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Intramolecular Direct Aldol Reactions of Sugar 2,7-Diketones: Syntheses of Hydroxylated Cycloalka(e)nones

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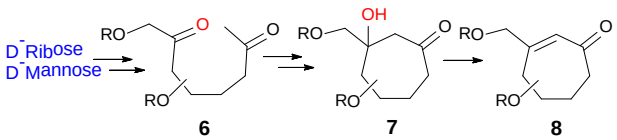


A regio- and stereoselective intramolecular direct aldol reaction of 2,7-diketones derived from carbohydrates has been developed to construct cycloalkanones **7** which were dehydrated to give heavily oxygenated cycloalkenones **8**.

Introduction

Since monosaccharides are designed by nature to choose five- and six-membered rings as the favourable structures to perform various functions,[1] most organic chemists focus their endeavor towards the formation of hydroxylated-cyclopentanes and -cyclohexanes[2] while leaving the medium-sized carbasugar synthesis as a relatively tangential research.[3] The sparse existence of medium-ring carbocyclic analogues of sugars and their unknown but potentially intriguing biological properties, together with our long standing interest in the construction of heavily hydroxylated carbocycles,[4] prompted us to engage in a synthetic excursion targeting cyclohepta(e)noid carbasugars. Nonetheless, the densely oxygenated cycloheptanoid skeleton is found in natural products, examples are urechitol A (**1**),[5a,b] 6α,7α,10α-trihydroxyisoducane (**2**),[5c] daucuside (**3**),[5d] daucusol (**4**)[5d] and **5**[5e] (Figure 1). These are also challenging synthetic targets.

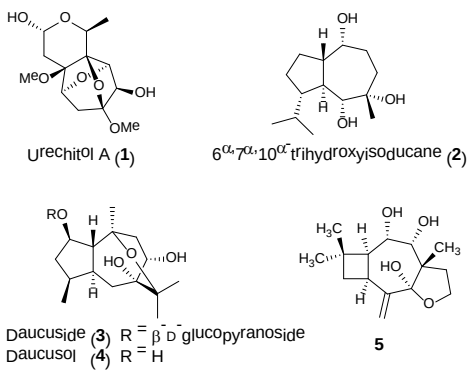


Fig. 1 Cycloheptanoid natural products

The direct aldol reaction has been regarded by organic chemists as one of the most succinct and efficient carbon-carbon bond forming reactions.[6] Recently, we reported the assembly of multi-hydroxylated cyclohexanoid natural products using the intramolecular variant of the direct aldol reaction on 2,6-diketones derived from sugars.[4e] Thus, valiolamine, validoxylamine G,[4e] gabosines A, D, and E,[4g] and 1,1-bis-valienamine[4h] were harvested efficiently by this protocol. On the other hand, the intramolecular aldol reactions of 2,7-diketones to furnish cycloheptyl aldols have received relatively less attention. In this article, we now describe the facile construction of cycloalkanones **7** via the same reaction on 2,7-diketones **6**, that were derived swiftly from D-ribose and D-mannose, and the dehydration of the cyclized aldols **7** into cycloalkenones **8** (Figure 2).

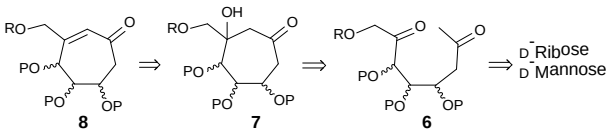
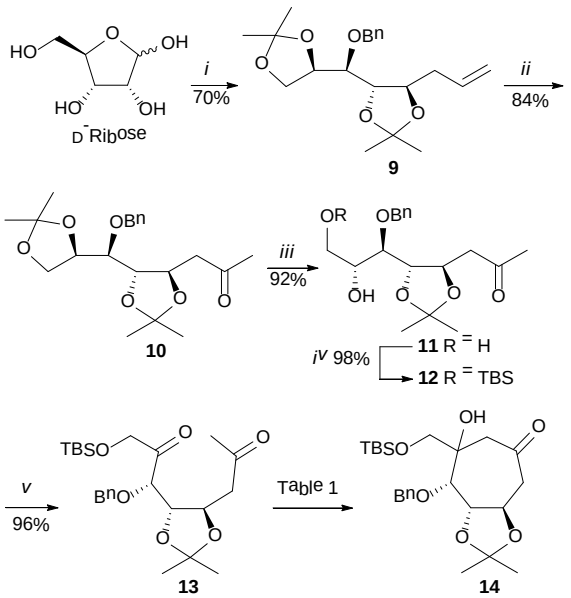


Fig. 2 Retrosynthetic analysis.

Results and discussion

The synthesis of a 2,7-diketone **13**, bearing a trans-isopropylidene blocking group, is indicated in Scheme 1. Alkene **9** was efficiently accessible from D-ribose in 3 steps with 70% overall yield according to our recent effort.[4b] Modified Wacker oxidation[7] of the terminal olefin in **9** using atmospheric molecular oxygen as the sole oxidant and water as the nucleophile provided ketone **10** in 84% yield. Regioselective acid hydrolysis of the terminal isopropylidene group in **10** afforded diol **11** in 92% yield. The primary

hydroxyl group in the diol **11** was selectively blocked with *t*-butyldimethylsilyl chloride (TBSCl) to give silyl ether **12**. 2,7-Diketone **13**, obtained by oxidation of the free alcohol in **12** with PDC, was then subjected to the intramolecular direct aldol reaction under different conditions and the results are revealed in Table 1.



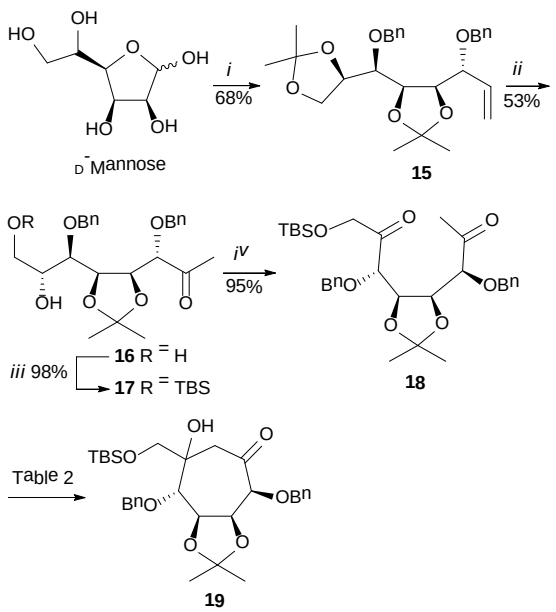
Scheme 1 Synthesis of diketone **13** from D-ribose *Reagents and conditions: i* 3 steps, Ref 4b; *ii* $PdCl_2$, O_2, DMA, H_2O, 80 °C, 6h; *iii* 80% AcOH; *iv* TBSCl, imidazole; *v* PDC, 3Å MS, CH_2Cl_2.

