Geminal Difunctionalization of Vinylarenes: Concise Synthesis of 1,3-Dioxolan-4-ones

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1. General Experimental Methods

All reactions were carried out in oven-dried apparatus using dry solvents under anhydrous conditions, unless otherwise noted. Reaction mixtures were stirred magnetically unless otherwise stated. Analytical grade solvents were distilled and dried according to literature procedures. Analytical TLC was performed on commercial plates coated with silica gel GF254 (0.25 mm). Visualization of TLC was accomplished using UV light or PMA stain. Silica gel (230 - 400 mesh) was used for column chromatography. NMR spectra were recorded on 400 MHz spectrometer. The chemical shifts (δ, ppm) are reported with reference to either internal standard SiMe₄ (for ¹H) or the central line (77.0 ppm) of CDCl₃. The following abbreviations explain the multiplicity s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of a doublet, quint = quintet, m = multiplet, and br = broad. IR spectra were recorded as thin films on NaCl plates on a FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Micromass Q-TOF mass spectrometer. Isolated yields refer to chromatographically and spectroscopically (¹H-NMR) homogeneous materials, unless otherwise stated.

All the α-hydroxy carboxylic acids 1c, 1d, and 1f were synthesized starting from aminoacids L-valine, L-leucine, and L-isoleucine respectively according to the literature procedure. All commercially available reagent grade styrenes 2a-2s, the R-(−)-mandelic acid 1a, L-lactic acid 1b, D-3-phenyl lactic acid 1e, α-hydroxy isobutyric acid 1g, glycolic acid 1h, benzoic acid 4, p-tolylacetic acid 6, 3-phenyl-1-propanol 8, benzamide 10, acetamide 12, NBS, and AgOTf were used as received, without further purification.

2. General procedure for the synthesis of 1,3-dioxolan-4-ones 3a-3s

To a well-stirred colorless solution of the appropriate α-hydroxy carboxylic acid (0.50 mmol) and the appropriate styrene (0.75 mmol) in CH₂Cl₂ (5 mL) in a well dried Schlenk flask under argon atmosphere was added NBS (0.60 mmol) and AgOTf (0.70 mmol) at room temperature [25 °C]. The reaction mixture turned from colorless to a white cloudy solution, then to a colorless solution with a pale yellow suspension, and finally to a colorless solution with the formation of pale grey precipitate in 1 h. The progress of the reaction was monitored by TLC. After stirring the reaction mixture for 1 h at room temperature, H₂O (3 mL), sat. soln. of aq. NaHCO₃ (4mL) and sat. soln. of aq. Na₂S₂O₃ (4 mL) were added in succession and extracted with CH₂Cl₂ (3 x 5 mL). The combined organic layers were dried (anhyd. Na₂SO₄), filtered and concentrated in vacuo. The crude product obtained was purified by flash chromatography (pentane: Et₂O, 25:1) to furnish 1,3-dioxolan-4-ones in pure form.
(5R)-2-Benzyl-5-phenyl-1,3-dioxolan-4-one (3a) (97 mg, 76%): Diastereomer A: white solid; mp 82-84 °C; $[\alpha]_D^{24}$ -89.7 (c 1.0, CHCl$_3$); IR (thin film): 3032, 2924, 1796, 1496, 1454, 1401, 1274, 1214 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36-7.21 (m, 10H), 5.86 (t, $J$ = 4.5 Hz, 1H), 5.19 (s, 1H), 3.30-3.20 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.3, 133.5, 133.0, 130.2, 129.2, 128.6, 128.5, 127.3, 127.0, 103.9, 76.8, 40.5; HRMS (ESI-QTOF) m/z: [M+ Na]$^+$ calcd for C$_{16}$H$_{14}$O$_3$Na, 277.0841; found, 277.0843.

