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# Regioselective oxidative cleavage of benzylidene acetals: synthesis of highly functionalized chiral intermediates

Pon Minor Senthilkumar, Appu Aravind and Sundarababu Baskaran*

*Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India*

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**Abstract**—A mild and efficient method for the regioselective oxidative cleavage of benzylidene acetals with $KBrO_3/Na_2S_2O_4$ under bi-phasic conditions ($EtOAc/H_2O$), leading to highly functionalized chiral intermediates, is reported.


## 1. Introduction

Chemoselective transformation of multifunctional organic compounds is a synthetic challenge for organic chemists and success depends on efficient manipulation of the functional groups involved. The selective protection and deprotection of polyhydroxylated substrates is a key step in the chemical synthesis of complex molecules.[1] Benzylidene acetals are widely used in organic synthesis due to their tolerance to a wide variety of reagents and reaction conditions.[2] Regioselective reductive[3] as well as oxidative cleavage of benzylidene acetals are important as they lead to synthetically useful intermediates. Benzylidene acetals can be oxidatively cleaved using trityl fluoroborate ($Ph_3C^+BF_4^-$),[4] ozone,[5] pyridinium dichromate/*t*-butyl hydroperoxide,[6] NBS/$H_2O$,[7] $NaBO_3$,[8] $Co(OAc)_2$/*N*-hydroxyphthalimide[9] and 2,2′-bipyridinium chlorochromate/*m*-CPBA.[10] Iadonisi and co-workers[11] have reported a new method for the deprotection of benzyl ethers in carbohydrate substrates using the sodium bromate–sodium dithionite reagent system under bi-phasic conditions. During the course of their studies, they also observed the oxidative cleavage of benzylidene acetal under the reaction conditions. However, the synthetic potential of sodium bromate–sodium dithionite as a novel reagent system for the regioselective oxidative cleavage of benzylidene acetals was not fully explored.

Our continued interest in the regioselective cleavage of bis-benzylidene acetals of D-mannitol under both oxidative and reductive conditions, recently resulted in the synthesis of highly functionalized chiral intermediates and their further application in the stereoselective synthesis of biologically active and pharmaceutically important molecules.[3]

In this Letter, we report a highly regioselective method for the oxidative cleavage of benzylidene acetals to novel chiral intermediates using the potassium bromate–sodium dithionite reagent system. Following the reported procedure,[11] we initially studied the regioselective oxidative cleavage of bis-benzylidene acetal **1a** with sodium bromate–sodium dithionite under bi-phasic ($EtOAc/H_2O$) conditions. However, unfortunately, this reaction resulted in the isolation of diol **2a** in a low yield with a poor regioselectivity. In order to improve the yield and regioselectivity, we investigated several variables, such as temperature, stoichiometry of the reagents ($KBrO_3/Na_2S_2O_4$), and volume of the solvent. After much experimentation, we realized that the volume of ethyl acetate plays a key role in deciding the yield and regioselectivity of the reaction (Table 1). Under the modified reaction conditions (entry 3), oxidative cleavage of bis-benzylidene acetal **1a** gave terminal diol **2a** as the major product and internal diol **3a** as a minor product in an 88% yield (86:14). Notably, the other possible product was not observed under the reaction conditions (Scheme 1).

In order to test the efficiency of our modified conditions, the regioselective oxidative cleavage was attempted with the known substrate **4**[11] and the results are shown in Scheme 2. Under our modified conditions, we achieved a better regioselectivity (77:23) compared to the reported procedure (65:35).[11]

* Corresponding author. Tel.: +91 44 2257 5280; fax: +91 44 2257 0545; e-mail: sbhaskar@iitm.ac.in

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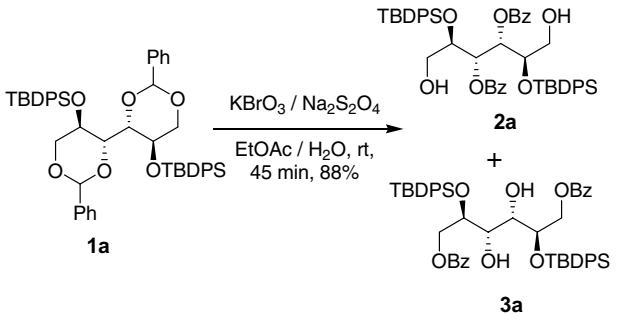
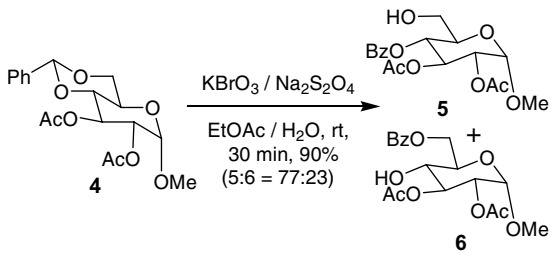
**Table 1.** Effect of concentration on the oxidative cleavage of **1a**