It is noteworthy that L-proline catalyzed the direct aldol reaction of 2,7-diketone **13** to give cycloheptanone **14** in 92% yield (entry 1, Table 1) whereas D-proline only provided the same product **14** in 76% yield, hinting at a mismatched asymmetric catalysis (entry 2). The diastereomeric aldol was not detected. Strong bases caused decomposition of the starting material and no desired aldol was observed (entries 3). Tertiary amines displayed poor performance as catalysts (entries 4–5) whereas cyclic secondary amines afforded good yields of the aldol product **14** (entries 6–7), albeit the reaction was sluggish. We were unable to confirm the stereochemistry of the tertiary alcohol in **14** at this stage. Addition of acetic acid as a non-chiral co-catalyst to cyclic secondary amines proved rewarding and the reaction time was shortened to 24 hours (entries 8–11). The desired product **14** was harvested in comparable yields and the best yield of 83% was accomplished by using pyrrolidine-acetic acid in DMSO (entry 10). We did not investigate the assignment of the stereochemistry of the tertiary alcohol in the aldols as it would be lost in the subsequent dehydration step.

Table 1. Aldol-cyclization conditions of diketone **13**

entry	conditions	results
1	L-Proline (0.3 equiv), DMSO, 24h	92%
2	D-Proline (0.3 equiv), DMSO, 7 d	76%
3	KHMDS (1 equiv), THF, –78 °C, 15 min	Decomposed
4	Et_3N (1.5 equiv), CH_2Cl_2, 21 d	38%
5	DIPEA (1.5 equiv), CH_2Cl_2, 21 d	35%
6	Pyrrolidine (1.5 eq), CH_2Cl_2, 21 d	80%
7	Piperidine (1.5 eq), CH_2Cl_2, 21 d	85%
8	Pyrrolidine (1.5 eq), AcOH (1.5 eq), CH_2Cl_2, 24 h	78%
9	Piperidine (1.5 eq), AcOH (1.5 eq), CH_2Cl_2, 24 h	75%
10	Pyrrolidine (1.5 eq), AcOH (1.5 eq), DMSO, 24 h	83%
11	Piperidine (1.5 eq), AcOH (1.5 eq), DMSO, 24 h	76%

The practicability to make cycloheptanones from a 2,7-diketone with a cis-isopropylidene blocking group was then explored. The preparation of 2,7-diketone **18** is highlighted in Scheme 2. Alkene **15** was promptly attained from D-mannose in 3 steps with 68% overall yield.[8] With the use of the aforesaid $PdCl_2$-DMA catalytic system[7] under prolonged heating, oxidation of the alkene in **15** occurred with concomitant hydrolysis of the terminal acetonide protecting group, forming diol **16** in 53% yield. The diol **16** was then converted into 2,7-diketone **18** by regioselective silylation followed by PDC oxidation.



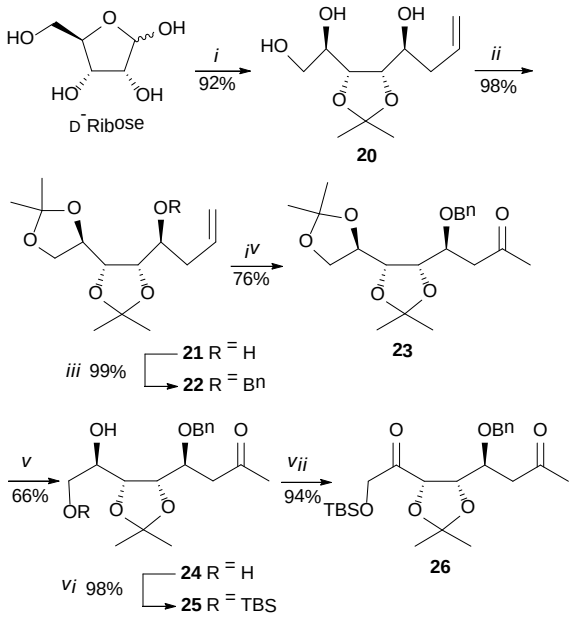
Scheme 2 Synthesis of diketone **18** from D-mannose. *Reagents and conditions: i* 3 steps, Ref 8; *ii* $PdCl_2$, O_2, DMA, H_2O, 80 °C, 48h; *iii* TBSCl, imidazole; *iv* PDC, 3Å MS, CH_2Cl_2.

Carbocyclization of the 2,7-diketone **18** was then studied and the results are presented in Table 2. Diketone **18** was induced to aldolize with L-proline in DMSO and cycloheptanone **19** was achieved in 87% yield with excellent diastereoselectivity (entry 1). The other diastereomer was not observed. When D-proline was used, the reaction also gave aldol product **19**, but in only 56% yield (entry 2). This might be another mismatched catalysis as indicated above. Strong bases (entry 3), aliphatic and cyclic amines (entries 4–7) produced aldol **19** in poor yields (35–38%). The aldolizations with amines were again sluggish. Fortunately, addition of acetic acid to cyclic amines effectively promoted the aldol cyclization to give **19** within one day (entries 8–11). Piperidine/acetic acid combination gave the best yields of cycloheptanone **19** (entry 9 and 11). The poor yields of the adolisation with triethylamine as base to form 7-membered rings suggested that the reaction might proceed through an enamine activation rather than a simple base promoted enolisation.

Table 2. Aldol-cyclization conditions of diketone **18**

entry	conditions	results
1	L-Proline (0.3 equiv), DMSO, 21 d	87%
2	D-Proline (0.3 equiv), DMSO, 21 d	56%
3	KHMDS (1 equiv), THF, –78 °C, 15 min	42%
4	Et_3N (1.5 equiv), CH_2Cl_2, 21 d	38%
5	DIPEA (1.5 equiv), CH_2Cl_2, 21 d	35%
6	Pyrrolidine (1.5 eq), CH_2Cl_2, 21 d	37%
7	Piperidine (1.5 eq), CH_2Cl_2, 21 d	36%
8	Pyrrolidine (1.5 eq), AcOH (1.5 eq), CH_2Cl_2, 24 h	67%
9	Piperidine (1.5 eq), AcOH (1.5 eq), CH_2Cl_2, 24 h	86%
10	Pyrrolidine (1.5 eq), AcOH (1.5 eq), DMSO, 24 h	68%
11	Piperidine (1.5 eq), AcOH (1.5 eq), DMSO, 24 h	83%

One more example on the production of cycloheptanone from a 2,7-diketone with a cis-isopropylidene was also examined. Alkene **20**[4a,9] was accessed quickly from D-ribose in 2 steps with 92% yield (Scheme 3). Standard acetonation of **20** followed by benzylation gave the completely protected alkene **22**. Then, performing the same synthetic transformation of alkene **9** on alkene **22** afforded 2,7-diketone **26** without incident.

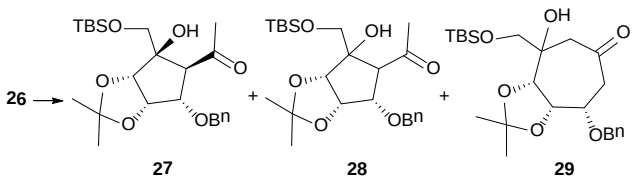


Scheme 3 Synthesis of diketone **26** from D-ribose.. *Reagents and conditions: i* 2 steps, Ref 4a; *ii* 2,2-DMP, Acetone, *p*-TsOH; *iii* BnBr, NaH, $^nBu_4NI$, THF; *iv* $PdCl_2$, O_2, DMA, H_2O, 80 °C, 6h; *v* 80% AcOH; *vi* TBSCl, imidazole, CH_2Cl_2; *vii* PDC, 3Å MS, CH_2Cl_2.