Diastereomer B: white solid; mp 53 - 54°C; $[\alpha]_D^{24}$ -38.2 (c 1.0, CHCl$_3$); IR (thin film): 3031, 2924, 1797, 1495, 1454, 1215, 1177, 992, 934 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38-7.25 (m, 10H), 6.02 (t, $J$ = 3.9 Hz, 1H), 5.11 (s, 1H), 3.21 (d, $J$ = 4.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.1, 126.6, 126.0, 123.2, 122.0, 121.9, 121.6, 120.4, 118.9, 97.9, 68.3, 34.3; HRMS (ESI-QTOF) m/z: [M+ Na]$^+$ calcd for C$_{16}$H$_{14}$O$_3$Na, 277.0841; found, 277.0850.

(5S)-2-Benzyl-5-methyl-1,3-dioxolan-4-one (3b) (92 mg, 63%): Diastereomer A: colourless oil; $[\alpha]_D^{24}$ +28.9 (c 1.0, CHCl$_3$); IR (thin film): 3032, 2930, 1797, 1495, 1542, 1260, 1131, 978 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.25 (m, 5H), 5.68 (m, 1H), 4.34- 4.28 (m, 1H), 3.12 (d, $J$ = 4.6 Hz, 2H), 1.38 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.5, 133.3, 130.0, 128.5, 127.3, 103.8, 71.4, 40.8, 16.3; HRMS (ESI-QTOF) m/z: [M+ Na]$^+$ calcd for C$_{11}$H$_{12}$O$_3$Na, 215.0684; found, 215.0686.

Diastereomer B: colorless oil; $[\alpha]_D^{24}$ -8.9 (c 1.0, CHCl$_3$); IR (thin film): 3030, 2930, 1800, 1218, 981 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44-7.22 (m, 5H), 5.87 (t, $J$ = 4.3 Hz, 1H), 4.17 (q, $J$ = 7.0 Hz, 1H), 3.09 (d, $J$ = 4.3 Hz, 2H), 1.39 (d, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.4, 132.8, 130.1, 128.6, 127.3, 104.1, 70.2, 41.2, 16.2; HRMS (ESI-QTOF) m/z: [M+ Na]$^+$ calcd for C$_{11}$H$_{12}$O$_3$Na, 215.0684; found, 215.0685.

(5S)-2-Benzyl-5-isopropyl-1,3-dioxolan-4-one (3c) (80 mg, 72%): Diastereomer A: colorless oil; $[\alpha]_D^{24}$ -3.6 (c 2.0, CHCl$_3$); IR (thin film): 2967, 2929, 1796, 1496, 1462, 1285, 1213, 1113, 997, 950, 909 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33-7.25 (m, 5H), 5.65 (t, $J$ = 4.6 Hz, 1H), 4.09 (d, $J$ = 3.9 Hz, 1H), 3.12 (d, $J$ = 4.6 Hz, 2H), 2.13-2.05 (m, 1H), 1.03(d, $J$ = 6.9 Hz, 3H), 0.90 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.4, 133.4, 130.0, 128.4, 127.2, 103.6, 79.2, 40.6, 29.6, 18.3, 16.5; HRMS (ESI-QTOF) m/z: [M+ Na]$^+$ calcd for C$_{13}$H$_{16}$O$_3$Na, 243.0997; found, 243.0996. Diastereomer B: colorless oil; $[\alpha]_D^{24}$ -24.6 (c 2.0, CHCl$_3$); IR (thin film): 3030, 2967, 2879, 1797, 1497, 1490, 1387, 1367, 1214, 1106, 991 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37-7.25 (m, 5H), 5.85 (t, $J$ = 3.6 Hz, 1H), 3.88 (d, $J$ = 3.5 Hz, 1H), 3.07 (t, $J$ = 3.3 Hz, 2H), 2.10-2.03 (m, 1H), 1.03(d, $J$ = 6.9 Hz, 3H), 0.96 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.4, 133.2, 130.2, 128.5, 127.3, 105.0, 78.5, 41.8, 30.6, 18.2, 16.9; HRMS (ESI-QTOF) m/z: [M+ Na]$^+$ calcd for C$_{13}$H$_{16}$O$_3$Na, 243.0997; found, 243.0993.
(5S)-2-Benzyl-5-isobutyl-1,3-dioxolan-4-one (3d) (72 mg, 61%): Diastereomer A: colorless oil; \([\alpha]_D^{21} -4.9 (c 2.5, \text{CHCl}_3)\); IR (thin film): 2958, 2930, 2873, 1798, 1461, 1307, 1118 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44-7.21 (m, 5H), 5.68 (t, J = 4.4 Hz, 1H), 4.24 (dd, J = 9.4, 3.5 Hz, 1H), 3.12 (d, J = 4.4 Hz, 2H), 1.87-1.78 (m, 1H), 1.67-1.60 (m, 1H), 1.43-1.36 (m, 1H), 0.93 (d, J = 6.6 Hz, 6H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 173.5, 133.3, 130.1, 128.4, 127.2, 103.9, 40.8, 39.7, 24.9, 22.8, 21.7; HRMS (ESI-QTOF) m/z: [M+ Na]\(^+\) calcd for C\(_{14}\)H\(_{18}\)O\(_3\)Na, 257.1154; found, 257.1155. Diastereomer B: colorless oil; \([\alpha]_D^{24} -17.7 (c 1.0, \text{CHCl}_3)\); IR (thin film): 2958, 2873, 1798, 1750, 1458, 1210, 990 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 (m, 5H), 5.85 (t, J = 4.2 Hz, 1H), 4.06 (dd, J = 18.8, 4.9 Hz, 1H), 3.09 (d, J = 4.1 Hz, 2H), 1.86-1.76 (m, 2H), 1.61-1.54 (m, 1H), 0.94 (d, J = 6.6 Hz, 3H), 0.91 (d, J = 6.6 Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 173.6, 133.3, 130.3, 129.6, 128.5, 127.3, 127.2, 104.2, 72.6, 41.3, 39.2, 24.9, 22.8, 21.6; HRMS (ESI-QTOF) m/z: [M+ Na]\(^+\) calcd for C\(_{14}\)H\(_{18}\)O\(_3\)Na, 257.1152.

