}NO_4$ ($[M+H]^+$): 298.1079; found: 298.1072.

3.7.5. X-ray crystallographic data for 19d. For the crystal of **19d**, four molecules were found in each unit cell. The compound crystallized in an orthorhombic space group $P2(1)2(1)2(1)$, with cell dimensions a=6.630(4) Å, b= 10.067(6) Å, c=21.631(11) Å. A total of 3479 unique reflection data were obtained to give a final R indices [$I>2\sigma(I)$] of $R1$=0.0626, $wR2$=0.1308 and R indices (all data) $R1$=0.0824, $wR2$=0.1444.

3.7.6. (1*S*,5*S*)-3-Aza-4-(ethoxycarbonyl)-7-trimethylsilanylethynyl-2-oxabicyclo[3.3.0]oct-3,7-diene-3-oxide (19e). ^1H NMR ($CDCl_3$, 250 MHz): δ 0.10 (s, 9H), 1.25 (t, 3H, J=7.0 Hz), 2.85–3.09 (m, 2H), 4.20 (m, 3H), 5.70 (d, 1H, J=8.7 Hz), 6.05 (d, 1H, J=2.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 0.5, 14.3, 40.9, 44.5, 62.0, 82.7, 99.4, 102.0, 111.2, 128.1, 136.2, 160.0 ppm; MS(ESI) m/z=294.1 $[M+H]^+$. HRESIMS calcd for $C_{14}H_{20}NO_4Si$ ($[M+H]^+$): 294.1162; found: 294.1165.

3.7.7. (1*S*,5*S*)-4-(Ethoxycarbonyl)-3-methyl-2-oxabicyclo[3.3.0]oct-3,7-diene (19f). Viscous liquid; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.20 (t, 3H, J=7.2 Hz), 2.09 (s, 3H), 2.3 (m, 1H), 2.6 (m, 1H), 3.7 (t, 1H, J=8.4 Hz), 4.10 (q, 2H, J=6.8 Hz), 5.53 (d, 1H, J=9.2 Hz), 5.7 (br s, 1H), 5.9 (br s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.5, 14.6, 40.1, 43.9, 59.5, 91.9, 106.6, 128.5, 137.0, 166.4, 167.1 ppm. HRESIMS calcd for $C_{11}H_{15}O_3$ ($[M+H]^+$): 195.1021; found: 195.1018.

3.7.8. (1*S*,5*S*)-4-(Ethoxycarbonyl)-3,7-dimethyl-2-oxabicyclo[3.3.0]oct-3,7-diene (19g). Viscous liquid; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.21 (t, 3H, J=7.0 Hz), 1.71 (m, 3H), 2.09 (d, 3H, J=1.2 Hz), 2.27–2.34 (m, 1H), 2.51–2.55 (m, 1H), 3.70 (dt, 1H, J=7.7, 1.0 Hz), 4.1 (m, 2H), 5.34 (m, 1H), 5.46 (d, 1H, J=8.8 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.42, 14.48, 16.5, 44.1, 44.6, 59.2, 92.3, 106.5, 123.0, 147.8, 166.3, 167.2 ppm. HRESIMS calcd for $C_{12}H_{17}O_3$ ($[M+H]^+$): 209.1178; found: 209.1181.

3.7.9. (1*S*,5*S*)-7-Butyl-4-(ethoxycarbonyl)-3-methyl-2-oxabicyclo[3.3.0]oct-3,7-diene (19h). Viscous liquid; ^1H NMR ($CDCl_3$, 250 MHz): δ 0.78 (t, 3H, J=7.0 Hz), 1.21 (m, 5H), 1.34 (m, 2H), 2.04 (m, 5H, CH_3+CH_2), 2.33 (dd, 1H, J=14.0, 1.0 Hz), 2.53 (dd, 1H, J=14.0, 8.0 Hz), 3.72 (m, 1H), 4.07 (m, 2H), 5.34 (d, 1H, J=1.25 Hz), 5.47 (d, 1H, J=9.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.8, 14.45, 14.49, 22.5, 29.6, 30.7, 42.5, 44.1, 59.2, 92.2, 106.5, 121.5, 152.2, 166.4, 167.2 ppm. HRESIMS calcd for $C_{15}H_{23}O_3$ ($[M+H]^+$): 251.1647; found: 251.1645.