The aldol-cyclization of 2,7-diketone **26** was then investigated and the results are documented in Table 3. In contrast to the previous 2,7-diketones **13** and **18**, L- and D-proline-catalyzed direct aldolization of 2,7-diketone **26** displayed different regioselectivity and furnished a mixture of three carbocycles, **27**, **28** and **29**, where cyclopentanone **27** was formed as the major regio- and diastereomer (entries 1–2). Tertiary amines yielded cyclopentanone **28** preponderantly (entries 4–5) whereas cyclic secondary amines afforded cyclopentanone **27** as the major diastereomer (entries 6–7). These aldolisations were again sluggish. A combination of cyclic secondary amine and acetic acid speeded up the cyclization and favored the assembly of cyclopentanone **27** (entries 8–11). Best yields of the cyclopentanones were achieved in using dichloromethane as the solvent (entries 8–9). The structure and stereochemistry of cyclopentanone **27** was confirmed by an X-ray crystallographic analysis. Acetic acid as the co-acid catalyst appears to be essential for an efficient aldolization. No aldol products derived from enolisation of the 7-keto group were observed. We believe that the *pKa* value of a methyl or methylene group without an oxygen substituent should be comparatively lower and hence 2-ketone was selectively enolised.

Regarding the regioselectivity of the intramolecular aldolization, it is not energetically feasible for the 2,7-diketone **13** to assemble a cyclopentane ring fused with a trans-acetonide ring. As for 2,7-diketone **18**, the difference in the pKa values of the methyl and the methine protons might dictate the selective deprotonation of the more acidic methyl group. Furthermore, the resultant cyclopentane ring would have had two adjacent tertiary carbons and would not be energetically favorable due to steric reasons. The selective formation of 5-membered rings from 2,7-diketone **26** appeared to be favorable under either kinetic or thermodynamic conditions. However, more aldolization examples are needed to confirm these rationalizations.

Table 3. Aldol-cyclization conditions of diketone **26**

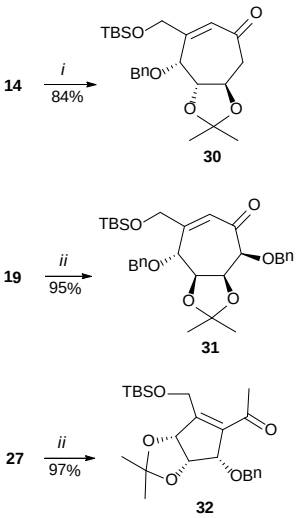


entry	conditions	results		
		27	**28**	**29**
1[a]	L-Proline (0.3 equiv), DMSO, 48 h	55%	19%	17%
2[a]	D-Proline (0.3 equiv), DMSO, 48 h	62%	17%	5%
3	KHMDS (1 equiv), THF, –78 °C, 15 min	decomposed		
4[b]	Et_3N (1.5 equiv), CH_2Cl_2, 21 d	25%	68%	-
5[b]	DIPEA (1.5 equiv), CH_2Cl_2, 21 d	24%	66%	-
6[b]	Pyrrolidine (1.5 eq), CH_2Cl_2, 21 d	79%	10%	-
7[b]	Piperidine (1.5 eq), CH_2Cl_2, 21 d	78%	14%	-
8[b]	Pyrrolidine (1.5 eq), AcOH (1.5 eq), CH_2Cl_2, 24 h	87%	7%	-
9[b]	Piperidine (1.5 eq), AcOH (1.5 eq), CH_2Cl_2, 24 h	84%	15%	-
10[b]	Pyrrolidine (1.5 eq), AcOH (1.5 eq), DMSO, 24 h	68%	23%	-
11[b]	Piperidine (1.5 eq), AcOH (1.5 eq), DMSO, 24 h	79%	9%	-

a Isolated yield

b Ratio was determined by NMR spectroscopy

With the cycloheptanones and cyclopentanones in hand, the next mission was the dehydration to give the corresponding enones. Elimination of the tertiary alcohol in cycloheptanone **14** proceeded with trifluoroacetic anhydride (TFAA) in pyridine to afford enone **30** in 84% yield (Scheme 4). The aldols **19** and **27** were inert to common elimination reagents, including $POCl_3$, $SOCl_2$ and TFAA. Eventually **19** and **27** reacted smoothly with Martin's sulfurane dehydrating agent[10] to give cycloalkenones **31** and **32** in 95% and 97% yield, respectively.



Scheme 4 Synthesis of Cycloalkeneones **5**, **31**, and **32**. *Reagents and conditions: i* TFAA, Pyridine, CH_2Cl_2; *ii* Martin's sulfurane, Benzene, reflux.

Conclusions

In conclusion, multi-hydroxylated cycloheptanones and cyclopentanones were assembled by an intramolecular direct aldol reaction of 2,7-diketones, derived from D-ribose and D-mannose. The regioselectiviy of the aldolization was substrate-controlled whereas the diastereoselectivity could be catalyst-controlled. More aldolization examples with different stereochemistries of the hydroxyl groups are needed to have a better understanding of the carbocyclization. The dehydration of the cycloheptyl or cyclopentyl aldol into the corresponding cycloheptenone or cyclopentenone was readiy executed. These heavily oxygenated carbocycles are also useful starting materials for complex natural product synthesis.

Experimental

General experimental procedures was described in the ESI†.

General procedure for intramolecular direct aldol reaction: Method A: To a suspension of 2,7-diketone (0.1 mmol) in 1 mL DMSO was added 0.03 mmol of L-proline or D-proline. After starting material was consumed, the solution was partitioned between EtOAc (10 mL) and water (5 mL). The aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine, dried ($MgSO_4$), and filtered. Concentration of the filtrate followed by flash chromatography afforded the cycloheptanone.

Method B: A solution of 2,7-diketone (0.1 mmoL) in 3 mL of THF at –78 °C was added 0.2 mL of potassium hexamethyldisilazide (KHMDS) (0.5 M solution in toluene, 0.1 mmL) or lithium diisopropylamide (0.5 M solution in THF, 0.1 mmL). After starting material was consumed, saturated NH_4Cl (1 mL) was added and the temperature was raised to room temperature. The solution was partitioned between EtOAc (10 mL) and water (5 mL), then extracted with EtOAc (20 mL × 3). The combined organic extracts were washed with brine, dried

($MgSO_4$), and filtered. Concentration of the filtrate followed by flash chromatography afforded the product.

Method C: A solution of 2,7-diketone (0.1 mmol) in 2 mL CH_2Cl_2 was added triethylamine (0.15 mmol), diisopropylethylamine (DIPEA) (0.15 mmol), pyrrolidine (0.15 mmol) or piperidine (0.15 mmol). After starting material was consumed, concentration of the solution followed by flash chromatography afforded the cycloalkanone.

