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3-Alkyl-1,2-cyclopentanediones by Negishi cross-coupling of a 3-bromo-1,2-cyclopentanedione silyl enol ether with alkylzinc reagents: an approach to 2-substituted carboxylic acid γ-lactones, homocitric and lycoperdic acids

Anne Paju [a], Diana Kostomarova [a], Katharina Matkevitš [a], Marit Laos [a], Tõnis Pehk [b], Tõnis Kanger [a], Margus Lopp [a,*]

[a] Department of Chemistry, Tallinn University of Technology, Akadeemia tee 15, 12618, Tallinn, Estonia
[b] National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618, Tallinn, Estonia

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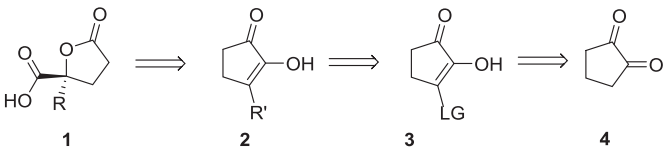
ABSTRACT

Negishi cross-coupling of the silyl-protected 3-bromoenol of 1,2-cyclopentanedione with primary and secondary alkylzinc reagents using Pd-catalysts affords 3-alkyl substituted 1,2-cyclopentanediones in good yield. The method was applied to obtain 3-methylalkoxycarbonyl- and 3(2-Boc-aminoethyl)-alkoxycarbonyl-1,2-cyclopentanediones—homocitric and lycoperdic acid precursors. Homocitric and lycoperdic acids were synthesized using asymmetric oxidation with the Ti(O*i*Pr)$_4$/tartaric ester/*t*BuOOH complex in two steps from the obtained precursors.

1. Introduction

Cross-coupling reactions are widely used tools for constructing C–C bonds of organic molecules from vinyl halides and other functionalized alkenes.[1,2] There are some examples in the literature of the replacement of leaving groups (LG) at the enol double bond.[3–7] The substitution of 3-bromine at a 1,2-diketone enol double bond was recently demonstrated in our group: the Sonogashira coupling of 2-silylprotected 1,2-cyclopentanedione enol **3** (LG=Br) afforded 3-alkynylsubstituted 1,2-diketones **2**.[8] We proposed that the enol derivatives **3** like many similar vinylic compounds undergo a Negishi cross-coupling reaction affording 3-alkylsubstituted diketones **2** (R=alkyl). The resulting 3-alkylsubstituted 1,2-diones are common substrates for an asymmetric oxidation reaction leading to lactone carboxylic acids **1**.[13] In Scheme 1 a simple retrosynthetic pathway from 1,2-cyclopentanedione **4** to lactone carboxylic acids **1** is outlined.

the key intermediate



1 **2** **3** **4**

1a R = CH_2COOH
1b R = $CH_2CH(NH_2)COOH$

Scheme 1. Retrosynthetic sequence to lactone carboxylic acid derivatives.

In the present study the Negishi cross-coupling reaction of silylprotected 3-bromo-1,2-cyclopentenedione silyl enol ether **5** with primary and secondary alkylzinc reagents **7** by using Pd-catalysts was investigated. The obtained substituted 1,2-cyclopentenediones **2f** and **2i** were used as key intermediates for the synthesis of natural compounds homocitric acid **1a**[9] (previous syntheses[10]) and lycoperdic acid **1b**[11] (previous syntheses[12]) by using an asymmetric oxidation cascade of 3-substituted 1,2-cyclopentanediones **2**.[13] We have used this asymmetric oxidation reaction before for the synthesis of γ-lactone carboxylic acids[14] and several other biologically active compounds.[15]

* Corresponding author. E-mail address: margus.lopp@ttu.ee (M. Lopp).

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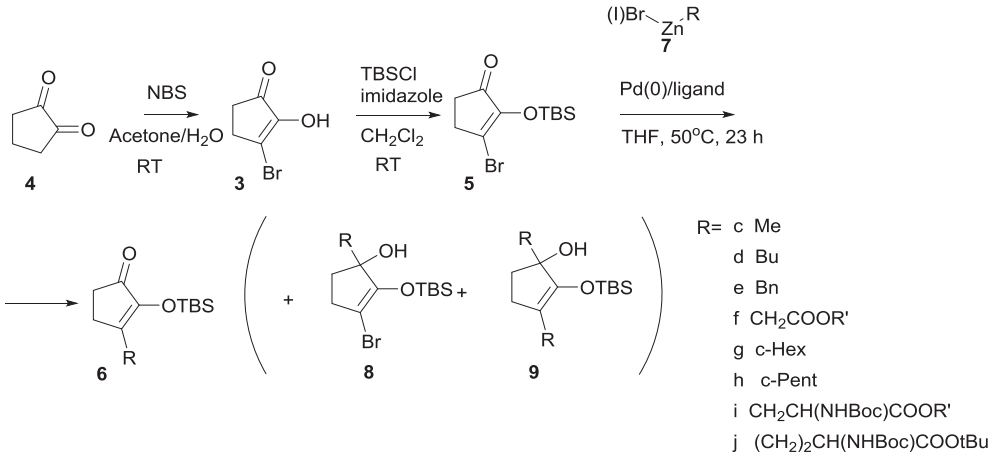
2. Results and discussion

2.1. Synthesis of 3-alkylsubstituted cyclopentane-1,2-diones

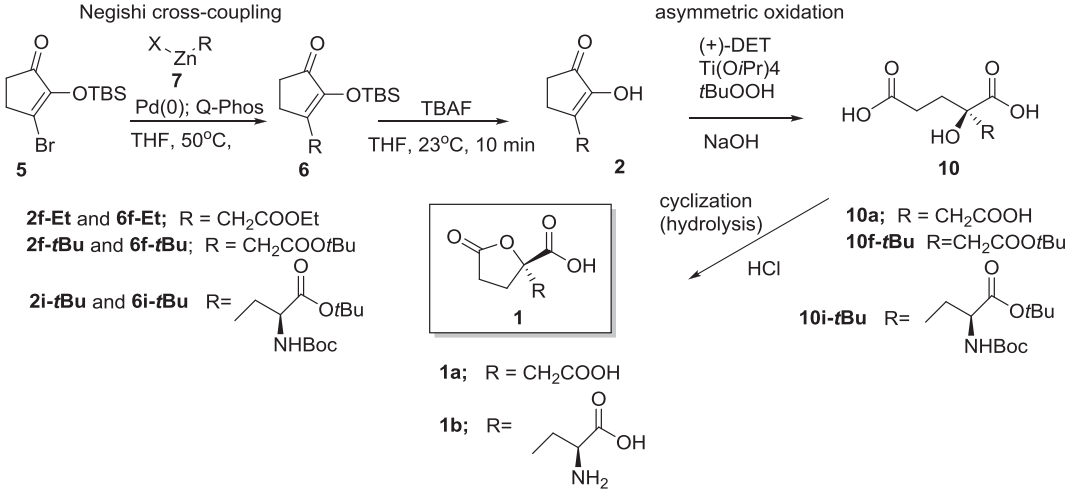
In Negishi cross-coupling reactions with differently functionalized zinc reagents, a number of Pd-catalyst/ligand combinations have been studied.[16] We initially investigated the coupling reactions of bromoenol ether **5** (prepared from cyclopentane-1,2-dione **4** by direct bromination with NBS[8] followed by silylation; Scheme 2) with butylzinc reagent (**7d**) using Pd(*t*Bu$_3$P)$_2$ as a catalyst,[17] and obtained the product (**6d**) in 69% yield (Table 1, entry 3). Zn reagent **7d** was prepared from equimolar amounts of *n*BuLi and $ZnBr_2$. Zn reagents with Me (**7c**) and Bn (**7e**) groups were prepared from the corresponding alkyl halides and activated zinc dust.[18] In these cases the products **6c** and **6e** were obtained in low yield (35% and 40%, respectively, Table 1, No 1 and 5). Using a higher reaction temperature (50 °C) increases the yield to 70–90% (Table 1, entries 2 and 6).

Also, with the unprotected 3-bromoenol **3** several minor side-products form, making purification of **2d** more complicated than that of **6d**. Therefore, in the following experiments only the protected substrate **5** was used.

