Supporting Information

Palladium-catalyzed Synthesis of Terminal Acetals via Highly Selective Anti-Markovnikov Nucleophilic Attack of Pinacol on Vinylarenes, Allyl Ethers, and 1,5-Dienes

Mayumi Yamamoto, Sonoe Nakaoka, Yasuyuki Ura* and Yasutaka Kataoka

Department of Chemistry, Faculty of Science, Nara Women’s University, Kitauoyanishi-machi, Nara 630-8506, Japan
ura@cc.nara-wu.ac.jp

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General Information

PdCl₂(MeCN)₂, 2-methyl-1,2-propanediol, methyl 4-(allyloxy)benzoate and allyl 2,6-dimethylphenyl ether and were prepared as described in the literature. Dehydrated DMF was purchased from Kanto Chemical Co. Ltd. Pinacol was obtained from Nacalai Tesque, Inc. Ethylene glycol was purchased from Wako Pure Chemical Industries, Ltd. and was dried over MgSO₄ and distilled before use. Other chemicals were also commercially available and were used without further purification. All reactions were performed under an argon atmosphere. Flash column chromatography was performed using silica gel SILICYCLE SiliaFlash F60 (40-63 μm, 230-400 mesh). NMR spectra were recorded on either a JEOL AL-400 (400 MHz (¹H), 100 MHz (¹³C)) or a Bruker AV-300N (300 MHz (¹H), 75 MHz (¹³C)) spectrometer. Chemical shift values (δ) were expressed relative to SiMe₄. GC analyses were performed on a Shimadzu GC-14B gas chromatograph with a capillary column (Shinwa Chemical Industries, ULBON HR-1701, 0.25 mm i.d. × 25 m). Mass spectra were recorded on a SHIMADZU GCMS-QP5050 spectrometer.

Reaction of Styrene with Several 1,2-Diols

A procedure for 2-benzyl-4,4,5,5-tetramethyl-1,3-dioxolane (2d) is representative. To a reaction vessel, PdCl₂(MeCN)₂ (31 mg, 0.12 mmol), p-benzoquinone (259 mg, 2.39 mmol), styrene (137 μL, 1.20 mmol) and dehydrated DMF (1.2 mL) were added. Pinacol (1.42 g, 12.0 mmol) was then added, and the reaction mixture was stirred at 60 °C for 48 h. After cooling to room temperature, the solvent and the volatile materials were removed from the reaction mixture under vacuum. To the residue, small amounts of silica gel and ethyl acetate were added and the mixture was stirred, and the solvent was again removed to dry to adsorb the residue to the silicagel, which was mounted on silicagel column. Purification by flash chromatography (eluent: hexane/ethyl acetate = 20:1) afforded 2d (159 mg, 0.72 mmol) as a colorless oil in 60% yield.

To examine the yields and the formation ratios for acetals 2a–c and 3a–c, ¹H NMR analyses were performed. The reaction mixtures were prepared in a similar manner as described above, to which an internal standard (mesitylene) was also added. The mixtures were sampled and mixed with CDCl₃. Integrations of the characteristic triplet peaks which appear in the range of 5.0–5.4 ppm for 2a–c and those of the singlet peaks which appear at around 1.6 ppm for 3a–c were compared to those of the peaks for the internal standard to calculate the NMR yields and the formation ratios. The spectral data for 2a, 3a, 2b, 2c and 2d are listed below.

![2b](image)

2-Benzyl-4,4-dimethyl-1,3-dioxolane (2b). ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.13 (m, 5H, arom.), 5.20 (t, J = 4.5 Hz, 1H, H²), 3.59 (d, J = 7.8 Hz, 1H, H⁵), 3.54 (d, J = 7.8 Hz, 1H, H⁶), 2.97 (dd, J = 14.1, 4.2 Hz, 1H, H⁷).
H'), 2.90 (dd, J = 14.1, 5.1 Hz, 1H, H\textsuperscript{b}), 1.26 (s, 3H, Me), 1.24 (s, 3H, Me). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 136.2 (C\textsuperscript{7}), 129.8 (C\textsuperscript{8} or C\textsuperscript{9}), 128.1 (C\textsuperscript{8} or C\textsuperscript{9}), 126.4 (C\textsuperscript{10}), 103.9 (C\textsuperscript{5}), 78.6 (C\textsuperscript{3}), 76.0 (C\textsuperscript{4}), 41.5 (C\textsuperscript{6}), 26.6 (Me), 25.0 (Me).