Method D: Acetic acid (0.15 mmol) was added to a solution of pyrrolidine (0.15 mmol) or piperidine (0.15 mmol) in CH_2Cl_2 (1 mL) at 0 °C. The resulting mixture was added to a solution of 2,7-diketone (0.1 mmol) in 1 mL of CH_2Cl_2. After starting material was consumed, concentration of the solution followed by flash chromatography afforded the cycloalkanone..

Ketone 10. To a two-neck flask equipped with a reflux condenser and a balloon (oxygen) were added $PdCl_2$ (51 mg, 0.288 mmol), *N*,*N*-dimethylacetamide (35 mL) and H_2O (3 mL). The mixture was heated at 80 °C under O_2 for 4 h. Alkene **9** (4.89 g, 13.5mmol) was added. The mixture was vigorously stirred at 80 °C for 8 h, then cooled to room temperature, and quenched with saturated $NaHCO_3$ solution (5 mL). Water (30 mL) was added and the aqueous phase was extracted with EtOAc (4 × 50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and filtered. Concentration of the filtrate followed by flash chromatography (hexane:Et_2O, 2:1) afforded ketone **10** (4.29 g, 84%) as a colorless oil: $[\alpha]^{20}_D$ +10.1 (*c* 0.63, $CHCl_3$); R_f 0.2 (hexane:Et_2O, 3:1); IR (thin film) 2986, 2934, 1718, 1362 cm^{-1}; ^1H NMR δ 1.35 (3H, s), 1.37 (3H, s), 1.39 (3H, s), 1.44 (3H, s), 2.10 (3H, s), 2.59−2.73 (2H, m), 3.63 (1H, dd, *J* = 7.8, 6.3 Hz), 3.79 (1H, dd, *J* = 6.0, 4.5 Hz), 3.93 (1H, t, *J* = 7.8 Hz), 4.03 (1H, dd, *J* = 8.1, 6.9 Hz), 4.26 (1H, dt, *J* = 6.9, 4.5 Hz), 4.41 (1H, dt, *J* = 8.1, 3.9 Hz), 4.68 (1H, d, *J* = 11.4 Hz), 4.82 (1H, d, *J* = 11.1 Hz), 7.28−7.34 (5H, m); ^{13}C NMR δ 25.6, 26.9, 27.3, 27.5, 31.1, 48.3, 65.9, 75.0, 75.3, 76.5, 79.2, 80.3, 109.5, 109.8, 128.4, 128.7, 128.9, 138.4, 206.5; MS (ESI) *m/z* (relative intensity) 401 ([M+Na]$^+$, 100); HRMS (quadrupole analyzer, ESI) calcd for $C_{21}H_{30}O_6$ [M+Na]$^+$ 401.1940, found 401.1945.

Diol 11. A solution of the ketone **10** (1.29 g, 3.41 mmol) in 80% aqueous AcOH (16 mL) was stirred at room temperature for 14 h. Solvent removal followed by flash chromatography (hexane:EtOAc, 1:2) gave diol **11** (1.06 g, 92%) as a colorless oil: $[\alpha]^{20}_D$ +2.71 (*c* 0.82, $CHCl_3$); R_f 0.17 (hexane:EtOAc, 1:2); IR (thin film) 3442, 2986, 2933, 1716 cm^{-1}; ^1H NMR δ 1.38 (3H, s), 1.39 (3H, s), 2.11 (3H, s), 2.61−2.69 (3H, m), 2.79 (1H, dd, *J* = 16.2, 2.7 Hz), 3.63 (1H, dd, *J* = 7.2, 5.4 Hz), 3.77 (1H, d, *J* = 4.2 Hz), 3.84 (1H, t, *J* = 7.5 Hz), 3.90 (1H, q, *J* = 4.8 Hz), 4.44 (1H, dt, *J* = 8.1, 2.7 Hz), 4.58 (1H, d, *J* = 10.8 Hz), 4.73 (1H, d, *J* = 11.1 Hz), 7.27−7.35 (5H, m); ^{13}C NMR δ 27.3, 27.5, 31.2, 48.1, 63.3, 72.5, 74.6, 75.8, 79.4, 81.0, 110.0, 128.6, 128.7, 129.0, 137.8, 207.0; MS (ESI) *m/z* (relative intensity) 361 ([M+Na]$^+$, 100); HRMS (ESI) calcd for $C_{18}H_{26}O_6$ [M+Na]$^+$ 361.1627, found 361.1613.

Silyl ether 12. A solution of diol **11** (820 mg, 2.42 mmol), imidazole (495 mg, 7.27 mmol) and *tert*-butyl dimethyl silyl chloride (548 mg, 3.64 mmol) in dry CH_2Cl_2 (30 mL) was stirred at room temperature for 3 h. The mixture was quenched with saturated $NaHCO_3$ solution and the aqueous phase was extracted with Et_2O (2 × 50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and filtered. Concentration of the filtrate followed by flash chromatography (hexane:Et_2O, 2:1) yielded silyl ether **12** (1.07g, 98%) as a colorless oil: $[\alpha]^{20}_D$ +12.7 (*c* 0.48, $CHCl_3$); R_f 0.2 (hexane:Et_2O, 2:1); IR (thin film) 3459, 2930, 2857, 1714 cm^{-1}; ^1H NMR δ 0.07 (3H, s), 0.07 (3H, s), 0.90 (9H, s), 1.38 (3H, s), 1.40 (3H, s), 1.62 (3H, s), 2.14 (3H, s), 2.63–2.82 (3H, m), 3.66–3.76 (4H, m), 3.94 (1H, dd, *J* = 7.8, 4.8 Hz), 4.51 (1H, dt, *J* = 8.7, 2.7 Hz), 4.67−4.75 (2H, m), 7.28−7.36 (5H, m); ^{13}C NMR δ –4.9, 18.7, 26.4, 27.4, 27.5, 31.2, 48.4, 64.0, 72.5, 74.4, 74.9, 79.3, 80.3, 109.5, 128.3, 128.6, 128.9, 138.5, 206.9; MS (FAB) *m/z* (relative intensity) 475 ([M+Na]$^+$, 10), 337 (45), 269 (100); HRMS (quadrupole analyzer, FAB) calcd for $C_{24}H_{40}O_6Si$ [M+Na]$^+$ 475.2486, found 475.2505.

Diketone 13. A mixture of 3Å molecular sieves (ca. 1.4 g) and pyridinium dichromate (2.04 g, 5.42 mmol) was added to a solution of silyl ether **12** (1.07 g, 2.36 mmol) in dry CH_2Cl_2 (30 mL) under N_2 at 0 °C. The mixture was stirred for 5 h at room temperature and was then filtered through a pad of Celite. The residue was washed with Et_2O until no product was observed in the eluent (checked with TLC). Concentration of the filtrate followed by flash chromatography (hexane:Et_2O, 2:1) yielded diketone **13** (1.02 g, 96%) as a colorless oil: $[\alpha]^{20}_D$ –3.99 (*c* 0.77, $CHCl_3$); R_f 0.25 (hexane:Et_2O, 1:1); IR (thin film) 2987, 2931, 1721 cm^{-1}; ^1H NMR δ –0.07 (6H, s), 0.90 (9H, s), 1.35 (3H, s), 1.37 (3H, s), 2.13 (3H, s), 2.62–2.79 (2H, m), 3.86 (1H, dd, *J* = 7.8, 6.0 Hz), 4.15 (1H, d, *J* = 6 Hz), 4.36−4.54 (4H, m), 4.59 (1H, d, *J* = 11.7 Hz), 7.26−7.36 (5H, m); ^{13}C NMR δ –4.9, 18.9, 26.3, 27.2, 27.5, 31.2, 47.6, 69.4, 73.7, 75.2, 80.3, 81.6, 110.1, 128.8, 129.1, 137.2, 206.3, 208.0; MS (FAB) *m/z* (relative intensity) 473 ([M+Na]$^+$, 21), 285 (100); HRMS (FAB) calcd for $C_{24}H_{38}O_6Si$ [M+Na]$^+$ 473.2330, found 473.2342.