We carried out a number of preliminary experiments with functionalized Zn reagent **7f-*t*Bu** (Reformatsky reagent from *t*Bu bromoacetate). This Zn reagent,[19] bearing a primary carbon affords 1,2-addition product **8f-*t*Bu** and disubstituted addition/cross-coupling product **9f-*t*Bu** with Pd(*t*Bu$_3$P)$_2$ catalyst (2 mol %) in a 8:1 ratio according to the NMR spectrum. No formation of the cross-coupling product **6f** was observed. It is well known that in several cases an additional phosphorus ligand is necessary to achieve the coupling reaction.[16e,f,20] When we used Zn reagent **7f-*t*Bu** (5 equiv)[21] with $Pd_2(dba)_3$ (2 mol %) and with ligand X-Phos (8 mol %), only 1,2-addition product **8f-*t*Bu** was isolated in 84% yield (Table 1, entry 8). The system $Pd(OAc)_2$ (2 mol %)/X-Phos (8 mol %) was less active, resulting in 20% yield of **8f-*t*Bu** with the main amount of substrate **5** unreacted (Table 1, entry 9). For the coupling of zinc



Scheme 2. Negishi coupling of 3-bromo-cyclopentane-1,2-dione silyl ether **5**.



Scheme 3. A general sequences for homocitric acid **1a** and lycoperdic acid **1b** synthesis.

The unprotected 3-bromoenol **3** also underwent the cross-coupling reaction with *n*BuZnBr, using Pd(*t*Bu$_3$P)$_2$ catalyst (2 mol %), resulting in *n*Bu-substituted product **2d** in 60% yield (Table 1, No 4). The obtained yield is lower than that for **6d** (69%, Table 1, No 3). ester enolates with haloarenes, sterically hindered ferrocenyl ligand Q-phos has been used in the synthesis of α-aryl esters.[22] However, in our case, use of the same system, Pd_2dba_3/Q-Phos (5 mol %/5 mol %), in the same substrate/reagent ratio (1:5) mainly

Table 1
Negishi cross-coupling of 3-bromo-cyclopentane-1,2-dione silyl enolate **5** with alkyl Zn reagents **7**[a]

No	Hal-Zn-R 7	Catalyst: Ligand (mol %)	Product/yield%
1	IZnMe	Pd(*t*Bu$_3$P)$_2$ (5)	**6c**/35[b]
2	IZnMe	Pd(*t*Bu$_3$P)$_2$, (5)	**6c**/68
3	BrZn*n*Bu	Pd(*t*Bu$_3$P)$_2$, (2)	**6d**/69[b]
4	BrZn*n*Bu	Pd(*t*Bu$_3$P)$_2$, (2)	**2d**/60[c]
5	BrZnBn	Pd(*t*Bu$_3$P)$_2$, (5)	**6e**/40[b]
6	BrZnBn	Pd(*t*Bu$_3$P)$_2$, (5)	**6e**/88
7	IZnCH$_2$COO*t*Bu	Pd(*t*Bu$_3$P)$_2$, (2)	**8f-*t*Bu**:**9f-*t*Bu** (ratio 8:1)[d]
8	IZnCH$_2$COO*t*Bu	Pd$_2$(dba)$_3$: X-Phos, (2:8)	**8f-*t*Bu**/84
9	IZnCH$_2$COO*t*Bu	Pd(OAc)$_2$: X-Phos, (2:8)	**8f-*t*Bu**/20 **5**/67
10	IZnCH$_2$COOMe	Pd$_2$(dba)$_3$: Q-Phos, (5:5)	**6f-Me**/44
11	IZnCH$_2$COOEt	Pd$_2$(dba)$_3$: Q-Phos, (5:5)	**6f-Et**/60
12	IZnCH$_2$COO*t*Bu	Pd$_2$(dba)$_3$: Q-Phos, (5:5)	**6f-*t*Bu**/77
13	IZnCH$_2$COO*t*Bu[d]	Pd$_2$(dba)$_3$: Q-Phos, (5:5)	**6f-*t*Bu**/15 **9f-*t*Bu**/65
14	BrZncHex	Pd(*t*Bu$_3$P)$_2$, (5)	**6g**/0
15	BrZncHex	Pd$_2$(dba)$_3$: Q-Phos, (1:2)	**6g**/82
16	BrZncPent	Pd$_2$(dba)$_3$: Q-Phos, (1:2)	**6h**/83
17	IZnCH$_2$CH(NHBoc)COOMe	Pd$_2$(dba)$_3$: Q-Phos, (5:5)	**6i-Me**/64
18	IZnCH$_2$CH(NHBoc)COO*t*Bu	Pd$_2$(dba)$_3$: Q-Phos, (7.5:7.5)	**6i-*t*Bu**/88[e]
19	IZn(CH$_2$)$_2$CH(NHBoc)COO*t*Bu	Pd$_2$(dba)$_3$: Q-Phos, (5:5)	**6j**/61[f]

[a] Conditions: THF, 50 °C, 21–24 h, substrate/reagent ratio 1:3.
[b] Reaction at 23 °C.
[c] Unprotected substrate **3**.
[d] Substrate/reagent ratio 1:5.
[e] Reaction time 44 h.
[f] Solvent DMF, reaction time 48 h.[25]

lead to dialkylated product **9f-*t*Bu** in 65% yield, while the mono-substituted product **6f-*t*Bu** was isolated in only 15% yield (Table 1, No 13).

Reducing the amount of Zn reagent **7f-*t*Bu** to 1.5 equiv (towards substrate **5**) using Pd$_2$(dba)$_3$ catalyst (5 mol %) and ligand Q-Phos (5 mol %), the cross-coupling product **6f-*t*Bu** was isolated in only 5% yield without formation of the double addition product and with a considerable amount of recovered unreacted starting compound **5**. By using substrate **5**/Zn reagent **7f-*t*Bu** in a 1:3 ratio and by using the same catalytic system (Pd$_2$(dba)$_3$ 5 mol %, Q-Phos 5 mol %), we finally obtained the cross-coupling product **6f-*t*Bu** in 77% isolated yield (Table 1, entry 12). As such the substrate **5**/reagent **7** ratio (1:3) was used later in the following experiments. With these conditions, Zn reagents **7f-Me**, **7f-Et** and **7f-*t*Bu** after reacting with **5** afforded the coupling products **6f-Me**, **6f-Et and 6f-*t*Bu** in 44%, 60% and 77% yield, respectively (Table 1, Nos 10–12). In these cases, when the Zn reagents were prepared directly from metallic Zn and the corresponding halide (all cases except reagent 7**d**), activation with TMSCl[21] or with 1,2-dibromoethane/TMSCl[18] was applied.

With *c*HexZnBr (**7g**) when using only the Pd(*t*Bu$_3$P)$_2$ catalyst the coupling reaction did not proceed either(Table 1, No 14). So we turned to the combination of Pd$_2$(dba)$_3$/ligand Q-Phos system for secondary zinc reagents, also. Thus, with *c*Hex and *c*Pent Zn reagents **7g** and **7h** with substrate **5**, using Pd$_2$(dba)$_3$ and Q-Phos system, afforded substitution products **6g** and **6h**, respectively, in 82% and 83% isolated yield (Table 1, entries 15 and 16).

Zn reagents with a more complex nature **7i-Me, 7i-*t*Bu** and **7j** bearing a Boc-protected amino group afforded products **6i-Me**, **6i-*t*Bu** and **6j** in 64%, 88% and 61% isolated yield with the same catalytic system (Table 1, entries 17–19).

2.2. Synthesis of homocitric and lycoperdic acids

Homocitric and lycoperdic acids were synthesized, using a similar general sequence of the main steps: Negishi cross-coupling, asymmetric oxidation, cyclization (Scheme 2).

For the asymmetric oxidation, substituted unprotected enols **2** have to be used. Thus, the silyl protecting groups of compounds **6f-Et** and **6f-*t*Bu** were removed. Desilylation with TBAF in THF at room temperature was fast (10 min) and resulted in substituted enols **2f-Et** and **2f-*t*Bu** in 53% and 68% isolated yields, respectively. For homocitric acid synthesis, enols **2f-Et** and **2f-*t*Bu** were subjected to asymmetric oxidation.[14]