| Entry | Substrate | Volume of EtOAc (mmol) | Yield[b] (%) | Selectivity (**2a**:**3a**) |
|---|---|---|---|---|
| 1 | **1a** | 15[a] | 67 | 76:24 |
| 2 | | 20 | 75 | 78:22 |
| 3 | | **25** | **88** | **86:14** |
| 4 | | 30 | 86 | 86:14 |

[a] Reported conditions.[11]
[b] Isolated yield of the mixture of isomers.




**Scheme 1.** Regioselective oxidative cleavage of bis-benzylidene acetals.



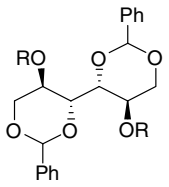
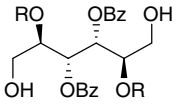
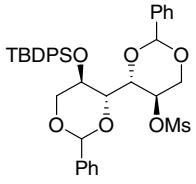
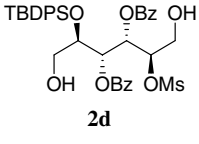
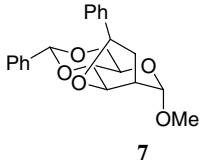
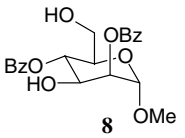

**Scheme 2.** Regioselective oxidative cleavage of mono-benzylidene acetals.

After successful modification of the reaction conditions, the generality of this methodology was tested with several bis-benzylidene acetals and the results are summarized in Table 2.

A high degree of regioselectivity was observed when the method was applied to both symmetrical and unsymmetrical (Table 2, entries 1 and 2) bis-benzylidene acetals derived from D-mannitol. Benzylidene acetals **1a**–**c** having labile functional groups such as TBDPS, OMs and OAc underwent smooth oxidative cleavage to give the corresponding $C_2$-symmetric terminal diols **2a**–**c**, respectively, in good yields. Conspicuously, the migration of the silyl group or acetate was not observed under the reaction conditions. Unsymmetrical benzylidene acetal **1d** underwent a smooth oxidative cleavage to give the corresponding highly functionalized diol **2d** in good yield. Furthermore, substrate **7** having both five- and six-membered benzylidene acetals (Table 2, entry 3), derived from methyl-α-D-mannopyranoside, underwent smooth oxidative cleavage to give diol **8** in good yield.

Our modified oxidative cleavage procedure was also tested with chiral mono-benzylidene acetals having various sensitive functional groups and the results are summarized in Table 3.

**Table 2.** Regioselective oxidative cleavage of bis-benzylidene acetals[a]

| Entry | Substrate | Product | Yield[b,c] (%) |
|---|---|---|---|
| 1 |  **1b** R = Ms, **1c** R = Ac |  **2b** R = Ms, **2c** R = Ac | 73 75 |
| 2 |  **1d** |  **2d** | 75 |
| 3 |  **7** |  **8** | 76 |

[a] Reaction time: 30–45 min.
[b] Isolated yield of the major isomer.
[c] In addition, the minor regioisomer was isolated in 3–15% yield.