2-Benzyl-4,5-dimethyl-1,3-dioxolane (2c). Compound 2c was isolated as a mixture of three diastereomers.

For isomer I: \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.33–7.14 (m, 5H, arom.), 5.05 (t, J = 4.8 Hz, 1H, H\textsuperscript{a}), 4.13–4.04 (m, 2H, H\textsubscript{c}), 2.95 (d, J = 4.8 Hz, 2H, H\textsuperscript{b}), 1.13–1.05 (m, 6H, Me). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 136.3 (C\textsuperscript{6}), 129.8 (C\textsuperscript{7} or C\textsuperscript{8}), 128.2 (C\textsuperscript{7} or C\textsuperscript{8}), 126.5 (C\textsuperscript{9}), 103.2 (C\textsuperscript{4}), 74.6 (C\textsuperscript{3} and C\textsuperscript{3'}, 41.7 (C\textsuperscript{5}), 15.4 (Me).

For isomer II: \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.33–7.14 (m, 5H, arom.), 5.23 (t, J = 4.6 Hz, 1H, H\textsuperscript{a}), 3.63–3.45 (m, 2H, H\textsuperscript{c}), 2.93 (d, J = 4.6 Hz, 2H, H\textsuperscript{b}), 1.23 (d, J = 6.0 Hz, 3H, Me), 1.18 (d, J = 6.0 Hz, 3H, Me). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz) \(\delta\) 136.3 (C\textsuperscript{6}), 129.8 (C\textsuperscript{7} or C\textsuperscript{8}), 128.2 (C\textsuperscript{7} or C\textsuperscript{8}), 126.4 (C\textsuperscript{9}), 103.4 (C\textsuperscript{4}), 79.7 (C\textsuperscript{3}), 78.1 (C\textsuperscript{3'}), 41.6 (C\textsuperscript{5}), 17.1 (Me), 16.9 (Me).

For isomer III: \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.33–7.14 (m, 5H, arom.), 5.37 (t, J = 4.4 Hz, 1H, H\textsuperscript{a}), 4.19–4.10 (m, 2H, H\textsuperscript{c}), 2.87 (d, J = 4.4 Hz, 2H, H\textsuperscript{b}), 1.23 (d, J = 6.0 Hz, 3H, Me), 1.13–1.05 (m, 6H, Me). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz) \(\delta\) 136.3 (C\textsuperscript{6}), 129.8 (C\textsuperscript{7} or C\textsuperscript{8}), 128.2 (C\textsuperscript{7} or C\textsuperscript{8}), 126.4 (C\textsuperscript{9}), 102.7 (C\textsuperscript{4}), 74.3 (C\textsuperscript{3} and C\textsuperscript{3'}, 41.9 (C\textsuperscript{5}), 14.2 (Me).

2-Benzyl-4,4,5,5-tetramethyl-1,3-dioxolane (2d). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.30–7.15 (m, 5H, arom.), 5.21 (t, J = 4.9 Hz, 1H, H\textsuperscript{a}), 2.89 (d, J = 4.9 Hz, 2H, H\textsuperscript{b}), 1.16 (s, 6H, Me), 1.15 (s, 6H, Me). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 136.6 (C\textsuperscript{6}), 129.8 (C\textsuperscript{7} or C\textsuperscript{8}), 128.1 (C\textsuperscript{7} or C\textsuperscript{8}), 126.3 (C\textsuperscript{9}), 101.1 (C\textsuperscript{4}), 81.9 (C\textsuperscript{3}), 43.1 (C\textsuperscript{5}), 24.1 (C\textsuperscript{1} or C\textsuperscript{2}), 22.0 (C\textsuperscript{1} or C\textsuperscript{2}). MS (EI) \textit{m/z} 219 ([M-H\textsuperscript{+}]).