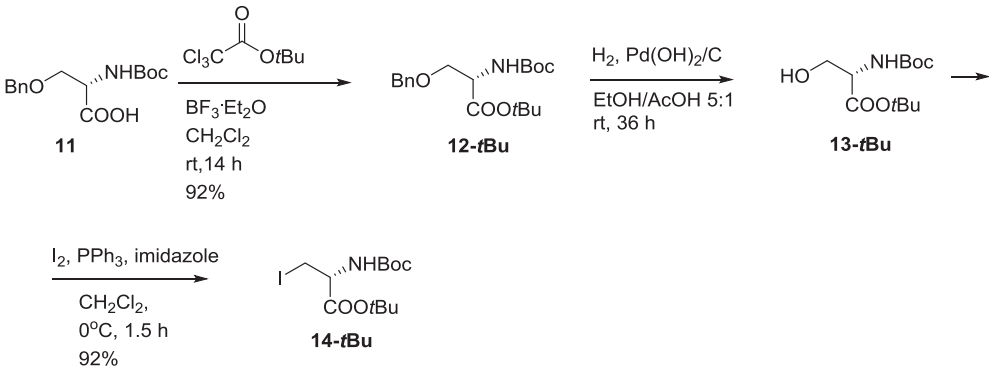
The asymmetric oxidation of substituted enol **2f-Et** with Ti(O*i*Pr)$_4$/diethyl tartrate/*t*BuOOH complex (1:1.6:2.5; −20 °C for 64 h[14]) proceeded smoothly with no starting compound **2f-Et** left. However, the common basic treatment of the reaction mixture with 30% NaOH solution also caused hydrolysis of the ethyl ester function, making the extraction of the resulted product **10a** from the reaction mixture complicated. To separate the reaction product, the triacid **10a** was lactonized by evaporating the reaction mixture to dryness and by subsequent treatment of the residue with 0.1 M hydrochloric acid. After extraction, the product was finally isolated by chromatography on silica gel. By this procedure, homocitric acid **1a** was obtained in 52% overall yield from enol **2f-Et**. When *t*-Bu ester **2f-*t*Bu** was used in asymmetric oxidation instead of alkali labile ethyl ester **2f-Et**, which is stable at these conditions, the extraction of the reaction product—mono *t*Bu ester **10f-*t*Bu** succeeded: after alkali work-up and neutralization with 1M HCl, the product **10f-*t*Bu** was extracted with ethyl acetate. The extract was subjected to acidic simultaneous hydrolysis and lactonization with conc. HCl. The product was purified on silica gel to afford homocitric acid **1a** in slightly better yield (53%) than that from the use of ester **2f-Et**. Therefore, the use of *t*-butyl ester **2f-*t*Bu**, which made the isolation and purification of the final product easier and more convenient, was considered preferable. Asymmetric oxidation of enol **2f-*t*Bu** proceeded with high enantioselectivity: compound **1a** was obtained with 97% *ee*, as determined by chiral HPLC analysis.

For the synthesis of lycoperdic acid **1b**, the precursor **14-*t*Bu** for the Zn reagent IZnCH$_2$CH(NHBoc)COO*t*Bu **7i-*t*Bu** was synthesized from commercial *N*-Boc-*O*-Bn-*L*-serine **11**[23,24] (see Supplementary). By converting it to *tert*-Bu ester **12-*t*Bu** with TBTA in the presence of BF$_3$·Et$_2$O which was then debenzylated with H$_2$ in the presence of Pd(OH)$_2$/C to afford aminoalcohol **13-*t*Bu**, conversion to iodide **14-*t*Bu** with I$_2$ in the presence of PPh$_3$ and imidazole was achieved in more than 80% overall yield from **11** (Scheme 4).

Zn reagent **7i-*t*Bu** was prepared from activated metallic Zn (analogous to **7f**–**h**) affording the coupling products **6i-*t*Bu** in 88% yield in their reaction with **5** (Table 1, No 18). Silyl enol ether **6i-*t*Bu** was desilylated with TBAF, resulting in the oxidation substrate enol **2i-*t*Bu** in 87% yield. Lycoperdic acid **1b** was synthesized directly from substituted enol **2i-*t*Bu** by using an asymmetric oxidation procedure with Ti(O*i*Pr)$_4$/diethyl tartrate/*t*BuOOH complex (1:1.6:2.5; −20 °C; 20 h). Removal of the protecting groups and lactonization of the intermediate **10-*t*Bu** were carried out in one step by refluxing with 6M hydrochloric acid[12] (Scheme 3). Lycoperdic acid **1b** was obtained after ion exchange chromatography in 48% yield from **2i-*t*Bu**. By using the conditions suitable for homocitric acid (concentrated hydrochloric acid in CH$_2$Cl$_2$), incomplete cyclization occurred (lactone/hydroxy-triacid ratio 2:1). Asymmetric oxidation of enol **2i-*t*Bu** (prepared from optically pure serine derivative **11**) proceeded with satisfactory selectivity affording **1b** and its epimer[12b] in 8:1 diastereomeric ratio, as determined by ^{1}H NMR.

3. Summary

The scope of the Negishi cross-coupling reaction is broadened to 3-halides of 1,2-cyclopentane diones, affording coupling products with primary and secondary alkyl Zn reagents and Reformatsky reagent. This reaction is an ideal tool to get 3-substituted 1,2-



Scheme 4. Synthesis of lycoperdic acid **1b** amino acid precursor **14-*t*Bu**.

cyclopentanediones, which are substrates of the asymmetric oxidation reaction. Thus, natural lactone carboxylic acids, homocitric acid and lycoperdic acid in pure enantiomeric form, were prepared in a very small number of simple steps from cyclopentanedione with reasonable yield.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were recorded in deuterated solvents on Bruker Avance II 400 and Avance III 800 spectrometers. Deuterated solvent peaks were used as reference. 2D FT methods were used for the full assignment of ^{1}H and ^{13}C chemical shifts. Mass spectra were measured on a GC–MS spectrometer using EI (70 eV). TLC was performed using 60 F_{254} silica gel plates. IR spectra were recorded on a Bruker PMA 50 spectrometer. Elemental analyses were performed on a varioMicro Analyzer. For column chromatography 40–63 μm and 100–160 μm silica gel was used. All reactions sensitive to oxygen or moisture were conducted under argon atmosphere in oven-dried glassware. Commercial reagents were generally used as received. THF was distilled from $LiAlH_4$ before use. CH_2Cl_2 and DMF were distilled from CaH_2.

4.2. Procedure for the coupling of bromo-diketone 5 with alkylzinc reagents 7c, 7e and 7g–7h

To a stirred suspension of zinc dust (131 mg, 2 mmol) in THF (1 mL), one drop of 1,2-dibromoethane was added. The mixture was heated to reflux, then two drops of Me_3SiCl were added and the mixture was stirred for 15 min at 60 °C. The formation of gas was observed and the zinc dust changed into dark grey fuzzy material. The alkyl halide (1 mmol, iodomethane for **6c**, benzyl bromide for **6e**, bromocyclohexane for **6g** and bromocyclopentane for **6h**) was added dropwise to the cooled mixture, stirred overnight at 50 °C and unreacted zinc was allowed to settle down for 30 min. The solution of zinc reagent was syringed away from the excess zinc and was added to a separate flask containing **5** (146 mg, 0.5 mmol), $Pd(tBu_3P)_2$ (12.8 mg, 0.025 mmol) for **6c** and **6e** or $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol)/Q-PHOS (7.1 mg, 0.01 mmol) for **6g** and **6h** in THF (0.5 mL). The resulting mixture was stirred at 50 °C for 21–24 h. Subsequently, saturated NH_4Cl solution (10 mL) was added to the cooled mixture and extracted with EtOAc (2×10 mL). The extracts were dried (Na_2SO_4) and the solvents were evaporated. The residue was purified by flash chromatography (silica gel, heptanes/EtOAc or heptanes/toluene) to give target compounds.

*4.2.1. 2-(tert-Butyl-dimethyl-silanyloxy)-3-methyl-cyclopent-2-enone (**6c**).* Obtained as a colorless oil (77 mg, 68%) after purification by flash chromatography (heptanes/EtOAc 60:1 to 30:1); [Found: C, 63.55; H, 9.72. $C_{12}H_{22}O_2Si$ requires C, 63.55; H, 9.80]; R_f=0.41 (heptanes/EtOAc 10:1); ν_{max} (neat, cm^{-1}): 2928, 1712, 1638, 1471, 1390, 1342, 1247, 1218, 1116, 862, 783. δ_H (400 MHz, $CDCl_3$): 2.42–2.39 (m, 2H, H-4), 2.33–2.31 (m, 2H, H-5), 1.95 (s, 3H, CH_3), 0.95 (s, 9H, $C(CH_3)_3$), 0.18 (s, 6H, $Si(CH_3)_2$); δ_C (101 MHz, $CDCl_3$): 203.0 (C-1), 151.6 (C-2), 149.7 (C-3), 32.3 (C-5), 27.1 (C-4), 25.9 ($C(CH_3)_3$), 18.5 ($C(CH_3)_3$), 15.0 (CH_3), −3.9 ($Si(CH_3)_2$). *m*/*z* (EI) 211 (M^+−15, 3.5), 169 (M^+−57, 100), 95 (15.1), 75 (23.3).