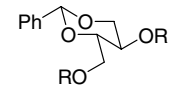
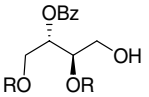
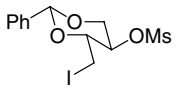
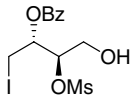
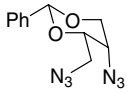
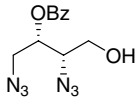
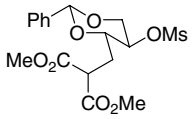
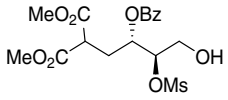
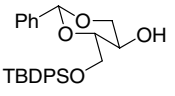
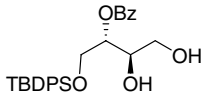
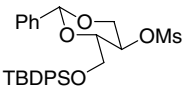
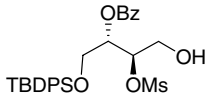
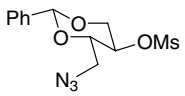
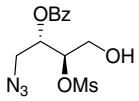
Benzylidene acetals **9a, 17** and **19** having labile TBDPS ether groups, underwent smooth reaction to give primary alcohols **10a**, **18** and **20**, respectively, in good yields. Benzylidene acetal **11**, having reactive iodide and mesylate functional groups, underwent facile oxidative cleavage to give highly functionalized chiral derivative **12**. Under similar reaction conditions, benzylidene acetals **13** and **21**, having sensitive functional groups, reacted readily to give the corresponding chiral azido alcohols **14** and **22**, respectively, in good yields. Interestingly, benzylidene acetal **15**, possessing a malonate ester and an OMs group, underwent a clean oxidative cleavage to give the corresponding chiral alcohol **16** in a good yield.

In conclusion, under the modified reaction conditions, $KBrO_3$–$Na_2S_2O_4$ was found to be a very efficient and mild reagent system for the regioselective oxidative cleavage of both bis- and mono-benzylidene acetals, leading to highly functionalized chiral intermediates in very good yields.[12] Synthetic application of this novel oxidative cleavage reaction in the stereoselective synthesis of biologically active molecules is in progress.

## 2. Experimental

A typical experimental protocol for the regioselective oxidative cleavage of benzylidene acetal is as follows:

**Table 3.** Regioselective oxidative cleavage of mono-benzylidene acetals[a]

| Entry | Substrate | Product | Yield[b,c] (%) |
|---|---|---|---|
| 1 |  **9a** R = TBDPS, **9b** R = TBDMS, **9c** R = Ms, **9d** R = Ac |  **10a** R = TBDPS, **10b** R = TBDMS, **10c** R = Ms, **10d** R = Ac | 77<br>78<br>77<br>74 |
| 2 |  **11** |  **12** | 76 |
| 3 |  **13** |  **14** | 76 |
| 4 |  **15** |  **16** | 73 |
| 5 |  **17** |  **18** | 72 |
| 6 |  **19** |  **20** | 67 |
| 7 |  **21** |  **22** | 73 |

[a] Reaction time: 30–45 min.
[b] Isolated yield of the major isomer.
[c] In addition, the minor regioisomer was isolated in 9–13% yield.

To a solution of benzylidene acetal **1a** (200 mg, 0.2397 mmol) in ethyl acetate (6 ml) was added a solution of $KBrO_3$ (240 mg, 1.44 mmol) in water (3.5 ml) followed by a solution of $Na_2S_2O_4$ (250 mg, 1.44 mmol) in water (3.5 ml) and the mixture stirred at room temperature for 45 min. After completion of the reaction, the organic layer was separated, washed with sodium thiosulfate solution and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous sodium sulfate, concentrated under reduced pressure and purified by column chromatography on silica gel using EtOAc–hexane, gradient elution, to furnish pure compound **2a** (179 mg, 86% yield) as a white foamy solid. Mp 180–184 °C ($CHCl_3$). $[\alpha]_D^{26}$ +74.5 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 2931, 2857, 1725, 1451, 1278, 1177, 1111, 741, 702, 675, 664, 509 $cm^{-1}$; $^1H$ NMR [400 MHz, $CDCl_3$] $\delta$: 7.93 (m, 4H), 7.68 (m, 2H), 7.62 (m, 2H), 7.53 (m, 4H), 7.36 (m, 10H), 7.24 (m, 4H), 7.15 (m, 4H), 5.70 (d, $J = 4.2$ Hz, 2H), 3.79 (dd, $J = 7.9$, 3.9 Hz, 2H), 3.57 (m, 4H), 1.10 (s, 18H); $^{13}C$ NMR [100 MHz, $CDCl_3$] $\delta$: 166.0, 135.9, 135.7, 133.8, 133.1, 132.3, 129.8, 129.8, 129.7, 129.5, 128.2, 127.6, 127.5, 72.6, 72.2, 62.5, 26.9, 19.2. HRMS (ESI) calcd for $C_{52}H_{59}O_8Si_2$ $(M+H)^+$: 867.3749. Found: 867.3781.