(5R)-2,5-Dibenzyl-1,3-dioxolan-4-one (3e) (73 mg, 54%): Diastereomer A: colorless oil; \([\alpha]_D^{21} +41.2 (c 1.0, \text{CHCl}_3)\); IR (thin film): 3063, 3031, 2923, 2854, 1797, 1497, 1218, 1178, 1118, 969 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34-7.20 (m, 10H), 5.67-5.64 (m, 1H), 4.50-4.47 (m, 1H), 3.14 (dd, J = 14.6, 3.8 Hz, 1H), 2.93 (d, J = 4.6 Hz, 2H), 2.84 (dd, J = 14.6, 7.2 Hz, 1H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.1, 135.8, 133.3, 130.0, 129.6, 128.5, 127.3, 127.1, 104.3, 75.6, 40.8, 37.0; HRMS (ESI-QTOF) m/z: [M+ Na]\(^+\) calcd for C\(_{17}\)H\(_{16}\)O\(_3\)Na, 291.0997; found, 291.0995. Diastereomer B: colorless oil; \([\alpha]_D^{24} +26.0 (c 1.0, \text{CHCl}_3)\); IR (thin film): 3063, 3031, 2924, 2852, 1797, 1751, 1496, 1453, 1221, 1175, 1113, 1078, 990 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32-7.19 (m, 5H), 5.50-5.48 (m, 1H), 4.35-4.38 (m, 1H), 3.11-2.96 (m, 4H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.3, 135.3, 133.0, 130.1, 129.5, 128.6, 128.5, 127.3, 127.2, 104.8, 74.9, 41.3, 37.0; HRMS (ESI-QTOF) m/z: [M+ Na]\(^+\) calcd for C\(_{17}\)H\(_{16}\)O\(_3\)Na, 291.0997; found, 291.0995.