*4.2.2. 3-Benzyl-2-(tert-Butyl-dimethyl-silanyloxy)-cyclopent-2-enone (**6e**).* Obtained as a white solid (134 mg, 88%) after purification by flash chromatography (heptanes/EtOAc 60:1) mp 42–44 °C; [Found: C, 71.37; H, 8.68. $C_{18}H_{26}O_2Si$ requires C, 71.47; H, 8.66]; R_f=0.45 (heptanes/EtOAc 10:1); ν_{max} (KBr, cm^{-1}): 2928, 1709, 1637, 1493, 1408, 1362, 1249, 1109, 861, 783, 754, 694. δ_H (400 MHz, $CDCl_3$): 7.32–7.28 (m, 2H, *m*-Ph), 7.25–7.17 (m, 3H, *o,p*-Ph), 3.70 (s, 2H, Ph-CH_2–), 2.31–2.27 (m, 4H, H-4, H-5), 0.99 (s, 9H, $C(CH_3)_3$), 0.25 (s, 6H, $Si(CH_3)_2$); δ_C (101 MHz, $CDCl_3$): 203.3 (C-1), 152.7 (C-2), 149.4 (C-3), 138.0 (*s*-Ph), 129.0 (2C, *o*-Ph), 128.8 (2C, *m*-Ph), 126.7 (1C, *p*-Ph), 35.2 (Ph-CH_2–), 32.3 (C-5), 26.0 ($C(CH_3)_3$), 24.5 (C-4), 18.5 ($C(CH_3)_3$), −3.8 ($Si(CH_3)_2$). *m*/*z* (EI) 245 (M^+−57, 100), 167 (8.1), 91 (13.2), 75 (18.2).

*4.2.3. 2-(tert-Butyl-dimethyl-silanyloxy)-3-cyclohexyl-cyclopent-2-enone (**6g**).* Obtained as a white solid (120 mg, 82%) after purification by flash chromatography (heptanes/toluene 1:1 to toluene); mp 57–59 °C; [Found: C, 69.20; H, 10.25. $C_{17}H_{30}O_2Si$ requires C, 69.33; H, 10.27]; R_f=0.47 (toluene); ν_{max} (KBr, cm^{-1}): 2931, 2854, 1700, 1633, 1472, 1407, 1247, 1202, 1112, 973, 864, 785. δ_H (400 MHz, $CDCl_3$): 2.73 (tt, *J*=8.1, 3.6 Hz, 1H, H-1′), 2.39–2.37 (m, 2H, H-4), 2.30–2.28 (m, 2H, H-5), 1.83–1.78 (m, 2H, H-3′,5′), 1.75–1.69 (m, 1H, H-4′), 1.68–1.63 (m, 2H, H-2′,6′), 1.39–1.17 (m, 5H, H-2′,3′,4′,5′,6′), 0.95 (s, 9H, $C(CH_3)_3$), 0.19 (s, 6H, $Si(CH_3)_2$); δ_C (101 MHz, $CDCl_3$): 203.5 (C-1), 159.8 (C-3), 148.1 (C-2), 37.7 (C-1′), 32.2 (C-5), 30.3 (2C, C-2′,6′), 26.3 (2C, C-3′,5′), 26.1 (C-4′), 25.9 ($C(CH_3)_3$), 21.9 (C-4), 18.5 ($C(CH_3)_3$), −4.0 ($Si(CH_3)_2$). *m*/*z* (EI) 279 (M^+−15, 3.2), 237 (M^+−57, 100), 155 (23.8), 75 (12.5).

*4.2.4. 2-(tert-Butyl-dimethyl-silanyloxy)-bicyclopentyl-1-en-3-one (**6h**).* Obtained as a white solid (116 mg, 83%) after purification by flash chromatography (heptanes/toluene 1:1 to toluene); mp 38–39 °C; [Found: C, 68.97; H, 10.02. $C_{16}H_{28}O_2Si$ requires C, 68.52; H, 10.06]; R_f=0.47 (toluene); ν_{max} (KBr, cm^{-1}): 2953, 2857, 1706,

1634, 1471, 1380, 1248, 1224, 1113, 1006, 938, 843, 788. δ_H (400 MHz, $CDCl_3$): 3.16 (p, J=8.7 Hz, 1H, H-1′), 2.41–2.37 (m, 2H, H-5), 2.33–2.28 (m, 2H, H-4), 1.87–1.80 (m, 2H, H-2′,5′), 1.75–1.60 (m, 4H, H-3′,4′), 1.54–1.45 (m, 2H, H-2′,5′), 0.95 (s, 9H, $C(CH_3)_3$), 0.19 (s, 6H, $Si(CH_3)_2$); δ_C (101 MHz, $CDCl_3$): 203.3 (C-3), 158.6 (C-1), 148.9 (C-2), 38.6 (C-1′), 32.2 (C-4), 30.9 (2C, C-2′,5′), 26.0 (2C, C-3′,4′), 25.9 ($C(CH_3)_3$), 21.7 (C-5), 18.6 ($C(CH_3)_3$), −3.9 ($Si(CH_3)_2$). m/z (EI) 265 (M^+−15, 3.2), 223 (M^+−57, 100), 155 (10.8), 129 (5.0), 75 (18.5).

4.3. Procedure for the coupling of bromo-diketone 5 and 3 with alkylzinc reagent 7d

Butyl-lithium (0.32 mL, 2.5 M in hexane, 0.8 mmol) was added to a solution of dried $ZnBr_2$ (180 mg, 0.8 mmol) in THF (2 mL) at 0 °C. The mixture was stirred at room temperature for 30 min. Then $Pd(tBu_3P)_2$ (6 mg, 0.01 mmol) and a solution of diketone **5** or **3** (0.5 mmol) was added. After stirring overnight at room temperature, saturated NH_4Cl solution (10 mL) was added and the mixture was extracted with EtOAc (2×10 mL). The extracts were dried (Na_2SO_4) and the solvents were evaporated. The residue was purified by flash chromatography (silica gel, heptanes/EtOAc or heptanes/toluene) to give target compounds.

*4.3.1. 3-Butyl-2-(tert-butyl-dimethyl-silanyloxy)-cyclopent-2-enone (**6d**).* Obtained as a colorless oil (92 mg, 69%) after purification by flash chromatography (heptanes/toluene 1:1 to toluene); [Found: C, 67.22; H, 10.47. $C_{15}H_{28}O_2Si$ requires C, 67.11; H, 10.51]; R_f=0.42 (toluene); ν_{max} (neat, cm^{-1}): 2931, 1713, 1641, 1464, 1375, 1251, 1116, 860, 785. δ_H (400 MHz, $CDCl_3$): 2.42–2.30 (m, 6H, H-4,5 and H-1′), 1.52–1.44 (m, 2H, H-2′), 1.39–1.30 (m, 2H, H-3′), 0.94–0.90 (m, 12H, $C(CH_3)_3$ and H-4′), 0.18 (s, 6H, $Si(CH_3)_2$); δ_C (101 MHz, $CDCl_3$): 203.3 (C-1), 155.5 (C-3), 149.3 (C-2), 32.3 (C-5), 29.3 (C-2′), 28.6 (C-1′), 25.9 ($C(CH_3)_3$), 24.9 (C-4), 22.9 (C-3′), 18.5 ($C(CH_3)_3$), 14.0 (C-4′), −3.9 ($Si(CH_3)_2$). m/z (EI) 211 (M^+−57, 100), 168 (9.3), 75 (10.8).

*4.3.2. 3-Butyl-2-hydroxy-cyclopent-2-enone (**2d**).* Obtained as a colorless oil (46 mg, 60%) after purification by flash chromatography (heptanes/EtOAc 10:1 to 10:2); R_f=0.30 (heptanes/EtOAc 10:3); δ_H (400 MHz, $CDCl_3$): 6.41 (s, 1H, OH), 2.44–2.38 (m, 6H, H-4,5 and H-1′), 1.56–1.49 (m, 2H, H-2′), 1.39–1.30 (m, 2H, H-3′), 0.91 (t, J=7.3 Hz, 3H, H-4′); δ_C (101 MHz, $CDCl_3$): 203.9 (C-1), 149.5 (C-2), 148.9 (C-3), 32.1 (C-5), 29.1 (C-2′), 28.5 (C-1′), 25.3 (C-4), 22.8 (C-3′), 13.9 (C-4′).