3.7.10. (1*S*,5*S*)-3-Phenyl-4-(phenylsulfonyl)-2-oxabicyclo[3.3.0]oct-3,7-diene (19i). Viscous liquid; ^1H NMR ($CDCl_3$, 250 MHz): δ 2.73 (dt, 1H, J=7.2, 2.2 Hz), 2.85 (p, 1H, J=2.2 Hz), 3.82 (dt, 1H, J=7.7, 5.2 Hz), 5.64 (doublet of p, 1H, J=7.2, 1.2 Hz), 5.74 (dq, 1H, J=5.7, 2.2 Hz), 6.06 (dt, 1H, J=5.7, 1.2 Hz), 7.18–7.6 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 40.1, 46.4, 91.9, 114.4, 127.0, 127.4, 127.9, 128.7, 128.8, 129.4, 130.7, 132.6, 137.2,

142.2, 163.9, 192.3 ppm. HRESIMS calcd for $C_{19}H_{17}O_3S$ ([M+H]$^+$): 325.0898; found: 325.0892.

3.7.11. (1*S*,5*S*)-7-Methyl-3-phenyl-4-(phenylsulfonyl)-2-oxabicyclo[3.3.0]oct-3,7-diene (19j). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.76 (s, 3H), 2.58–2.90 (m, 2H), 3.84 (dt, 1H, J=7.7, 2.2 Hz), 5.41 (t, 1H, J=2.0 Hz), 5.62 (d, 1H, J=9.0 Hz), 7.19–7.60 (m, 10H, $PhSO_2$+COPh) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 15.5, 43.2, 46.2, 91.6, 113.3, 121.5, 125.9, 126.6, 127.7, 128.0, 128.4, 129.6, 131.5, 141.3, 147.3, 163.1 ppm. HRESIMS calcd for $C_{20}H_{19}O_3S$ ([M+H]$^+$): 339.1055; found: 339.1050.

3.7.12. (1*S*,5*S*)-7-Butyl-3-phenyl-4-(phenylsulfonyl)-2-oxabicyclo[3.3.0]oct-3,7-diene (19k). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.80 (t, 3H, J=7.2 Hz), 1.19 (m, 2H), 1.31 (m, 2H), 2.05 (t, 2H, J=7.5 Hz), 2.58–2.90 (m, 2H), 3.80 (dt, 1H, J=7.7, 2.2 Hz), 5.40 (d, 1H, J=2.0 Hz), 5.60 (d, 1H, J=9.2 Hz), 7.19–7.60 (m, 10H, $PhSO_2$+COPh) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.9, 22.4, 29.5, 30.6, 42.5, 46.7, 92.4, 114.3, 121.1, 126.9, 127.7, 128.7, 129.1, 129.4, 130.6, 132.5, 142.4, 152.7, 164.1 ppm. HRESIMS calcd for $C_{23}H_{25}O_3S$ ([M+H]$^+$): 381.1524; found: 381.1522.

3.7.13. (1*S*,5*S*)-3-Phenyl-7-phenylethynyl-4-(phenylsulfonyl)-2-oxabicyclo[3.3.0]oct-3,7-diene (19l). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.89–3.17 (m, 2H), 3.94 (dt, 1H, J=8.2, 2.2 Hz), 5.70 (d, 1H, J=9.0 Hz), 6.00 (d, 1H, J=1.7 Hz), 7.26–7.61 (m, 15H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 43.7, 46.6, 84.5, 91.4, 94.8, 114.3, 122.5, 127.0, 127.7, 128.4, 128.6, 128.8, 129.4, 130.8, 131.0, 131.7, 131.9, 132.0, 132.7, 142.1, 164.2 ppm. HRESIMS calcd for $C_{27}H_{21}O_3S$ ([M+H]$^+$): 425.1211; found: 425.1203.

3.7.14. (1*S*,5*S*)-3-Phenyl-4-(phenylsulfonyl)-7-trimethylsilanyl-2-oxabicyclo[3.3.0]oct-3,7-diene (19m). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.14 (s, 9H), 2.85–3.05 (m, 2H), 3.99 (dt, 1H, J=8.5, 2.0 Hz), 5.72 (d, 1H, J=9.0 Hz), 6.10 (d, 1H, J=1.7 Hz), 7.26–7.65 (m, 10H, $PhSO_2$+COPh) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 0.5, 43.5, 46.7, 90.5, 98.0, 102.1, 114.2, 122.7, 127.5, 128.7, 129.0, 129.6, 131.4, 133.0, 134.4, 165.0 ppm. HRESIMS calcd for $C_{24}H_{25}O_3SSi$ ([M+H]$^+$): 421.1294; found: 421.1288.

3.7.15. 2-Cyclopent-2-enylidene-malonic acid dimethyl ester (19p). Viscous liquid; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.58 (m, 2H), 2.90 (m, 2H), 3.70 (s, 3H), 3.73 (s, 3H), 6.76 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 31.0, 32.9, 51.8, 52.0, 115.3, 132.4, 152.4, 166.2, 166.6, 168.3 ppm. HRESIMS calcd for $C_{10}H_{13}O_4$ ([M+H]$^+$): 197.0814; found: 197.0812.

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Supplementary data

ORTEP diagrams with structure factors for compounds **11** and **19d** are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.11.066.

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