**Reaction of Vinylarenes with Pinacol**

Same procedure was applied as described above for 2d. The products were obtained as colorless oils.
2-(p-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2e). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23 (d, $J = 8.3$ Hz, 2H, arom.), 7.16 (d, $J = 8.3$ Hz, 2H, arom.), 5.17 (t, $J = 4.9$ Hz, 1H, H$^a$), 2.85 (d, $J = 4.9$ Hz, 2H, H$^b$), 1.16 (s, 6H, Me), 1.13 (s, 6H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 135.0 (C$_6$ or C$_9$), 132.3 (C$_6$ or C$_9$), 131.3 (C$_7$ or C$_8$), 128.3 (C$_7$ or C$_8$), 100.7 (C$_4$), 82.0 (C$_3$), 42.3 (C$_5$), 24.1 (C$_1$ or C$_2$), 22.0 (C$_1$ or C$_2$). MS (EI) $m/z$ 253 ([M-H]$^+$).

2-(o-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2f). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34–7.30 (m, 2H, arom.), 7.20–7.11 (m, 2H, arom.), 5.23 (t, $J = 5.1$ Hz, 1H, H$^a$), 3.06 (d, $J = 5.1$ Hz, 2H, H$^b$), 1.20 (s, 6H, Me), 1.17 (s, 6H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.5 (C$_6$), 134.5 (C$_7$), 132.1 (arom.), 129.3 (arom.), 127.9 (arom.), 126.6 (arom.), 99.7 (C$_4$), 82.0 (C$_3$), 40.4 (C$_5$), 24.0 (C$_1$ or C$_2$), 22.0 (C$_1$ or C$_2$). MS (EI) $m/z$ 253 ([M-H]$^+$).

2-(m-Nitrobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2g). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (s, 1H, H$^c$), 8.07 (dt, $J = 8.0$, 1.1 Hz, 1H, H$^d$), 7.57 (dd, $J = 7.6$, 0.4 Hz, 1H, H$^e$), 7.43 (t, $J = 7.9$ Hz, 1H, H$^f$), 5.23 (t, $J = 4.7$ Hz, 1H, H$^g$), 2.98 (d, $J = 4.7$ Hz, 2H, H$^b$), 1.16 (s, 6H, Me), 1.10 (s, 6H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.1 (C$_8$), 138.4 (C$_9$), 136.4 (C$_{11}$), 128.9 (C$_{10}$), 124.9 (C$_7$), 121.6 (C$_6$), 100.0 (C$_4$), 82.2 (C$_3$), 42.3 (C$_5$), 24.0 (C$_1$ or C$_2$), 22.0 (C$_1$ or C$_2$). MS (EI) $m/z$ 264 ([M-H]$^+$).
2-(m-Trifluoromethylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2h). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50–7.34 (m, 4H, arom.), 5.22 (t, $J = 4.7$ Hz, 1H, H$^a$), 2.94 (d, $J = 4.7$ Hz, 2H, H$^b$), 1.16 (s, 6H, Me), 1.11 (s, 6H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.3 (C$^6$), 133.5 (q, $J_{CF} = 1.3$ Hz, C$^{10}$), 130.3 (q, $J_{CF} = 31.8$ Hz, C$^8$), 128.5 (C$^{11}$), 126.8 (q, $J_{CF} = 3.8$ Hz, C$^7$ or C$^9$), 124.2 (q, $J_{CF} = 272$ Hz, C$^{12}$), 123.3 (q, $J_{CF} = 3.8$ Hz, C$^7$ or C$^9$), 100.3 (C$^4$), 82.1 (C$^3$), 42.5 (C$^5$), 24.0 (C$^1$ or C$^2$), 22.1 (C$^1$ or C$^2$). MS (EI) m/z 287 ([M-H]$^+$).