Cycloheptanone 14. Following the general procedure for intramolecular direct aldol reaction, diketone **13** was converted into cycloheptanone **14**. Fractionation with flash chromatography (hexane:Et_2O, 2:1) afforded cycloheptanone **14** as a colorless oil: $[\alpha]^{20}_D$ –22.9 (*c* 0.69, $CHCl_3$); R_f 0.3 (hexane:Et_2O, 2:1); IR (thin film) 3468, 2953, 1709 cm^{-1}; ^1H NMR δ 0.04 (3H, s), 0.06 (3H, s), 0.89 (9H, s), 1.45 (3H, s), 1.47 (3H, s), 2.32 (1H, d, *J* = 13.2 Hz) and 2.96 (1H, d, *J* = 13.2 Hz) (2-H), 2.52 (1H, dd, *J* = 18.6, 11.7 Hz) and 2.96 (1H, dd, *J* = 18.3, 4.8 Hz) (7-H), 3.28 and 3.57 (each 1H, ABq, *J* = 9.6 Hz, $-CH_2O-$), 4.06 (1H, brs, 4-H), 4.19 (1H, dd, *J* = 9.3, 2.1 Hz, 5-H), 4.59−4.69 (1H, m, 6-H), 4.61 and 5.06 (each 1H, ABq, *J* = 10.8 Hz, $-CH_2O-$), 7.30−7.36 (5H, m); ^{13}C NMR δ –5.0, –4.9, 18.7, 26.3, 27.3, 27.6, 45.2, 47.2, 68.4, 70.0, 75.3, 75.9, 76.7, 82.5, 109.3, 128.3, 128.9, 138.7, 206.0; MS (ESI) *m/z* (relative intensity) 473 ([M+Na]$^+$, 100); HRMS (ESI) calcd for $C_{24}H_{38}O_6Si_1$ [M+Na]$^+$ 473.2335, found 473.2329.

Diol 16. To a two-neck flask equipped with a reflux condenser and a balloon (oxygen) were added $PdCl_2$ (5 mg, 0.068 mmol), *N*,*N*-dimethylacetamide (3 mL) and H_2O (0.3 mL). The mixture was heated at 80 °C under O_2 for 4 h and alkene **15** (420 mg, 0.896 mmol) was added. The mixture was vigorously stirred at 80 °C for 48 h, was then cooled to room temperature and quenched with saturated $NaHCO_3$ solution (5 mL). Water (30

mL) was added and the aqueous phase was extracted with EtOAc (4 × 30mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and filtered. Concentration of the filtrate followed by chromatography (hexane:EtOAc, 1:1) afforded diol **16** (211.1mg, 53%) as a colorless oil: $[\alpha]^{20}_D$ +72.0 (*c* 0.67, $CHCl_3$); R_f 0.37 (hexane:EtOAc, 1:1); IR (thin film) 3419, 2934, 1722, 1454 cm^{-1}; ^1H NMR δ 1.35 (3H, s), 1.47 (3H, s), 2.22 (3H, s), 3.09 (1H, brs), 3.38−3.44 (1H, m), 3.54−3.60 (3H, m), 3.87−3.90 (1H, m), 4.25 (1H, d, *J* = 10.8 Hz), 4.35−4.42 (3H, m), 4.59 (1H, d, *J* = 11.1 Hz), 4.74 (1H, d, *J* = 11.4 Hz), 7.23−7.39 (10H, m); ^{13}C NMR δ 26.0, 26.1, 27.7, 64.2, 72.7, 73.2, 74.0, 75.9, 76.4, 80.8, 83.2, 109.5, 128.3, 128.4, 128.6, 128.8, 129.1, 129.2, 135.9, 138.4, 207.2; MS (ESI) *m/z* (relative intensity) 467 ($[M+Na]^+$, 5), 409 (100); HRMS (ESI) calcd for $C_{25}H_{32}O_7$ $[M+Na]^+$ 467.2040, found 467.2050.

Silyl ether 17. Following the preparation procedure used for **12**, diol **16** was converted into silyl ether **17**. Fractionation with chromatography (hexane:Et_2O, 2:1) afforded **17** (272.1 mg, 98%) as a colorless oil: $[\alpha]^{20}_D$ +9.42 (*c* 0.64, $CHCl_3$); R_f 0.3 (hexane:Et_2O, 2:1); IR (thin film) 3472, 2929, 2857, 1721 cm^{-1}; ^1H NMR δ 0.03 (3H, s), 0.04 (3H, s), 0.88 (9H, s), 1.32 (3H, s), 1.44 (3H, s), 2.13 (3H, s), 2.88 (1H, d, *J* = 7.5 Hz), 3.62 (1H, dd, *J* = 9.9, 5.1 Hz), 3.68−3.83 (3H, m), 3.99 (1H, d, *J* = 8.7 Hz), 4.32−4.36 (2H, m), 4.40 (1H, d, *J* = 11.7 Hz), 4.48 (1H, t, *J* = 6.3 Hz), 4.62 (2H, s), 7.27−7.36 (10H, m); ^{13}C NMR δ −4.8, 18.8, 26.0, 26.4, 26.8, 27.4, 64.7, 72.5, 73.2, 73.4, 76.6, 76.9, 79.8, 82.9, 109.6, 128.0, 128.3, 128.8, 128.9, 129.0, 129.1, 136.6, 138.9, 208.2; MS (ESI) *m/z* (relative intensity) 581 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{31}H_{46}O_7Si$ $[M+Na]^+$ 581.2905, found 581.2911.

Diketone 18. Following the preparation procedure used for **13**, silyl ether **17** was converted into diketone **18**. Fractionation with chromatography (hexane:Et_2O, 3:1) afforded **18** (70.9 mg, 95%) as a colorless oil: $[\alpha]^{20}_D$ −75.3 (*c* 1.30, $CHCl_3$); R_f 0.37 (hexane:Et_2O, 2:1); IR (thin film) 2931, 1724 cm^{-1}; ^1H NMR δ 0.02 (3H, s), 0.03 (3H, s), 0.88 (9H, s), 1.29 (3H, s), 1.47 (3H, s), 2.16 (3H, s), 4.31 (1H, d, *J* = 18.6 Hz), 4.31 (1H, d, *J* = 18.6 Hz), 4.35 (1H, dd, *J* = 8.7, 6 Hz), 4.41 (1H, d, *J* = 4.2 Hz), 4.45 (1H, d, *J* = 4.2 Hz), 4.49 (1H, dd, *J* = 6, 4.2 Hz), 4.55 (1H, d, *J* = 18.6 Hz), 7.23−7.36 (10H, m); ^{13}C NMR δ −5.1, −4.9, 18.9, 25.9, 26.2, 26.2, 26.3, 27.0, 27.4, 68.8, 71.9, 73.2, 76.7, 78.1, 81.8, 81.9, 110.5, 128.0, 128.3, 128.7, 127.7, 127.9, 129.0, 129.1, 130.4, 136.8, 137.6, 208.2, 208.2; MS (ESI) *m/z* (relative intensity) 579 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{31}H_{44}O_7Si$ $[M+Na]^+$ 579.2749, found 579.2749.