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12. *Spectral data for selected compounds*: Compound **2b**: $[\alpha]_D^{26}$ +16.6 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 3514, 3031, 2939, 1721, 1601, 1451, 1343, 1263, 1174, 1093, 1069, 1025, 970, 921, 803, 710, 686, 521 $cm^{-1}$; $^1H$ NMR [400 MHz, $CDCl_3$] $\delta$: 7.99 (m, 4H), 7.52 (m, 2H), 7.38 (m, 4H), 5.80 (d,

$J = 6.3$ Hz, 2H), 4.94 (dd, $J = 9.2$, 3.7 Hz, 2H), 3.99 (dd, $J = 13.3$, 3 Hz, 2H), 3.73 (dd, $J = 13.3$, 2.9 Hz, 2H), 3.56 (br s, 2H), 3.02 (s, 6H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 165.8, 133.8, 129.9, 128.7, 128.6, 80.4, 69.8, 60.6, 38.6. HRMS (ESI) calcd for $C_{22}H_{26}O_{12}S_2Na$ $(M+Na)^+$: 569.0763. Found: 569.0756. Compound **2d**: $[\alpha]_D^{26}$ +56.6 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 3480, 2930, 2857, 1720, 1451, 1427, 1315, 1273, 1176, 1111, 1070, 1026, 772, 708, 687, 506 cm$^{-1}$; $^1$H NMR [400 MHz, $CDCl_3$] $\delta$: 8.03 (d, $J = 7.1$ Hz, 2H), 7.96 (d, $J = 7.1$, 2H), 7.67 (m, 2H), 7.58 (m, 4H), 7.42 (m, 5H), 7.34 (m, 2H) 7.1 (m, 3H), 5.96 (d, $J = 8$ Hz, 1H), 5.71 (dd, $J = 6.4$, 3.1 Hz, 1H), 4.98 (m, 1H), 3.99 (m, 2H), 3.92 (m, 1H), 3.82 (m, 1H), 3.56 (m, 1H) 3.1 (s, 3H), 1.04 (s, 9H), 2.04 (br s, 2H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 166, 165, 135.8, 135.7, 133.6, 133.5, 132.0, 129.98, 129.92, 129.89, 129.39, 129.0, 128.5, 127.8, 127.7, 79.6, 72.5, 71.2, 69.4, 62.4, 61.0, 38.7, 27.0, 19.1. HRMS (ESI) calcd for $C_{37}H_{42}O_{10}SSiNa$ $(M+Na)^+$: 729.2166. Found: 729.2184. Compound **8**: $[\alpha]_D^{26}$ +25.3 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 3473, 1716, 1601, 1451, 1317, 1262, 1112, 1068, 1026, 972, 908, 709 cm$^{-1}$; $^1$H NMR [400 MHz, $CDCl_3$] $\delta$: 8.1 (m, 4H), 7.52 (m, 2H), 7.46 (m, 4H), 5.49 (t, $J = 10$ Hz, 1H), 5.39 (dd, $J = 3.6$, 1.6 Hz, 1H), 4.92 (d, $J = 1.3$ Hz, 1H), 4.43 (dd, $J = 10$, 3.2 Hz, 1H), 3.9 (ddd, $J = 10$, 4, 2.4 Hz, 1H), 3.74 (m, 2H), 3.4 (s, 3H), 2.75 (br s, 1H), 2.56 (br s, 1H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 167.2, 166, 133.7, 133.5, 129.9, 129.2, 129.0, 128.6, 128.5, 98.5, 72.8, 70.4, 70.3, 68.5, 61.4, 55.4. HRMS (ESI) calcd for $C_{21}H_{22}O_8Na$ $(M+Na)^+$: 425.1212. Found: 425.1225. Compound **10a**: $[\alpha]_D^{26}$ +22.8 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 2930, 1718, 1450, 1427, 1314, 1269, 1104, 1068, 1026, 998, 907, 821, 758, 731, 698, 648, 611, 502 cm$^{-1}$; $^1$H NMR [400 MHz, $CDCl_3$] $\delta$: 8.09 (m, 2H), 7.73 (m, 8H), 7.52 (m, 1H), 7.42 (m, 14H), 5.57 (m, 1H), 4.23 (dd, $J = 9.1$, 4.4 Hz, 2H), 4.08 (m, 1H), 3.75 (m, 2H), 