(2S,5S)-2-Benzyl-5-((R)-sec-butyl)-1,3-dioxolan-4-one (3f): colorless oil (68 mg, 58%); \([\alpha]_D^{21} -0.9 (c 2.0, \text{CHCl}_3)\); IR (thin film): 2966, 2930, 2880, 1797, 1458, 1401, 1114, 999 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33-7.25 (m, 5H), 5.65-5.63 (m, 1H), 4.12 (d, J = 4.1 Hz, 1H), 3.12 (d, J = 4.6 Hz, 2H), 1.86-1.79 (m, 1H), 1.45-1.20 (m, 2H), 1.0 (d, J = 6.9 Hz, 3H), 0.88 (t, J = 7.5 Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.4, 133.4, 130.0, 128.4, 127.2, 103.6, 78.8, 40.6, 36.1, 24.0, 14.9, 11.5; HRMS (ESI-QTOF) m/z: [M+ Na]\(^+\) calcd for C\(_{14}\)H\(_{18}\)O\(_3\)Na, 257.1154; found, 257.1162.
2-Benzyl-5,5-dimethyl-1,3-dioxolan-4-one (3g): colorless oil (67 mg, 65%); IR (thin film): 3032, 2985, 2929, 1797, 1497, 1456, 1387, 1360, 1278, 1210, 1148, 983 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.26 (m, 5H), 5.74 (t, J = 4.4 Hz, 1H), 3.10 (d, J = 3.9 Hz, 2H), 1.39 (s, 3H), 1.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.4, 133.4, 130.1, 128.4, 127.2, 101.9, 77.2, 41.0, 24.4, 21.8; HRMS (ESI-QTOF) m/z: [M+ Na]⁺ calcd for C₁₂H₁₄O₃Na, 229.0841; found, 229.0839.

2-Benzyl-1,3-dioxolan-4-one (3h): colorless oil (43 mg, 48%); ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.25 (m, 5H), 5.81 (t, J = 4.5 Hz, 1H), 4.14 (d, J = 2.9 Hz, 2H), 3.13 (d, J = 3.0 Hz, 1H), 3.12 (d, J = 2.9 Hz, 1H).

5,5-Dimethyl-2-(2-methylbenzyl)-1,3-dioxolan-4-one (3i): colorless oil (64 mg, 58%); IR (thin film): 2982, 2930, 1800, 1460, 1390, 1280, 1151, 982 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.12 (m, 4H), 5.74 (t, J = 4.5 Hz, 1H), 3.12 (d, J = 4.5 Hz, 2H), 2.35 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.5, 137.2, 131.9, 130.8, 127.3, 125.9, 102.0, 77.2, 38.0, 24.5, 21.8, 19.9; HRMS (ESI-QTOF) m/z: [M+ Na]⁺ calcd for C₁₃H₁₆O₃Na, 243.0997; found, 243.0998.

5,5-Dimethyl-2-(3-methylbenzyl)-1,3-dioxolan-4-one (3j): colorless oil (68 mg, 61%); IR (thin film): 3024, 2983, 2926, 1799, 1391, 1360, 1280, 1206, 1151, 1103, 1033, 984 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.20-7.05 (m, 4H), 5.72 (t, J = 4.5 Hz, 1H), 3.05 (d, J = 4.6 Hz, 2H), 2.34 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.5, 137.2, 131.9, 130.8, 128.3, 127.9, 127.0, 102.1, 77.2, 41.1, 24.5, 21.8, 21.3; HRMS (ESI-QTOF) m/z: [M+ Na]⁺ calcd for C₁₃H₁₆O₃Na, 243.0997; found, 243.0996.

5,5-Dimethyl-2-(4-methylbenzyl)-1,3-dioxolan-4-one (3k): colorless oil (63 mg, 57%); IR (thin film): 2985, 2925, 1800, 1515, 1458, 1392, 1201, 1151, 982 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.17-7.11 (m, 4H), 5.71
5,5-Dimethyl-2-(4-tert-butyl benzyl)-1,3-dioxolan-4-one (3l): colorless oil (88 mg, 67%); IR (thin film): 2961, 1799, 1275, 1209, 1186, 1143, 984 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34 (dd, J = 6.5, 1.8 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 5.71 (t, J = 4.6 Hz, 1H), 3.06 (d, J = 4.5 Hz, 2H), 1.39 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.5, 150.1, 130.4, 129.7, 125.4, 102.2, 77.2, 40.6, 34.4, 31.3, 24.5, 21.8; HRMS (ESI-QTOF) m/z: [M+ Na]⁺ calcd for C₁₆H₂₂O₃Na, 285.1466; found, 285.1465.