Cycloheptanone 19. Following the general procedure for intramolecular direct aldol reaction, the diketone **18** was converted into cycloheptanone **19**. Fractionation with chromatography (hexane:Et_2O, 3:1) afforded **19** as a colorless oil: $[\alpha]^{20}_D$ +2.60 (*c* 0.78, $CHCl_3$); R_f 0.23 (hexane:Et_2O, 1:1); IR (thin film) 3434, 2929, 1717 cm^{-1}; ^1H NMR δ ^1H NMR (C_6D_6:$CDCl_3$, 8:1) δ −0.11 (3H, s), −0.09 (3H, s), 0.81 (9H, s), 1.22 (3H, s), 1.54 (3H, s), 2.00 (1H, brs), 2.54 (1H, dd, *J* = 12.6, 0.9 Hz) and 3.15 (1H, d, *J* = 12.6 Hz), 3.41 (1H, d, *J* = 9.6 Hz) and 3.44 (1H, d, *J* = 9.6 Hz) (−CH_2O−), 4.17 (1H, d, *J* = 0.9 Hz), 4.28 and 4.42 (each 1H, ABq, *J* = 11.7 Hz, −CH_2O−), 4.37 (1H, dd, *J* = 7.2, 2.1 Hz), 4.61 (1H, d, *J* = 7.8 Hz), 4.68 and 5.08 (each 1H, ABq, *J* = 11.4 Hz, −CH_2O−), 4.76 (1H, t, *J* = 7.5 Hz), 7.08−7.34 (10H, m); ^{13}C NMR δ −5.1, −4.9, 18.6, 25.0, 26.3, 27.1, 30.1, 48.1, 68.3, 73.9, 75.0, 76.8, 80.5, 81.5, 87.7, 109.2, 127.9, 128.2, 128.3, 128.7, 128.8, 128.9, 130.4, 137.8, 138.9, 209.5; MS (ESI) *m/z* (relative intensity) 579 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{31}H_{44}O_7Si$ $[M+Na]^+$ 579.2749, found 579.2741; Anal. Calcd for $C_{31}H_{44}O_7Si$: C, 66.88; H, 7.97, found: C, 67.02; H, 7.91.

Alcohol 21. A solution of triol **20** (3.41g, 14.69 μmol), 2,2-dimethoxypropane (3.6 mL, 29.4mmol) and a catalytic amount of *p*-toluenesulfonic acid (28 mg, 0.147 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature under N_2 for 1 h. The reaction was quenched with solid $NaHCO_3$ (60 mg) and filtered. Concentration of the filtrate followed by chromatography (hexane:Et_2O, 3:1) gave alcohol **21** (3.91 g, 98%) as a colorless oil: $[\alpha]^{20}_D$ +36.4 (*c* 0.94, $CHCl_3$); R_f 0.2 (hexane:Et_2O, 3:1); IR (thin film) 3497, 2987, 2934, 1641 cm^{-1}; ^1H NMR δ 1.33 (3H, s), 1.37 (6H, s), 1.41 (3H, s), 2.26 (1H, dt, *J* = 14.4, 7.8 Hz), 2.53−2.61 (1H, m), 3.78 (1H, brs), 3.90 (1H, td, *J* = 8.4, 2.7 Hz), 3.98 (1H, dd, *J* = 6.3, 3 Hz), 4.02−4.07 (2H, m), 4.12−4.17 (2H, m), 5.10−5.20 (2H, m), 5.90−6.04 (1H, m); ^{13}C NMR δ 25.8, 25.9, 27.0, 28.6, 38.8, 68.5, 68.8, 73.6, 79.0, 80.5, 109.2, 110.9, 117.7, 135.2; MS (ESI) *m/z* (relative intensity) 295 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{14}H_{24}O_5$ $[M+Na]^+$ 295.1521, found 295.1499.

Benzyl ether 22. Following the standard procedure used for benzylation, alcohol **21** was converted into benzyl ether **22**. Fractionation with chromatography (hexane:Et_2O, 4:1) afforded **22** (3.19 g, 99%) as a colorless oil: $[\alpha]^{20}_D$ +61.8 (*c* 3.16, $CHCl_3$); R_f 0.4 (hexane:Et_2O, 3:1); IR (thin film) 2986, 2935, 1454 cm^{-1}; ^1H NMR δ 1.32 (3H, s), 1.33 (3H, s), 1.35 (3H, s), 1.40 (3H, s), 2.40−2.49 (1H, m), 2.59−2.66 (1H, m), 3.81−3.92 (2H, m), 4.05−4.23 (4H, m), 4.53 (1H, d, *J* = 10.8 Hz), 4.64 (1H, d, *J* = 10.8 Hz), 5.09−5.20 (2H, m), 5.89−6.03 (1H, m), 7.28−7.38 (5H, m); ^{13}C NMR δ 25.7, 26.2, 27.0, 28.2, 35.3, 68.3, 71.4, 73.7, 76.2, 77.9, 79.1, 108.4, 110.1, 118.1, 127.9, 128.3, 128.7, 134.4, 138.9; MS (ESI) *m/z* (relative intensity) 385 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{21}H_{30}O_5$ $[M+Na]^+$ 385.1990, found 385.1979.

Ketone 23. Following the preparation procedure used for **10**, alkene **22** was converted into ketone **23**. Fractionation with chromatography (hexane:Et_2O, 3:1) afforded **23** (1.66 g, 76%) as a colorless oil: $[\alpha]^{20}_D$ +14.8 (*c* 1.23, $CHCl_3$); R_f 0.23 (hexane:Et_2O, 3:1); IR (thin film) 2986, 2936, 1717 cm^{-1}; ^1H NMR δ 1.31 (3H, s), 1.33 (3H, s), 1.36 (6H, s), 2.17 (3H, s), 2.75−2.88 (2H, m), 3.89 (1H, dd, *J* = 8.1, 5.7 Hz), 4.07−4.24 (4H, m), 4.35−4.42 (1H, m), 4.51 (1H, d, *J* = 11.1 Hz), 4.61 (1H, d, *J* = 11.1 Hz), 7.26−7.32 (5H, m); ^{13}C NMR δ 25.7, 26.0, 27.1, 27.9, 31.6, 46.6, 68.4, 72.2, 73.5, 73.9, 79.0, 79.2, 108.6, 110.3, 128.0, 128.2, 128.7, 138.8, 207.5; MS (ESI) *m/z* (relative intensity) 401 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{21}H_{30}O_6$ $[M+Na]^+$ 401.1935, found 401.1936.