2.29 (br s, 1H), 1.16 (s, 9H), 1.13 (s, 9H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 166.2, 136.3, 135.9, 135.9, 135.9, 133.9, 133.3, 133.2, 130.4, 130.2, 130.2, 130.2, 130.2, 130.2, 128.5, 128.1, 128.0, 75.8, 74.0, 63.7, 62.8, 27.2, 27.2, 19.7, 19.4. HRMS (ESI) calcd for $C_{43}H_{50}O_5Si_2Na$ $(M+Na)^+$: 725.3095. Found: 725.3089. Compound **10b**: $[\alpha]_D^{26}$ +3.7 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 3410, 2953, 2928, 2884, 2856, 1720, 1471, 1463, 1315, 1271, 1253, 1097, 1068, 1026, 1003, 938, 830, 811, 775, 734, 708, 686, 669, 461 cm$^{-1}$; $^1$H NMR [400 MHz, $CDCl_3$] $\delta$: 8.01 (m, 2H), 7.50 (m, 1H), 7.38 (m, 2H), 5.16 (dd, $J = 9.8$, 4.3 Hz, 1H), 4.12 (dd, $J = 9.8$, 4.3 Hz, 1H), 3.99 (dd, $J = 11.2$, 4.2 Hz, 1H), 3.88 (dd, $J = 11.2$, 4.3 Hz, 1H), 3.70 (dd, $J = 13.4$, 4 Hz, 1H), 3.67 (dd, $J = 13.4$, 4.1 Hz, 1H), 2.4 (br s, 1H), 0.89 (s, 9H), 0.84 (s, 9H), 0.10 (s, 6H), −0.0073 (s, 6H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 167.5, 134.7, 131.8, 131.4, 130.0, 76.6, 73.2, 65.1, 62.7, 27.5, 27.4, 19.9, 19.7, −2.8, −3.170, −3.72, −3.76. HRMS (ESI) calcd for $C_{23}H_{42}O_5Si_2Na$ $(M+Na)^+$: 477.2469. Found: 477.2454. Compound **12**: $[\alpha]_D^{26}$ −3.8 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 3514, 2938, 1719, 1601, 1584, 1451, 1357, 1268, 1173, 1116, 1070, 1025, 967, 918, 848, 752, 709, 667, 521, 460 cm$^{-1}$; $^1$H NMR [400 MHz, $CDCl_3$] $\delta$: 7.97 (t, $J = 7.3$ Hz, 2H), 7.49 (d, $J = 7.4$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 2H), 5.41 (m, 1H), 5.23 (m, 1H), 4.10 (m, 2H), 3.39 (dd, $J = 10.6$, 4 Hz, 1H), 3.88 (dd, $J = 9.7$, 5.8 Hz, 1H), 2.88 (s, 3H); 1.80 (br s, 1H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 165.8, 133.7, 129.8, 129.7, 128.9, 128.6, 128.5, 76.8, 71.6, 71.0, 96.6, 38.2. HRMS (ESI) calcd for $C_{12}H_{15}IO_6SNa$ $(M+Na)^+$: 436.9532. Found: 436.9531. Compound **14**: $[\alpha]_D^{26}$ −6.8 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 3451, 2928, 2093, 1716, 1601, 1584, 1492, 1450, 1384, 1315, 1265, 1177, 1096, 1069, 1025, 936, 755, 707, 554, 499, 429 cm$^{-1}$; $^1$H NMR [400 MHz, $CDCl_3$] $\delta$: 7.97 (m, 2H), 7.52 (m, 1H), 7.37 (t, $J = 7.6$ Hz, 2H), 4.62 (dd, $J = 11.7$, 4.6 Hz, 1H), 4.45 (dd, $J = 11.5$, 7.5 Hz, 1H), 3.80 (m, 2H), 3.43 (m, 2H), 2.44 (d, $J = 6.1$ Hz, 1H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 166.2, 133.5, 129.8, 129.1, 128.6, 69.9, 64.1, 61.9, 53.6. HRMS (ESI) calcd for $C_{11}H_{12}N_6O_3Na$ $(M+Na)^+$: 299.0869. Found: 299.0868. Compound **16**: $[\alpha]_D^{26}$ +12.2 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 3451, 2955, 