5,5-Dimethyl-2-(4-bromobenzyl)-1,3-dioxolan-4-one (3m): colorless oil (89 mg, 62%); IR (thin film): 2984, 2924, 2850, 1797, 1489, 1182, 1147, 985 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 5.70 (t, J = 8.5 Hz, 1H), 3.05 (d, J = 2.2 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.2, 132.2, 131.9, 131.5, 121.3, 101.3, 77.2, 40.3, 24.4, 21.8; HRMS (ESI-QTOF) m/z: [M+ Na]⁺ calcd for C₁₂H₁₃BrO₃Na, 308.9946; found, 308.9945.

5,5-Dimethyl-2-(4-fluorobenzyl)-1,3-dioxolan-4-one (3n): colorless oil (68 mg, 60%); IR (thin film): 2986, 2929, 1790, 1512, 1221, 1149, 985 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.22 (dd, J = 8.4, 5.5 Hz, 2H), 7.0 (dd, J = 8.6 Hz, 2H), 5.70 (t, J = 4.3 Hz, 1H), 3.06 (dd, J = 3.9 Hz, 2H), 1.39 (s, 3H), 1.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.32, 162.1 (d, J_C-F = 243.9 Hz), 131.7 (d, J_C-F = 8.0 Hz), 129.0 (d, J_C-F = 3.0 Hz), 115.3 (d, J_C-F = 21.2 Hz), 101.6, 77.3, 40.0, 24.4, 21.8; HRMS (ESI-QTOF) m/z: [M+ Na]⁺ calcd for C₁₂H₁₁FO₃Na, 247.0746; found, 247.0749.

2-Benzhydryl-5,5-dimethyl-1,3-dioxolan-4-one (3o): colorless oil (122 mg, 86%); IR (thin film): 3030, 2984, 2909, 1800, 1496, 1454, 1386, 1284, 1184, 1151, 972 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.26 (m, 10H), 6.16 (d, J = 3.3 Hz, 1H), 4.36 (d, J = 3.3 Hz, 1H), 1.42 (s, 3H), 1.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.2, 137.83, 137.76, 129.6, 129.5, 128.4, 127.25, 127.22, 102.7, 77.1, 55.2, 24.0, 22.5; HRMS (ESI-QTOF) m/z: [M+ Na]⁺ calcd for C₁₈H₁₈O₃Na, 305.1154; found, 305.1150.
5,5-Dimethyl-2-(1-phenylethyl)-1,3-dioxolan-4-one (3q): [mixture of diastereomers; inseparable in $^1$H NMR]; colorless oil (100 mg, 90%); IR (thin film): 2982, 2908, 1799, 1457, 1279, 1210, 964 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.24 (m, 5H), 5.65 (d, $J$ = 3.8 Hz, 0.5H, $^1A$), 5.63 (d, $J$ = 3.7 Hz, 0.5H, $^1B$), 3.16-3.09 (m, 1H), 1.40-1.37 (m, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.6, 175.5, 139.4, 139.2, 128.7, 128.5, 128.4, 128.31, 128.26, 127.23, 104.3, 77.2, 77.1, 43.6, 24.3, 24.2, 22.1, 21.8, 14.2, 14.1; HRMS (ESI-QTOF) m/z: [M+ Na]$^+$ calcd for C$_{13}$H$_{16}$O$_3$Na, 243.0997; found, 243.0995.

5,5-Dimethyl-2-(phenylmethyl-$^2$H$_2$)-1,3-dioxolan-4-one (3s): colorless oil (66 mg, 63%); IR (thin film): 2984, 2926, 1798, 1387, 1281, 1183, 1008, 986 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.25 (m, 5H), 5.72 (s, 1H, $^1HCCD_2$Ph), 1.38 (s, 3H), 1.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.4, 133.3, 130.1, 128.4, 127.2, 101.9, 77.2, 40.4 (quint, $^3J_{C-D}$ = 19.6 Hz), 24.4, 21.8; HRMS (ESI-QTOF) m/z: [M+ Na]$^+$ calcd for C$_{12}$H$_{12}$D$_2$O$_3$Na, 231.0966; found, 231.0969.