4.4. Procedure for the coupling of bromo-diketone 5 with alkylzinc reagents 7f-Me, 7f-Et and 7f-*t*Bu

To a stirred suspension of zinc dust (196 mg, 3 mmol) in THF (1.2 mL), one drop of Me_3SiCl and alkyl bromoacetate (1.5 mmol, methyl bromoacetate for **7f-Me**, ethyl bromoacetate for **7f-Et** and *tert*-butyl bromoacetate for **7f-*t*Bu**) were sequentially added and the mixture was stirred for 1 h at room temperature. The zinc was allowed to settle, and the solution of zinc reagent was syringed from the excess zinc and was added to a separate flask containing **5** (146 mg, 0.5 mmol), $Pd_2(dba)_3$ (23 mg, 0.025 mmol) and Q-PHOS (18 mg, 0.025 mmol) in THF (1 mL). The resulting mixture was stirred overnight at room temperature. Subsequently, saturated NH_4Cl solution (40 mL) was added to the mixture and extracted with CH_2Cl_2 (3×30 mL). The extracts were dried (Na_2SO_4) and the solvents were evaporated. The residue was purified by flash chromatography (silica gel, heptanes/EtOAc) to give target compounds.

*4.4.1. [2-(tert-Butyl-dimethyl-silanyloxy)-3-oxo-cyclopent-1-enyl]-acetic acid methyl ester (**6f-Me**).* Obtained as a colorless oil (62 mg, 44%) after purification by flash chromatography (heptanes/EtOAc 50:1 to 15:1); [Found: C, 59.25; H, 8.42. $C_{14}H_{24}O_4Si$ requires C, 59.12; H, 8.51]; R_f=0.18 (heptanes/EtOAc 10:1); ν_{max} (neat, cm^{-1}): 2955, 1744, 1650, 1472, 1253, 1111, 856, 787. δ_H (400 MHz, $CDCl_3$): 3.69 (s, 3H, OMe), 3.39 (s, 2H, CH_2CO), 2.53–2.51 (m, 2H, H-5), 2.36–2.34 (m, 2H, H-4), 0.92 (s, 9H, $C(CH_3)_3$), 0.18 (s, 6H, $Si(CH_3)_2$); δ_C (101 MHz, $CDCl_3$): 202.9 (C-3), 170.0 (COO), 151.0 (C-2), 145.0 (C-1), 52.2 (OMe), 34.1 CH_2CO), 32.4 (C-4), 25.8 ($C(CH_3)_3$), 25.1 (C-5), 18.4 ($C(CH_3)_3$), −4.0 ($Si(CH_3)_2$). m/z (EI) 227 (M^+−57, 100), 195 (13.9), 167 (41.1), 89 (27.6), 73 (24.9).

*4.4.2. [2-(tert-Butyl-dimethyl-silanyloxy)-3-oxo-cyclopent-1-enyl]-acetic acid ethyl ester (**6f-Et**).* Obtained as a colorless oil (89 mg, 60%) after purification by flash chromatography (heptanes/EtOAc 50:1 to 20:1); [Found: C, 60.52; H, 8.74. $C_{15}H_{26}O_4Si$ requires C, 60.37; H, 8.78]; R_f=0.21 (heptanes/EtOAc 10:1); ν_{max} (neat, cm^{-1}): 2956, 1739, 1716, 1650, 1472, 1369, 1253, 1111, 855, 787. δ_H (400 MHz, $CDCl_3$): 4.14 (q, J=7.1 Hz, 2H, OCH_2CH_3), 3.37 (s, 2H, CH_2CO), 2.53–2.51 (m, 2H, H-5), 2.36–2.34 (m, 2H, H-4), 1.24 (t, J=7.1 Hz, 3H, OCH_2CH_3), 0.92 (s, 9H, $C(CH_3)_3$), 0.18 (s, 6H, $Si(CH_3)_2$); δ_C (101 MHz, $CDCl_3$): 202.9 (C-3), 169.5 (COO), 150.9 (C-2), 145.3 (C-1), 61.2 (OCH_2CH_3), 34.4 CH_2CO), 32.4 (C-4), 25.8 ($C(CH_3)_3$), 25.1 (C-5), 18.4 ($C(CH_3)_3$), 14.3 (CH_2CH_3), −4.0 ($Si(CH_3)_2$). m/z (EI) 241 (M^+−57, 100), 213 (21.3), 195 (7.5), 167 (33.9), 75 (24.9).

*4.4.3. [2-(tert-Butyl-dimethyl-silanyloxy)-3-oxo-cyclopent-1-enyl]-acetic acid tert-butyl ester (**6f-tBu**).* Obtained as a white solid (125 mg, 77%) after purification by flash chromatography (heptanes/EtOAc 60:1 to 20:1); mp 87–88 °C; [Found: C, 62.71; H, 9.26. $C_{17}H_{30}O_4Si$ requires C, 62.54; H, 9.26]; R_f=0.29 (heptanes/EtOAc 10:1); ν_{max} (KBr, cm^{-1}): 2955, 1732, 1709, 1655, 1465, 1261, 1150, 843, 788. δ_H (400 MHz, $CDCl_3$): 3.32 (s, 2H, CH_2CO), 2.55–2.52 (m, 2H, H-5), 2.38–2.36 (m, 2H, H-4), 1.45 (s, 9H, $C(CH_3)_3$), 0.95 (s, 9H, $SiC(CH_3)_3$), 0.20 (s, 6H, $Si(CH_3)_2$); δ_C (101 MHz, $CDCl_3$): 203.1 (C-3), 168.8 (COO), 150.8 (C-2), 146.3 (C-1), 81.6 ($OC(CH_3)_3$), 35.8 CH_2CO), 32.5 (C-4), 28.2 (C-5), 25.9 ($C(CH_3)_3$), 25.2 ($SiC(CH_3)_3$) 18.5 ($SiC(CH_3)_3$), −4.0 ($Si(CH_3)_2$). m/z (EI) 311 (M^+−15, 0.5), 269 (M^+−57, 48.9), 213 (M^+−113, 100), 185 (3.6), 169 (14.2), 167 (23.0), 75 (18.0).

*4.4.4. [3-Bromo-2-(tert-butyl-dimethyl-silanyloxy)-1-hydroxy-cyclopent-2-enyl]-acetic acid tert-butyl ester (**8f-tBu**).* Obtained as a colorless oil (207 mg, containing succinic acid di-*tert*-butyl ester ~4:1 molar ratio:172 mg of **8f-*t*Bu**=84%) according to the general procedure using 2.5 mmol of zinc reagent **7f-*t*Bu** and $Pd_2(dba)_3$ (8 mg, 0.01 mmol)/X-Phos (19 mg (0.04 mmol) catalytic system after purification by flash chromatography (heptanes/EtOAc 60:1 to 20:1); R_f=0.43 (heptanes/EtOAc 10:1); δ_H (400 MHz, $CDCl_3$): 3.87 (s, 1H, OH), 2.70–2.57 (m, 2H, CH_2CO and H-4), 2.43–2.34 (m, 2H, H-4 and CH_2CO), 2.19–2.13 (m, 1H, H-5), 2.07–2.00 (m, 1H, H-5), 1.47 (s, 9H, $OC(CH_3)_3$), 0.98 (s, 9H, $SiC(CH_3)_3$), 0.27 (s, 3H, $Si(CH_3)_2$), 0.26 (s, 3H, $Si(CH_3)_2$); δ_C (101 MHz, $CDCl_3$): 172.2 (COO), 151.8 (C-2), 100.1 (C-3), 82.0 ($OC(CH_3)_3$), 79.0 (C-1), 43.1 (CH_2CO), 35.8 (C-5), 31.8 (C-4), 28.2 ($C(CH_3)_3$), 26.1 ($SiC(CH_3)_3$), 18.7 ($SiC(CH_3)_3$), −3.3 ($Si(CH_3)_2$), −3.8 ($Si(CH_3)_2$).

*4.4.5. [3-tert-Butoxycarbonylmethyl-2-(tert-butyl-dimethyl-silanyloxy)-1-hydroxy-cyclo-pent-2-enyl]-acetic acid tert-butyl ester (**9f-tBu**).* Obtained as a colorless oil (144 mg, 65%) according to the general procedure using 2.5 mmol of zinc reagent **7f-*t*Bu** after purification by flash chromatography (heptanes/EtOAc 60:1 to 20:1); R_f=0.27 (heptanes/EtOAc 10:1); δ_H (400 MHz, $CDCl_3$): 3.84 (s, 1H, OH), 3.01 and 2.94 (2d, J=15.6 Hz, 2H, CH_2CO), 2.65 (d, J=15.4 Hz, 1H, 1-CH_2CO), 2.41–2.34 (m, 1H, H-4), 2.32 (d, J=15.4 Hz, 1H, 1-CH_2CO), 2.17–2.30 (m, 2H, H-4 and H-5), 1.95–1.88 (m, 1H, H-5), 1.46 (s, 9H, $C(CH_3)_3$), 1.43 (s, 9H, $C(CH_3)_3$), 0.96 (s, 9H, $SiC(CH_3)_3$), 0.22 (s, 3H, $Si(CH_3)_2$), 0.15 (s, 3H, $Si(CH_3)_2$); δ_C (101 MHz, $CDCl_3$): 172.8 (COO), 170.5 (COO), 150.8 (C-2), 113.0 (C-3), 81.7 ($OC(CH_3)_3$), 80.6 (C-1), 80.4 ($OC(CH_3)_3$), 43.0 (CH_2CO), 35.3 (C-5), 34.3 (CH_2CO),

28.3 (C(CH_3)$_3$), 28.2 (C(CH_3)$_3$), 27.7 (C-4), 26.1 (SiC(CH_3)$_3$), 18.5 (SiC(CH_3)$_3$), −3.1 (Si(CH_3)$_2$), −4.0 (Si(CH_3)$_2$).