Diol 24. Following the preparation procedure used for **11**, ketone **23** was converted into diol **24**. Fractionation with chromatography (hexane:EtOAc, 1:2) afforded **24** (432 mg, 66%) as a colorless oil: $[\alpha]^{20}_D$ +6.5 (*c* 0.52, $CHCl_3$); R_f 0.37

(hexane:EtOAc, 1:2); IR (thin film) 3448, 2985, 2934, 1714 cm^{-1}; ^1H NMR δ 1.31 (3H, s), 1.33 (3H, s), 2.19 (3H, s), 2.75 (1H, dd, *J* = 17.1, 4.8 Hz), 3.01 (1H, dd, *J* = 17.1, 4.8 Hz), 3.63 (1H, dd, *J* = 10.8, 5.4 Hz), 3.72−3.84 (2H, m), 4.05−4.13 (2H, m), 3.35 (1H, dt, *J* = 8.4, 4.8 Hz), 4.51 (1H, d, *J* = 10.8 Hz), 4.56 (1H, d, *J* = 10.8 Hz), 7.29−7.36 (5H, m); ^{13}C NMR δ 26.1, 27.9, 31.5, 45.9, 65.0, 69.3, 72.4, 74.6, 78.1, 78.7, 109.5, 128.8, 128.9, 129.2, 136.8, 206.9; MS (ESI) *m/z* (relative intensity) 361 ($[M+Na]^+$, 100), 361 (56); HRMS (ESI) calcd for $C_{18}H_{26}O_6$ $[M+Na]^+$ 361.1622, found 361.1620.

Silyl ether 25. Following the preparation procedure used for **12**, diol **24** was converted into silyl ether **25**. Fractionation with chromatography (hexane:Et_2O, 2:1) afforded **25** (272.1 mg, 98%) as a colorless oil: $[\alpha]^{20}_D$ +11.2 (*c* 0.80, $CHCl_3$); R_f 0.47 (hexane:Et_2O, 1:1); IR (thin film) 3503, 2929, 2856, 1718 cm^{-1}; ^1H NMR δ 0.07 (6H, s), 0.90 (9H, s), 1.30 (3H, s), 1.33 (3H, s), 2.17 (3H, s), 2.76 (1H, dd, *J* = 16.8, 5.7 Hz), 2.92 (1H, dd, *J* = 16.8, 4.5 Hz), 3.24 (1H, d, *J* = 3.9 Hz), 3.68−3.73 (2H, m), 3.82−3.87 (1H, m), 4.12−4.20 (2H, m), 4.38 (1H, dt, *J* = 7.2, 5.4 Hz), 4.51 (1H, d, *J* = 11.1 Hz), 4.56 (1H, d, *J* = 11.1 Hz), 7.29−7.32 (5H, m); ^{13}C NMR δ –4.9, –4.8, 18.9, 25.9, 26.4, 27.8, 31.6, 46.2, 65.1, 69.7, 72.3, 74.6, 77.7, 78.7, 109.0, 128.5, 128.7, 129.0, 137.6, 207.4; MS (ESI) *m/z* (relative intensity) 475 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{24}H_{40}O_6Si_1$ $[M+Na]^+$ 475.2486, found 475.2487.

Diketone 26. Following the preparation procedure used for **13**, silyl ether **25** was converted into silyl ether **25**. Fractionation with chromatography (hexane:Et_2O, 2:1) afforded **26** (338 mg, 94%) as a colorless oil: $[\alpha]^{20}_D$ –33.6 (*c* 1.31, $CHCl_3$); R_f 0.4 (hexane:Et_2O, 1:1); IR (thin film) 2952, 2930, 1732, 1717 cm^{-1}; ^1H NMR δ –0.07 (3H, s), –0.07 (3H, s), 0.86 (9H, s), 1.35 (3H, s), 1.51 (3H, s), 2.13 (3H, s), 2.67 (1H, dd, *J* = 16.8, 5.4 Hz), 2.83 (1H, dd, *J* = 16.8, 4.8 Hz), 3.94−4.01 (2H, m), 4.11 (1H, d, *J* = 17.7 Hz), 4.22 (1H, d, *J* = 11.1 Hz), 4.35 (1H, d, *J* = 11.1 Hz), 4.42 (1H, dd, *J* = 8.4, 6.3 Hz), 5.06 (1H, d, *J* = 6 Hz), 7.23−7.29 (5H, m); ^{13}C NMR δ –5.4, –5.1, 18.6, 25.8, 26.2, 27.7, 31.5, 45.7, 69.2, 71.9, 74.3, 79.3, 79.7, 110.0, 128.2, 128.6, 128.7, 138.0, 205.4, 206.9; MS (ESI) *m/z* (relative intensity) 473 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{24}H_{38}O_6Si$ $[M+Na]^+$ 473.2335, found 473.2332.

Carbocycles 27, 28 and 29. Following the general procedure for intramolecular direct aldol reaction, diketone **26** was converted into cyclohexanones. Fractionation with chromatography afforded firstly cyclopentane **27** as a white solid (25.2 mg, 55%), secondly cycloheptane **29** as a colorless oil (7.8 mg, 17%) and thirdly cyclopentane **28** as a colorless oil (8.9 mg, 19%). **27**: $[\alpha]^{20}_D$ –60.6 (*c* 3.02, $CHCl_3$); R_f 0.5 (hexane:Et_2O, 2:1); IR (thin film) 3433, 2931, 2857, 1698 cm^{-1}; ^1H NMR δ –0.02 (3H, s), –0.03 (3H, s), 0.86 (9H, s), 1.30 (3H, s), 1.53 (3H, s), 2.29 (3H, s), 3.22 (1H, d, *J* = 10.8 Hz), 3.66 (1H, d, *J* = 10.5 Hz), 3.72 (1H, d, *J* = 10.5 Hz), 4.17−4.23 (2H, m), 4.49 (1H, d, *J* = 11.7 Hz), 4.65−4.69 (2H, m), 7.29−7.33 (5H, m); ^{13}C NMR δ –5.0, 18.8, 24.4, 26.2, 26.6, 34.1, 56.3, 67.7, 72.5, 77.0, 81.9, 82.0, 84.6, 111.9, 128.3, 128.8, 138.2, 213.2; MS (ESI) *m/z* (relative intensity) 473 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{24}H_{38}O_6Si_1$ $[M+Na]^+$ 473.2330, found 473.2329.

28: $[\alpha]^{20}_D$ –15.4 (*c* 0.72, $CHCl_3$); R_f 0.13 (hexane:Et_2O, 2:1); IR (thin film) 3491, 2926, 2853, 1713 cm^{-1}; ^1H NMR δ −0.01 (6H, s), 0.83 (9H, s), 1.38 (3H, s), 1.61 (3H, s), 2.26 (3H, s), 3.28 (1H, d, *J* = 10.8 Hz), 3.34−3.43 (2H, m), 4.24−4.29 (2H, m), 4.49 (1H, t, *J* = 5.1 Hz), 4.57 (1H, d, *J* = 12 Hz), 4.68 (1H, d, *J* = 12 Hz), 7.27−7.39 (5H, m); ^{13}C NMR δ –5.4, –5.3, 18.6, 25.0, 26.2, 26.7, 32.0, 63.0, 66.4, 72.7, 76.0, 77.5, 81.3, 111.9, 128.1, 128.5, 128.7, 128.8, 138.7, 207.4; MS (ESI) *m/z* (relative intensity) 473 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{24}H_{38}O_6Si_1$ $[M+Na]^+$ 473.2330, found 473.2333.