2-(p-Methylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2i). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.15 (d, $J = 8.0$ Hz, 2H, arom.), 7.09 (d, $J = 8.0$ Hz, 2H, arom.), 5.20 (t, $J = 5.0$ Hz, 1H, H$^a$), 2.86 (d, $J = 5.0$ Hz, 2H, H$^b$), 2.31 (s, 3H, Me), 1.19 (s, 6H, Me), 1.17 (s, 6H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 135.8 (C$^6$ or C$^9$), 133.5 (C$^6$ or C$^9$), 129.7 (C$^7$ or C$^8$), 128.9 (C$^3$ or C$^5$), 101.2 (C$^4$), 81.9 (C$^3$), 42.7 (C$^5$), 24.1 (C$^1$ or C$^2$), 22.0 (C$^1$ or C$^2$), 21.0 (C$^{10}$). MS (EI) m/z 233 ([M-H]$^+$).

2-(o-Methylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2j). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21–7.18 (m, 1H, arom.), 7.14–7.09 (m, 3H, arom.), 5.23 (t, $J = 5.0$ Hz, 1H, H$^a$), 2.91 (d, $J = 5.0$ Hz, 2H, H$^b$), 2.33 (s, 3H, Me), 1.16 (s, 6H, Me), 1.15 (s, 6H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.9 (C$^6$ or C$^9$), 135.0 (C$^6$ or C$^9$), 130.5 (arom.), 130.1 (arom.), 126.5 (arom.), 125.7 (arom.), 100.9 (C$^4$), 81.8 (C$^3$), 42.1 (C$^5$), 24.0 (C$^1$ or C$^2$), 22.0 (C$^1$ or C$^2$), 20.0 (C$^{12}$). MS (EI) m/z 233 ([M-H]$^+$).
2-\((p\text{-Methoxybenzyl})\)-4,4,5,5-tetramethyl-1,3-dioxolane (2k). 1H NMR (400 MHz, CDCl₃) δ 7.16 (d, \(J = 8.4\) Hz, 2H, H‴), 6.82 (d, \(J = 8.4\) Hz, 2H, H‴), 5.17 (t, \(J = 5.0\) Hz, 1H, H‴), 3.76 (s, 3H, OMe), 2.78 (d, \(J = 5.0\) Hz, 2H, H‴), 1.16 (s, 6H, Me), 1.16 (s, 6H, Me). 13C NMR (100 MHz, CDCl₃) δ 158.2 (Ċ), 130.8 (C⁸), 128.7 (C⁶), 113.6 (C⁰), 101.2 (C⁴), 81.9 (C³), 55.2 (C¹₀), 42.1 (C⁵), 24.1 (C¹ or C²), 22.1 (C¹ or C²). MS (EI) m/z 249 ([M-H]+).

2-\((m\text{-Methoxybenzyl})\)-4,4,5,5-tetramethyl-1,3-dioxolane (2l). 1H NMR (400 MHz, CDCl₃) δ 7.19 (t, \(J = 7.9\) Hz, 1H, H‴), 6.84 (dd, \(J = 7.5\), 0.4 Hz, 1H, H‴ or H‴), 6.81 (s, 1H, H‴), 6.75 (dd, \(J = 8.2\), 2.6 Hz, 1H, H‴ or H‴), 5.22 (t, \(J = 5.0\) Hz, 1H, H‴), 3.78 (s, 3H, OMe), 2.87 (d, \(J = 5.0\) Hz, 2H, H‴), 1.17 (s, 12H, Me). 13C NMR (100 MHz, CDCl₃) δ 159.4 (C⁸), 138.1 (C³), 129.1 (C¹₀), 122.2 (C⁹ or C¹¹), 115.6 (C⁷), 111.7 (C⁹ or C¹¹), 100.0 (C⁴), 81.9 (C³), 55.1 (C¹²), 43.2 (C⁵), 24.1 (C¹ or C²), 22.0 (C¹ or C²). MS (EI) m/z 249 ([M-H]+).