4.5. Procedure for the coupling of bromo-diketone 5 with alkylzinc reagents 7i-Me and 7i-*t*Bu

To a stirred suspension of zinc dust (131 mg, 2 mmol, dried under vacuum using a heat gun), THF (0.8 mL) and one drop of Me_3SiCl were added. Protected 3-iodopropionic ester (1 mmol, methyl 2-[(*tert*-butoxycarbonyl)amino]-3-iodopropanoate for **6i-Me** and *tert*-butyl 2-[(*tert*-butoxycarbonyl)amino]-3-iodopropanoate for **6i-*t*Bu**) in THF (1.4 mL) and an additional drop of Me_3SiCl were sequentially added and the mixture was stirred for 1 h at room temperature. The zinc was allowed to settle and the solution of zinc reagent was syringed from the excess zinc and was added to a separate flask containing **5** (146 mg, 0.5 mmol), $Pd_2(dba)_3$ (23 mg, 0.025 mmol) and Q-PHOS (18 mg, 0.025 mmol) in THF (0.8 mL). The resulting mixture was stirred for 20 h at 50 °C. Subsequently, saturated NH_4Cl solution (20 mL) was added to the mixture and extracted with EtOAc (2×20 mL). The extracts were dried (Na_2SO_4) and the solvents were evaporated. The residue was purified by flash chromatography (silica gel, heptanes/EtOAc) to give target compounds.

*4.5.1. 2-tert-Butoxycarbonylamino-3-[2-(tert-butyl-dimethyl-silanyloxy)-3-oxo-cyclopent-1-enyl]-propionic acid methyl ester (**6i-Me**).-* Obtained as a white solid (133 mg, 64%) after purification by flash chromatography (heptanes/EtOAc 10:1 to 10:2); mp 88−90 °C; [Found: C, 58.23; H, 8.52; N, 3.35. $C_{20}H_{35}NO_6Si$ requires C, 58.08; H, 8.53; N, 3.39]; R_f=0.20 (heptanes/EtOAc 10:2); ν_{max} (KBr, cm^{-1}): 3401, 2956, 1710, 1511, 1377, 1247, 1214, 1163, 1120, 846, 787. δ_H (800 MHz, $CDCl_3$, 258 K), 12 to 1 mixture of *E*-and *Z*-conformers from urethane bond, *E*-conformer: 5.17 (d, *J*=8.3 Hz, 1H, NH), 4.49 (td, *J*=2×7.2 and 8.3 Hz, 1H, H-2), 3.75 (s, 3H, OCH_3), 2.78 (d, *J*=7.2 Hz, 2H, H-3), 2.55 (m, 1H, H-5′), 2.40 (m, 1H, H-5′), 2.36 (m, 2H, H-4′), 1.39 (s, 9H, Boc (CH_3)$_3$, 0.93 (s, 9H, SiC(CH_3)$_3$, 0.20 and 0.19 (2s, 2×3H, Si(CH_3)$_2$); δ_C (201 MHz, $CDCl_3$): 203.0 (C-3′), 172.4 (COO), 155.1 (Boc CO), 151.3 (C-1′), 148.2 (C-2′), 80.1 (O*C*(CH_3)$_3$), 52.7 (OCH_3), 51.7 (C-2), 32.2 (C-4′), 31.6 (C-3), 28.1 (Boc C(*C*H_3)$_3$), 25.6 (SiC(*C*H_3)$_3$), 24.6 (C-5′), 18.2 (Si*C*(CH_3)$_3$), −4.0 and −4.1 (Si(CH_3)$_2$). *Z*-conformer δ_H: 4.90 (d, *J*=7.5 Hz, 1H, NH), 4.32 (ddd, *J*=5.3, 7.5 and 8.9 Hz, 1H, H-2), 3.74 (s, 3H, OCH_3), 2.77 (dd, *J*=13.4 and 5.3 Hz, 1H, H-3), 2.70 (dd, *J*=13.4 and 8.9 Hz, 1H, H-3), 2.46 (m, 2H, H-5′), 2.38 (m, 2H, H-4′), 1.41 (s, 9H, Boc (CH_3)$_3$, 0.93 (s, 9H, SiC(CH_3)$_3$; δ_C 202.7 (C-3), 172.3 (COO), 154.2 (Boc CO), 151.3 (C-1′), 147.7 (C-2′), 80.7 (O*C*(CH_3)$_3$), 52.6 (OCH_3), 51.6 (C-2), 32.2 (C-4′), 31.6 (C-3), 28.1 (Boc C(*C*H_3)$_3$), 25.6 (SiC(*C*H_3)$_3$), 24.6 (C-5′), 18.2 (Si*C*(CH_3)$_3$), −4.0 and −4.1 (Si(CH_3)$_2$). *m*/*z* (EI) 340 (5.1), 300 (M^+−113, 67.4), 282 (9.5), 256 (22.0), 239 (60.0), 169 (100).

*4.5.2. 2-tert-Butoxycarbonylamino-3-[2-(tert-butyl-dimethyl-silanyloxy)-3-oxo-cyclopent-1-enyl]-propionic acid tert-butyl ester (**6i-tBu**).* Obtained as a colorless oil (200 mg, 88%); %) after purification by flash chromatography (heptanes/EtOAc 30:1 to 10:1); [Found: C, 60.50; H, 9.02; N, 3.08. $C_{23}H_{41}NO_6Si$ requires C, 60.63; H, 9.07; N, 3.07]; R_f=0.33 (heptanes/EtOAc 10:2); $[\alpha]_D^{25}$ +14.5 (*c* 1.14, $CHCl_3$); ν_{max} (neat, cm^{-1}): 3443, 2932, 2859, 1714, 1643, 1502, 1368, 1251, 1154, 1113, 859, 786. δ_H (800 MHz, $CDCl_3$, 268 K), 10 to 1 mixture of *E*- and *Z*-conformers from urethane bond, *E*-conformer: 5.18 (d, *J*=8.2 Hz, 1H, NH), 4.36 (ddd, *J*=6.4, 8.2 and 8.3 Hz, 1H, H-2), 2.78 (dd, *J*=6.4 and 13.6 Hz, 1H, H-3), 2.71 (dd, *J*=8.3 and 13.6 Hz, 1H, H-3), 2.54 (dt, *J*=17.8 and 2×4.3 Hz, 1H, H-5′), 2.48 (dt, *J*=17.8 and 2×4.3 Hz, 1H, H-5′), 2.35 (t, *J*=4.3 Hz, 2H, H-4′), 1.42 (s, 9H, ester C(CH_3)$_3$, 1.40 (s, 9H, Boc C(CH_3)$_3$, 0.93 (s, 9H, SiC(CH_3)$_3$), 0.20 and 0.18 (2s, 2×3H, Si(CH_3)$_2$); δ_C (201 MHz, $CDCl_3$): 203.1 (C-3′), 170.8 (COO), 155.0 (Boc CO), 150.8 (C-1′), 149.2 (C-2′), 82.3 (ester O*C*(CH_3)$_3$), 79.8 (Boc O*C*(CH_3)$_3$), 52.2 (C-2), 32.2 (C-4′), 32.1 (C-3), 28.1 (Boc C(*C*H_3)$_3$), 27.8 (ester C(*C*H_3)$_3$), 25.7 (SiC(*C*H_3)$_3$), 24.5 (C-5′), 18.3 (Si*C*(CH_3)$_3$), −3.9 and −4.1 (Si(CH_3)$_2$). *Z*-conformer δ_H: 4.87 (d, *J*=7.5 Hz, 1H, NH), 4.20 (ddd, *J*=6.8, 7.5 and 8.4 Hz, 1H, H-2), 2.80 (dd, *J*=13.8 and 6.8 Hz, 1H, H-3), 2.61 (dd, *J*=13.8 and 8.4 Hz, 1H, H-3), 2.53 (m, 1H, H-5′), 2.44 (m, 1H, H-5′), 2.36 (m, 2H, H-4′), 1.43 (s, 9H, Boc (CH_3)$_3$, 1.42 (s, 9H, ester (CH_3)$_3$), 0.93 (s, 9H, SiC(CH_3)$_3$), 0.20 and 0.18 (2s, 2×3H, Si(CH_3)$_2$); δ_C 202.7 (C-3′), 170.7 (COO), 154.3 (Boc CO), 150.9 (C-1′), 148.6 (C-2′), 82.2 (ester O*C*(CH_3)$_3$), 80.5 (Boc O*C*(CH_3)$_3$), 53.4 (C-2), 32.2 (C-4′), 32.0 (C-3), 28.1 (Boc C(*C*H_3)$_3$), 27.8 (ester C(*C*H_3)$_3$), 25.7 (SiC(*C*H_3)$_3$), 24.8 (C-5′), 18.3 (Si*C*(CH_3)$_3$), −3.9 and −4.2 (Si(CH_3)$_2$). *m*/*z* (EI) 342 (M^+−113, 14.9), 326 (7.6), 310(5.7), 286 (100), 268 (21.6), 242 (13.1), 225 (42.5), 169 (19.4), 114 (9.8).