1780, 1719, 1601, 1451, 1348, 1316, 1269, 1171, 1109, 1070, 1025, 971, 918, 805, 753, 710, 686, 525, 449 cm$^{-1}$; $^1$H NMR [400 MHz, $CDCl_3$] $\delta$: 8.02 (m, 2H), 7.59 (m, 1H), 7.37 (t, $J = 7.6$ Hz, 2H), 5.39 (dd, $J = 6.7$, 3.2 Hz, 1H), 4.97 (dd, $J = 7.7$, 3.7 Hz, 1H), 3.95 (dd, $J = 12.6$, 3.8 Hz, 1H), 3.89 (dd, $J = 12.6$, 6.8 Hz, 1H), 3.63 (s, 3H), 3.62 (s, 3H), 3.56 (t, $J = 7$ Hz, 1H), 3.11 (s, 3H), 2.45 (t, $J = 7.1$ Hz, 1H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 169.2, 169.0, 165.8, 133.6, 129.8, 129.0, 128.6, 82.5, 70.4, 61.4, 52.8, 52.7, 48.0, 38.7, 28.6; (ESI) $C_{17}H_{22}O_{10}S$ $(M+Na)^+$ 441. Compound **18**: $[\alpha]_D^{26}$ +15.4 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 3411, 2930, 2856, 2360, 2341, 1718, 1471, 1450, 1314, 1268, 1177, 1069, 1040, 1026, 996, 822, 740, 699, 613, 503, 488 cm$^{-1}$; $^1$H NMR [400 MHz, $CDCl_3$] $\delta$: 7.95 (m, 2H), 7.59 (m, 4H), 7.54 (m, 1H), 7.37 (m, 6H), 7.17 (m, 2H), 5.05 (m, 1H), 3.96 (m, 3H), 3.64 (m, 1H), 3.57 (m, 1H), 3.13 (br s, 1H), 2.78 (br s, 1H), 0.95 (s, 9H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 166.2, 135.1, 132.9, 132.4, 132.3, 129.5, 129.4, 129.1, 128.0, 127.4, 127.3, 73.7, 70.3, 62.8, 62.4, 26.3, 18.7. HRMS (ESI) calcd for $C_{27}H_{32}O_5$-SiNa $(M+Na)^+$: 487.1917. Found: 487.1917. Compound **20**: $[\alpha]_D^{26}$ +1.5 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 2342, 1723, 1360, 1272, 1176, 1112, 922, 828, 773, 742, 708, 505 cm$^{-1}$; $^1$H NMR [400 MHz, $CDCl_3$] $\delta$: 7.97 (d, $J = 7.6$ Hz, 2H), 7.60 (m, 5H), 7.35 (m, 8H), 5.03 (m, 1H), 4.60 (dd, $J = 12.2$, 2.7 Hz, 1H), 4.50 (dd, $J = 6.4$, 2.8 Hz, 1H), 3.92 (m, 1H), 3.77 (m, 2H), 3.28 (s, 3H), 2.2 (s, 1H), 1.016 (s, 9H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 166.18, 135.60, 135.59, 133.37, 132.50, 132.45, 130.09, 129.77, 129.39, 128.53, 127.94, 79.37, 70.47, 63.38, 63.18, 38.73, 26.84, 19.21. HRMS (ESI) calcd for $C_{28}H_{34}O_7SSiNa$ $(M+Na)^+$: 565.1692. Found: 565.1689. Compound **22**: $[\alpha]_D^{26}$ −2.3 (*c* 1, $CHCl_3$); IR ($CHCl_3$): 3509, 3034, 2937, 2869, 2347, 2101, 1719, 1472, 1457, 1397, 1357, 1293, 1219, 1176, 1126, 1093, 1064, 1001, 962, 899, 869, 833, 756, 699, 660, 525 cm$^{-1}$; $^1$H NMR [400 MHz, $CDCl_3$] $\delta$: 8.07 (m, 2H), 7.63 (m, 1H), 7.49 (m, 2H), 5.46 (m, 1H), 5.02 (m, 1H), 4.03 (dd, $J = 12.9$, 3.8 Hz, 1H), 3.8 (dd, $J = 5.5$, 12.9 Hz, 1H), 3.74 (m, 2H), 3.1 (s, 3H), 2.0 (s, 1H); $^{13}$C NMR [100 MHz, $CDCl_3$] $\delta$: 165.6, 133.9, 129.7, 128.7, 128.6, 80.2, 70.6, 61.3, 50.4, 38.8. HRMS (ESI) calcd for $C_{12}H_{15}N_3O_6SNa$ $(M+Na)^+$: 352.0579. Found: 352.0574.