29: $[\alpha]^{20}_D$ –7.4 (*c* 0.12, $CHCl_3$); R_f 0.21 (hexane:Et_2O, 2:1); IR (thin film) 3467, 2924, 2850, 1708 cm^{-1}; ^1H NMR δ 0.07 (6H, s), 0.89 (9H, s), 1.40 (3H, s), 1.56 (3H, s), 2.34 (1H, d, *J* = 13.2 Hz), 2.68 (1H, d, *J* = 14.4 Hz), 2.89 (1H, d, *J* = 13.2 Hz), 3.21 (1H, dd, *J* = 13.2, 11.1 Hz), 3.32 (1H, d, *J* = 9.6 Hz), 3.55 (1H, d, *J* = 9.6 Hz), 4.18 (1H, d, *J* = 8.4 Hz), 4.23–4.27 (1H, m), 4.52 (1H, d, *J* = 12 Hz), 4.63−4.67 (2H, m), 7.27−7.34 (5H, m); ^{13}C NMR δ –5.04, –4.94, 18.84, 24.44, 26.34, 26.84, 44.84, 46.84, 69.14, 72.04, 72.64, 73.34, 76.84, 78.44, 109.34, 128.24, 128.44, 128.84, 206.54; MS (ESI) *m/z* (relative intensity) 473 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{24}H_{38}O_6Si_1$ $[M+Na]^+$ 473.2330, found 473.2338.

Enone 30. To a solution of β-hydroxy ketone **14** (49.4 mg, 0.11 mmol), pyridine (0.55 mL, 6.83 mmol) in dry CH_2Cl_2 (2 mL) at 0 °C was added trifluoroacetic anhydride (0.33 mL, 2.34 mmol). The mixture was stirred for 2 h at 0°C, warmed to room temperature and then stirred for 7 d. Concentration of the filtrate followed by chromatography (hexane:Et_2O, 3:1) afforded firstly enone **30** (30.5 mg, 0.0706 mmol, 84% BOSMR) as a colorless oil and then secondly the starting material (11.5 mg, 0.0255 mmol, 23.2% recovered). Data for **30**: $[\alpha]^{20}_D$ –135 (*c* 0.28, $CHCl_3$); R_f = 0.37 (hexane:Et_2O, 3:1); IR (thin film) 2930, 2851, 1660 cm^{-1}; ^1H NMR δ 0.01 (3H, s), 0.02 (3H, s), 0.87 (9H, s), 1.49 (3H, s), 1.50 (3H, s), 2.67 (1H, dd, *J* = 16.8, 11.7 Hz), 3.16 (1H, ddd, *J* = 16.8, 4.5, 0.6 Hz), 4.03–4.10 (2H, m), 4.28 (1H, d, *J* = 2.4 Hz), 4.60–4.71 (2H, m), 5.01 (1H, d, *J* = 11.4 Hz), 6.18 (1H, s); ^{13}C NMR δ –5.02, –4.91, 18.8, 26.3, 27.1, 27.8, 46.7, 65.6, 69.6, 72.8, 76.6, 83.6, 110.5, 128.3, 128.6, 128.8, 129.0, 138.1, 150.5, 196.9; MS (ESI) *m/z* (relative intensity) 433 ($[M+H]^+$, 11), 343 (100), 285 (25), 227 (49); HRMS (ESI) calcd for $C_{24}H_{37}O_5Si$ $[M+H]^+$ 433.2410, found 433.2409.

Enone 31. To a solution of ketone **19** (10.1 mg, 0.018 mmol) in benzene (2 mL) was added Martin sulfurane (18.3 mg, 0.027 mmol) and the solution was heated under reflux for 2 h. After cooling, solvent removal followed by chromatography (hexane:Et_2O, 3:1) afforded enone **31** (9.2 mg, 95%) as a colorless oil: $[\alpha]^{20}_D$ –30.9 (*c* 1.47, $CHCl_3$); R_f = 0.32 (hexane:Et_2O, 3:1); IR (thin film) 2954, 2929, 1680 cm^{-1}; ^1H NMR δ 0.07 (6H, s), 0.91 (9H, s), 1.27 (6H, s), 3.97 (1H, brs), 4.06 (1H, d, *J* = 17.4 Hz), 4.16 (1H, d, *J* = 17.4 Hz), 4.42 (1H, d, *J* = 11.7 Hz), 4.49–4.56 (2H, m), 4.60–4.69 (2H, m), 4.96 (1H, d, *J* = 12 Hz), 5.22 (1H, s), 6.39 (1H, s), 7.13–7.37 (10H, m); ^{13}C NMR δ –5.04, 18.8, 24.6, 26.2, 57.4, 73.0, 73.3, 75.9, 78.5, 80.9, 110.3, 126.9, 128.0, 128.2, 128.5, 128.6, 128.7, 128.9, 137.4, 138.4, 155.4, 196.1; MS (ESI) *m/z* (relative intensity) 561

([M+H]$^+$, 100); HRMS (ESI) calcd for $C_{31}H_{42}O_6Si$ [M+Na]$^+$ 561.2643, found 561.2640.

Enone 32. Following the preparation procedure used for **31**, ketone **27** was converted into enone **32**. Fractionation with chromatography (hexane:Et_2O, 6:1) afforded **32** (18.1 mg, 97%) as a colorless oil: $[\alpha]^{20}_D$ –40 (*c* 0.59, $CHCl_3$); R_f 0.5 (hexane:Et_2O, 2:1); IR (thin film) 2929, 2856, 1685 cm^{-1}; ^{1}H NMR δ 0.04 (3H, s), 0.06 (3H, s), 0.88 (9H, s), 1.40 (6H, s), 2.22 (3H, s), 4.40 (1H, d, *J* = 15.6 Hz), 4.58 (1H, d, *J* = 11.1 Hz), 4.64 (1H, brs), 4.78–4.83 (2H, m), 4.87 (1H, d, *J* = 11.4 Hz), 5.15 (1H, d, *J* = 5.7), 7.32–7.41 (5H, m); ^{13}C NMR δ –5.0, 18.8, 26.3, 27.3, 28.0, 29.9, 59.3, 72.4, 76.6, 80.8, 82.8, 112.9, 128.4, 128.8, 137.2, 138.0, 153.2, 199.3; MS (ESI) *m/z* (relative intensity) 455 ([M+H]$^+$, 100); HRMS (ESI) calcd for $C_{24}H_{36}O_5Si$ [M+Na]$^+$ 455.2224, found 455.2227.

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Notes and references

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† Electronic Supplementary Information (ESI) available: General procedure, crystallographic data of compound **27** and copies of ^{1}H and ^{13}C NMR spectra of all new compounds. See DOI:10.1039/b000000x/

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