3. General procedure for the addition of mono-functionalized nucleophiles 4-12 to styrene 2a

To a well-stirred colorless solution of the appropriate nucleophile (1.2 mmol) and styrene 2a (0.50 mmol) in 5 mL of CH$_2$Cl$_2$ in a well dried Schlenk flask under argon atmosphere was added NBS (0.60 mmol) and AgOTf (0.70 mmol) at room temperature [25 °C]. The reaction mixture turned from colorless to a white cloudy solution, then to a colorless solution with a pale yellow suspension, and finally to a colorless solution with the formation of pale grey precipitate in 1 h. The progress of the reaction was monitored by TLC. After stirring the reaction mixture for 1 h at room temperature 3 mL of H$_2$O (3 mL), sat. soln. of aq. NaHCO$_3$ (4 mL) and sat. soln. of aq. Na$_2$S$_2$O$_3$ (4 mL) were added in succession and extracted with CH$_2$Cl$_2$ (3 x 5 mL). The combined organic layers were dried (anhyd. Na$_2$SO$_4$), filtered and concentrated in vacuo. The crude product obtained was purified by flash chromatography (petroleum ether: EtOAc) to furnish the respective products in pure form.
1-Phenylethane-1,2-diyl dibenzoate (5): white solid (118 mg, 68%); mp 99 °C (lit. mp 94-95 °C); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11-7.98 (m, 4H), 7.57-7.32 (m, 11H), 6.42 (dd, $J = 8.0$, 3.7 Hz, 1H), 4.78-4.65 (m, 2H).

1-Phenylethane-1,2-diyl bis(2-(p-tolyl)acetate) (7): colorless oil (110 mg, 54%); IR (thin film): 3028, 2950, 2971, 2858, 1727, 1493, 1451, 1300, 1021 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30-7.07 (m, 13H), 6.0 (dd, $J = 7.3$, 4.6 Hz, 1H), 4.29 (t, $J = 4.2$ Hz, 2H), 3.57 (s, 2H), 3.48 (s, 2H), 2.32 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.2, 170.6, 136.7, 136.2, 130.64, 130.59, 129.21, 129.19, 129.12, 129.10, 128.53, 128.49, 126.6, 73.4, 66.2, 40.9, 40.6, 21.0; HRMS (ESI-QTOF) $m/z$: [M+ Na]$^+$ calcd for C$_{26}$H$_{26}$O$_4$Na, 425.1729; found, 425.1733.

(((2-phenylethane-1,1-diyl)bis(oxy))bis(propane-3,1-diyl))Dibenene (9): colorless oil (97 mg, 52%); IR (thin film): 3027, 2932, 2866, 1602, 1495, 1452, 1351, 1121, 1057 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31-7.09 (m, 15H), 4.61 (t, $J = 5.7$ Hz, 1H), 3.66-3.61 (m, 2H), 3.41-3.36 (m, 2H), 2.94 (d, $J = 5.6$ Hz, 2H), 2.61 (t, $J = 7.4$ Hz, 4H), 1.90-1.789 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.9, 137.3, 129.6, 128.4, 128.3, 128.2, 126.3, 125.7, 104.2, 65.5, 40.8, 32.3, 31.4; HRMS (ESI-QTOF) $m/z$: [M+ Na]$^+$ calcd for C$_{26}$H$_{30}$O$_2$Na, 397.2143; found, 397.2150.
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of diastereomer A of compound 3a
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of diastereomer B of compound 3a
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of diastereomer A of compound 3b
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of diastereomer B of compound 3b
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of diastereomer $A$ of compound $3c$
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of diastereomer B of compound 3c
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of diastereomer A of compound 3d
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of diastereomrer B of compound 3d
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of diastereomer $A$ of compound 3e
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of diastereomer B of compound 3e
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3f
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3g
$^1$H NMR spectrum (400, CDCl$_3$) of compound 3h
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3i
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3j
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3k
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3I
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3m
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3n
Supporting Information

$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3o
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3q
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 3s
$^{1}H$ and $^{13}C$ NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 7
$^1$H and $^{13}$C NMR spectrum (400; 100 MHz, CDCl$_3$) of compound 9
References