2-\((o\text{-Methoxybenzyl})\)-4,4,5,5-tetramethyl-1,3-dioxolane (2m). 1H NMR (400 MHz, CDCl₃) δ 7.24–7.20 (m, 1H, H‴), 7.21–7.16 (dt, \(J = 1.7\), 1H, H‴), 6.88 (dt, \(J = 0.8\), 7.4 Hz, 1H, H‴), 6.82 (d, \(J = 8.2\) Hz, 1H, H‴), 5.26 (t, \(J = 5.2\) Hz, 1H, H‴), 3.79 (t, \(J = 5.2\) Hz, 2H, H‴), 1.20 (s, 6H, Me), 1.16 (s, 6H, Me). 13C NMR (100 MHz, CDCl₃) δ 157.6 (C⁷), 131.5 (C¹¹), 127.7 (C⁹), 125.2 (C⁸), 120.4 (C¹⁰), 110.3 (C⁶), 100.1 (C⁴), 81.7 (C³), 55.3 (C¹²), 37.5 (C⁵), 24.1 (C¹ or C²), 22.1 (C¹ or C²). MS (EI) m/z 249 ([M-H]+).
2-(2-Naphthylmethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2n). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$7.81–7.75 (m, 3H, H$^d$, H$^f$ and H$^h$), 7.70 (s, 1H, H$^c$), 7.47–7.39 (m, 3H, H$^e$, H$^i$ and H$^j$), 5.33 (t, $J = 4.9$ Hz, 1H, H$^a$), 3.08 (d, $J = 4.9$ Hz, 2H, H$^b$), 1.19 (s, 12H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$134.2 (C$^6$, C$^8$ or C$^{13}$), 133.5 (C$^6$, C$^8$ or C$^{13}$), 132.3 (C$^6$, C$^8$ or C$^{13}$), 128.4 (C$^{10}$, C$^{11}$ or C$^{15}$), 128.2 (C$^7$), 127.6 (C$^9$, C$^{12}$ or C$^{14}$), 127.5 (C$^9$, C$^{12}$ or C$^{14}$), 125.7 (C$^{10}$, C$^{11}$ or C$^{15}$), 125.3 (C$^{10}$, C$^{11}$ or C$^{15}$), 101.1 (C$^4$), 82.0 (C$^3$), 43.2 (C$^5$), 24.1 (C$^1$ or C$^2$), 22.1 (C$^1$ or C$^2$). MS (EI) $m/z$ 270 (M$^+$).

2-Naphthyl-4,4,5,5-tetramethyl-1,3-dioxolane. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$7.94 (s, 1H, arom.), 7.87–7.79 (m, 3H, arom.), 7.60 (d, $J = 8.6$ Hz, 1H, arom.), 7.50–7.43 (m, 2H, arom.), 6.14 (s, 1H, H$^a$), 1.36 (s, 6H, Me), 1.30 (s, 6H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$137.2 (arom.), 133.5 (arom.), 133.0 (arom.), 128.2 (arom.), 128.1 (arom.), 127.7 (arom.), 126.1 (arom.), 126.0 (arom.), 125.4 (arom.), 123.9 (arom.), 99.9 (C$^4$), 82.7 (C$^3$), 24.3 (C$^1$ or C$^2$), 22.2 (C$^1$ or C$^2$). MS (EI) $m/z$ 256 (M$^+$).

Reaction of Allyl Ethers with Pinacol
Same procedure was applied as described above for 2d. The products were obtained as colorless oils.

2-(Phenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5a). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$7.27–7.22 (m, 2H, H$^c$), 6.92–6.86 (m, 3H, H$^d$ and H$^f$), 5.25 (t, $J = 5.3$ Hz, 1H, H$^a$), 4.08 (t, $J = 6.7$ Hz, 2H, H$^b$), 2.10–2.05 (s, 2H, H$^j$), 1.19 (s, 6H, Me), 1.19 (s, 6H, Me). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$158.8 (C$^7$), 129.3 (C$^9$), 120.5 (C$^{10}$), 114.4 (C$^8$), 98.1 (C$^4$), 81.9 (C$^3$), 63.7 (C$^6$), 36.3 (C$^5$), 24.2 (C$^1$ or C$^2$), 22.0 (C$^1$ or C$^2$). MS (EI) $m/z$ 250 (M$^+$).
2-(Phenoxymethyl)-2,4,4,5,5-pentamethyl-1,3-dioxolane (6a). Compound 6a was obtained as a mixture with 5a. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.27–7.22 (m, 2H, H\(b\)), 6.92–6.86 (m, 3H, H\(a\) and H\(c\)), 3.86 (s, 2H, C\(H\_2\)), 1.56 (s, 3H, Me), 1.30 (s, 6H, Me), 1.25 (s, 6H, Me). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.8 (C\(7\)), 129.3 (C\(9\)), 120.8 (C\(10\)), 114.6 (C\(8\)), 105.5 (C\(4\)), 83.1 (C\(3\)), 74.0 (C\(6\)), 25.1 (C\(5\)), 24.7 (C\(1\) or C\(2\)), 24.6 (C\(1\) or C\(2\)). MS (EI) \(m/z\) 235 ([M-CH\(_3\)]\(^+\)).