4.6. Procedure for the coupling of bromo-diketone 5 with alkylzinc reagents 7j

To a stirred suspension of zinc dust (393 mg, 6 mmol) in DMF (0.45 mL), 1,2-dibromoethane (26 μL, 0.3 mmol) was added. The mixture was heated at 60 °C for 30 min and cooled to room temperature. A drop of Me_3SiCl was added and the mixture was stirred for 30 min. Then a solution of *tert*-butyl 2-[(*tert*-butoxycarbonyl) amino]-4-iodobutanoate (385 mg, 1 mmol) in DMF 0.45 mL) was added and the mixture was stirred at 35 °C for 30 min, cooled and unreacted zinc was allowed to settle down. The solution of zinc reagent was syringed from the excess zinc and was added to a separate flask containing **5** (146 mg, 0.5 mmol), $Pd_2(dba)_3$ (23 mg, 0.025 mmol) and Q-PHOS (18 mg, 0.025 mmol) in DMF (0.2 mL). The resulting mixture was stirred for 48 h at 50 °C. Subsequently, saturated NH_4Cl solution (20 mL) was added to the mixture and extracted with EtOAc (2×20 mL). The extracts were dried (Na_2SO_4) and the solvents were evaporated. The residue was purified by flash chromatography (silica gel, heptanes/EtOAc) to give 2-*tert*-butoxycarbonylamino-4-[2-(*tert*-butyl-dimethyl-silanyloxy)-3-oxo-cyclopent-1-enyl]-butyric acid *tert*-butyl ester (**6j**) as a colorless oil (138 mg, 59%) after purification by flash chromatography (heptanes/EtOAc 30:1 to 10:1); [Found: C, 61.16; H, 9.21; N, 2.84. $C_{24}H_{43}NO_6Si$ requires C, 61.37; H, 9.23; N, 2.98]; R_f=0.27 (heptanes/EtOAc 10:2); ν_{max} (neat, cm^{-1}): 3435, 3350, 2930, 1714, 1641, 1498, 1368, 1251, 1155, 859, 785. δ_H (800 MHz, $CDCl_3$, 268 K), 10 to 1 mixture of *E*- and *Z*-conformers from urethane bond, *E*-conformer: 5.14 (d, *J*=8.4 Hz, 1H, NH), 4.24 (ddd, *J*=4.6, 7.6 and 8.4 Hz, 1H, H-2), 2.45−2.33 (m, 6H, H-4, H-4′, H-5′), 2.00 (m, 1H, H-3), 1.77 (m, 1H, H-3), 1.46 (s, 9H, ester (CH_3)$_3$), 1.44 (s, 9H, Boc (CH_3)$_3$), 0.94 (s, 9H, SiC(CH_3)$_3$), 0.19 and 0.17 (2s, 2×3H, Si(CH_3)$_2$); δ_C (201 MHz, $CDCl_3$): 203.2 (C-3′), 171.4 (COO), 155.3 (Boc CO), 153.4 (C-1′), 149.4 (C-2′), 82.2 (ester O*C*(CH_3)$_3$), 79.7 (Boc O*C*(CH_3)$_3$), 53.6 (C-2), 32.1 (C-4′), 30.1 (C-3), 28.2 (Boc C(*C*H_3)$_3$), 27.9 (ester C(*C*H_3)$_3$), 25.7 (SiC(*C*H_3)$_3$), 24.7 (C-5′), 24.4 (C-4), 18.3 (Si*C*(CH_3)$_3$), −4.0 and −4.1 (Si(CH_3)$_2$). *Z*-conformer δ_H: 4.85 (d, *J*=7.9 Hz, 1H, NH), 4.04 (ddd, *J*=5.3, 7.3 and 7.9 Hz, 1H, H-2), 2.45−2.33 (m, 6H, H-4, H-4′, H-5′), 1.94 (m, 1H, H-3), 1.76 (m, 1H, H-3), 1.46 (s, 9H, ester (CH_3)$_3$), 1.44 (s, 9H, Boc (CH_3)$_3$), 0.94 (s, 9H, SiC(CH_3)$_3$), 0.19 and 0.17 (2s, 2×3H, Si(CH_3)$_2$); δ_C 203.2 (C-3), 171.9 (COO), 155.3 (Boc CO), 152.9 (C-3), 149.6 (C-2′), 81.8 (ester O*C*(CH_3)$_3$), 80.4 (Boc O*C*(CH_3)$_3$), 55.0 (C-2), 32.0 (C-4′), 30.2 (C-3), 28.2 (Boc C(*C*H_3)$_3$), 27.9 (ester C(*C*H_3)$_3$), 25.7 (SiC(*C*H_3)$_3$), 24.8 (C-5′), 24.5 (C-4), 18.3 (Si*C*(CH_3)$_3$), −4.0 and −4.1 (Si(CH_3)$_2$). *m*/*z* (EI) 470 (M^++1, 0.5) 356 (M^+−113, 7.2), 340 (11.0), 324 (11.9), 312 (10.8), 300 (97.7), 282 (53.9), 239 (11.2), 223 (13.7), 210 (32.2), 167 (36.9), 57 (100).

4.7. Procedure for deprotection of silyl enol ethers 6f-*t*Bu and 6i-*t*Bu

A solution of (2-(*tert*-butyl-dimethyl-silanyloxy)-3-oxo-cyclopent-1-enyl)-acetic acid *tert*-butyl ester **6f-*t*Bu** (48 mg,

0.147 mmol) in THF (2 mL) was treated with TBAF (0.162 mL, 0.162 mmol, 1M solution in THF). After 10 min of stirring the reaction was quenched with saturated NH_4Cl solution (3 mL), the phases were separated and the aqueous phase was extracted with EtOAc (2×2 mL). The organic phases were combined, dried over $MgSO_4$, the solvent was evaporated and the residue was purified by flash chromatography (silica gel, heptanes/EtOAc) to give target compound.

*4.7.1. (2-Hydroxy-3-oxo-cyclopent-1-enyl)-acetic acid tert-butyl ester (**2f-tBu**).* Obtained as white crystals (21 mg, 68%) after purification by flash chromatography (heptanes/EtOAc 10:1.5 to 10:3); mp 84–86 °C; [Found: C, 62.21; H, 7.61. $C_{11}H_{16}O_4$ requires C, 62.25; H, 7.60]; R_f=0.20 (heptanes/EtOAc 10:3); ν_{max} (KBr, cm^{-1}): 3307, 2999, 2973, 1728, 1699, 1665, 1415, 1384, 1366, 1151, 699. δ_H (400 MHz, $CDCl_3$): 6.35 (s, 1H, OH), 3.37 (s, 2H, CH_2CO), 2.56–2.53 (m, 2H, H-5), 2.46–2.43 (m, 2H, H-4), 1.44 (s, 9H, $C(CH_3)_3$); δ_C (125 MHz, $CDCl_3$): 203.1 (C-3), 169.1 (COO), 150.1 (C-2), 138.3 (C-1), 82.1 ($OC(CH_3)_3$)), 35.8 (CH_2CO), 32.2 (C-4), 28.2 ($OC(CH_3)_3$), 25.6 (C-5). *m/z* (EI) 156 (M^+−56, 34.9), 139 (27.7), 111 (28.3), 57 (100).

*4.7.2. 2-tert-Butoxycarbonylamino-3-(2-hydroxy-3-oxo-cyclopent-1-enyl)-propionic acid tert-butyl ester (**2i-tBu**).* Obtained from **6i-tBu** (382 mg, 0.84 mmol) and TBAF (0.92 mL, 0.92 mmol, 1M solution in THF) in THF (8.4 mL) as a colorless viscous mass (249 mg, 87%) after purification by flash chromatography (heptanes/EtOAc 10:2 to 10:4); [Found: C, 59.58; H, 8.06; N, 4.03. $C_{17}H_{27}NO_6$ requires C, 58.81; H, 7.97; N, 4.10]; R_f=0.14 (heptanes/EtOAc 10:3); $[\alpha]_D^{25}$ +26.0 (*c* 1.39, $CHCl_3$); ν_{max} (neat, cm^{-1}): 3383, 2980, 2933, 1711, 1661, 1509, 1394, 1368, 1252, 1155. δ_H (400 MHz, $CDCl_3$), main *E*-conformer: 5.97 (s, 1H, OH), 5.24 (d, *J*=8.2 Hz, 1H, NH), 4.43 (td, *J*=2×6.9, 8.2 Hz), 2.82 (d, *J*=6.9 Hz, 2H, H-3), 2.59–2.44 (m, 2H, H-5′), 2.46–2.40 (m, 2H, H-4′), 1.44 (s, 9H, ester $OC(CH_3)_3$), 1.41 (s, 9H, Boc $OC(CH_3)_3$); δ_C (101 MHz, $CDCl_3$): 203.0 (C-3′), 170.9 (COO), 155.4 (COO), 150.3 (C-2′), 141.8 (C-1′), 82.6 ester ($OC(CH_3)_3$), 80.1 Boc ($OC(CH_3)_3$), 52.5 (C-2), 32.3 (C-4′), 32.1 (C-3), 28.4 Boc ($OC(CH_3)_3$), 28.0 ester ($OC(CH_3)_3$), 25.4 (C-5′). *m/z* (EI) 285 (M^+−56, 1.8), 229 (M^+−112, 12.2), 212 (9.7), 185 (15.0), 168 (8.2), 140 (17.0), 130 (6.3), 112 (42.2) 74 (14.9), 57 (100).

4.8. (R)-(−)-Homocitric acid lactone 1a (2-carboxymethyl-5-oxo-tetrahydrofuran-2-carboxylic acid)

To a solution of $Ti(OiPr)_4$ (0.3 mL, 1 mmol) and 4 Å powdered molecular sieves (100 mg) in CH_2Cl_2 (6 mL), (+)-DET (0.27 mL, 1.6 mmol) was added at −20 °C and the mixture was stirred for 15 min. Next diketone **2f-tBu** (1 mmol) in CH_2Cl_2 (2.0 mL) was added and the reaction mixture was stirred for 30 min. Next *t*BuOOH (0.38 mL, 2.5 mmol, 6.6M solution in decane) was added and the reaction was kept at −20 °C for 63 h. Water (6.0 mL) was added and the mixture was stirred for 1 h at room temperature, then 30%NaOH in saturated NaCl solution (1.2 mL) was added and the mixture was again stirred at room temperature for an additional 1 h. Then CH_2Cl_2 layer was removed and the mixture was acidified with 1M HCl solution (pH=1–2) and extracted with EtOAc (6×20 mL). The combined extracts were dried over $MgSO_4$ and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (40 mL) and concentrated HCl solution (0.4 mL) was added. The mixture was stirred for 2 h at room temperature, concentrated in vacuum and treated with EtOAc: toluene (2:1). The product purified by flash chromatography (silica gel, petroleum ether–acetone) to give **1a** as a white solid (100 mg, 53%); mp 152–154 °C (lit. 154–156 °C,[10b] 146–148 °C,[10c]); 97% ee (HPLC: Chiralpak AS-H, 250×4.6 mm, hexane/EtOH=85/15 +0.1% TFA, 0.8 mL/min, 210 nm; major 13.6 min, minor 12.6 min);; [Found: C, 44.74; H, 4.32. $C_7H_8O_6$ requires C, 44.69; H, 4.29]; $[\alpha]_D^{20}$ −50.8 (*c* 0.36, H_2O) (lit. $[\alpha]_D^{21}$ −50.5 (*c* 0.33, H_2O),[10b] $[\alpha]_D$ −50.0 (*c* 0.35, H_2O),[10d] $[\alpha]_D^{23}$ −57.0 (*c* 1, H_2O),[10j]); ν_{max} (KBr, cm^{-1}): 3129, 2982, 2936, 1755, 1722, 1674, 1386, 1185, 1061. δ_H (800 MHz, $(CD_3)_2CO$, 2.05): 3.14 and 2.94 (both d, 2H, *J*=17.2 Hz, CH_2COOH), 2.61 (ddd, *J*=9.7, 10.1 and 17.8 Hz, 1H, H-4), 2.57 (ddd, *J*=3.6, 9.8 and 17.8 Hz, 1H, H-4), 2.48 (ddd, *J*=3.6, 9.7 and 13.4 Hz, 1H, H-3), 2.42 (ddd, *J*=9.8, 10.1 and 13.4 Hz, 1H, H-3); δ_C (125 MHz, $(CD_3)_2CO$, 29.80): 176.8 (C-5), 172.7 (2-COOH), 170.8 (CH_2COOH), 83.6 (C-2), 41.7 (CH_2CO), 31.7 (C-3), 28.3 (C-4).

4.9. (S)-(+)-Lycoperdic acid (1b) [2-(2-amino-2-carboxyethyl)-5-oxo-tetrahydrofuran-2-carboxylic acid]

To a solution of $Ti(OiPr)_4$ (0.28 mL, 0.93 mmol) and 4 Å powdered molecular sieves (93 mg) in CH_2Cl_2 (5.5 mL), (+)-DET (0.26 mL, 1.49 mmol) was added at −20 °C and the mixture was stirred for 15 min. Next diketone **2i-tBu** (0.93 mmol) in CH_2Cl_2 (2.0 mL) was added and the reaction mixture was stirred for 30 min. Next *t*BuOOH (0.41 mL, 2.5 mmol, 5.68M solution in decane) was added and the reaction was kept at −20 °C for 21 h. Water (5.6 mL) was added and the mixture was stirred for 1 h at room temperature, then 30%NaOH in saturated NaCl solution (1.12 mL) was added and the mixture was again stirred at room temperature for an additional 1 h. The reaction mixture was filtered through a pad of Celite, washing with water. Then CH_2Cl_2 layer was removed and the mixture was acidified with 6M HCl solution (pH=2–3) and extracted with several portions of EtOAc. The combined extracts were dried over $MgSO_4$ and the solvent was evaporated to give crude diacid **10** as a slightly yellow solid (265 mg, 73%). A solution of **10** (237 mg, 0.606 mmol) in 6M HCl (10.5 mL) was refluxed for 8 h, then concentrated under reduced pressure. Purification the residue by ion-exchange chromatography (Dowex 1×8, 200–400 mesh, acetate form) eluting with 2M aqueous acetic acid gave 8:1 mixture of **1b** and its epimer (87 mg, 66%) as a white solid which was recrystallized from water to afford pure lycoperdic acid as colorless needles; mp 202–203 °C (lit. 200–201 °C,[12b] lit. 200–202 °C,[12c,d]); [Found: C, 44.19; H, 5.06; N, 6.44. $C_8H_{11}NO_6$ requires C, 44.24; H, 5.11; N, 6.45]; $[\alpha]_D^{22}$ +12.6 (*c* 0.32, H_2O) (lit. $[\alpha]_D^{21}$ +14.2 (*c* 0.46, H_2O),[12b]; $[\alpha]_D^{28}$ +12.7 (*c* 0.21, H_2O),[12c] $[\alpha]_D^{24}$ +14.4 (*c* 0.47, H_2O),[12f]); ν_{max} (KBr, cm^{-1}): 3440, 3239, 2940, 2590, 1770, 1732, 1634, 1522, 1277, 1210. δ_H (400 MHz, D_2O): 4.03 (dd, *J*=3.4, 10.1 Hz, 1H, H-2′), 2.92 (dd, *J*=3.4, 15.6 Hz, 1H, H-1′), 2.75–2.70 (m, 2H, H-4), 2.67–2.59 (m, 1H, H-3), 2.40–2.32 (m, 1H, H-3), 2.33 (dd, *J*=10.1, 15.6 Hz, 1H, H-1′); δ_C (101 MHz, D_2O): 179.7(C-5), 175.3 (COOH), 171.9 (COOH), 87.6 (C-2), 51.4 (C-2′), 37.6 (C-1′), 32.3 (C-3), 27.7 (C-4).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.10.014.

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