2-(p-Methoxycarbonylphenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5b). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 (dd, \(J = 9.0, 1.0\) Hz, 2H, H\(b\)), 6.87 (dd, \(J = 8.9, 0.9\) Hz, 2H, H\(d\)), 5.22 (t, \(J = 5.2\) Hz, 1H, H\(a\)), 4.11 (t, \(J = 6.6\) Hz, 2H, H\(f\)), 3.82 (s, 3H, OMe), 2.10–2.04 (m, 2H, H\(f\)), 1.18 (s, 6H, Me), 1.17 (s, 6H, Me). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.8 (C\(1\)), 162.6 (C\(7\)), 131.5 (C\(8\)), 122.4 (C\(10\)), 114.0 (C\(9\)), 97.8 (C\(3\)), 82.0 (C\(5\)), 64.1 (C\(6\)), 51.7 (C\(12\)), 36.0 (C\(5\)), 24.1 (C\(1\) or C\(2\)), 22.0 (C\(1\) or C\(2\)). MS (EI) \(m/z\) 308 (M\(^+\)).

2-(p-Methoxycarbonylphenoxyethyl)-2,4,4,5,5-pentamethyl-1,3-dioxolane (6b). Compound 6b was obtained as a mixture with 5b. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 (dd, \(J = 9.0, 1.0\) Hz, 2H, H\(b\)), 6.91 (d, \(J = 9.0\) Hz, 2H, H\(d\)), 3.88 (s, 2H, CH\(_2\)), 3.82 (s, 3H, OMe), 1.53 (s, 3H, Me), 1.27 (s, 6H, Me), 1.23 (s, 6H, Me). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.7 (C\(1\)), 162.5 (C\(7\)), 131.5 (C\(8\)), 122.7 (C\(10\)), 114.2 (C\(9\)), 105.2 (C\(4\)), 83.2 (C\(5\)), 74.1 (C\(6\)), 51.7 (C\(12\)), 25.1 (C\(5\)), 24.6 (C\(1\) or C\(2\)), 24.5 (C\(1\) or C\(2\)). MS (EI) \(m/z\) 293 ([M-CH\(_3\)]\(^+\)).
2-(2,6-Dimethylphenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5c). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.98 (d, $J = 7.3$ Hz, 2H, H$^d$), 6.89 (t, $J = 7.4$ Hz, 1H, H$^e$), 5.33 (t, $J = 5.0$ Hz, 1H, H$^a$), 3.84 (dt, $J = 0.8$, 6.7 Hz, 2H, H$^c$), 2.27 (s, 6H, Me), 2.13–2.07 (m, 2H, H$^b$), 1.20 (s, 12H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.0 (C$^7$), 130.9 (C$^8$), 128.7 (C$^9$), 123.6 (C$^{10}$), 98.1 (C$^4$), 81.8 (C$^3$), 68.1 (C$^6$), 37.2 (C$^5$), 24.2 (C$^1$ or C$^2$), 22.0 (C$^1$ or C$^2$), 16.3 (C$^{11}$). MS (EI) m/z 278 (M$^+$).

2-(2,6-Dimethylphenoxyethyl)-2,4,4,5,5-pentamethyl-1,3-dioxolane (6c). Compound 6c was obtained as a mixture with 5c. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.98 (d, $J = 7.3$ Hz, 2H, H$^d$), 6.89 (t, $J = 7.4$ Hz, 1H, H$^e$), 3.67 (s, 2H, C$\text{H}_2$), 2.30 (s, 6H, Me), 1.68 (s, 3H, Me), 1.31 (s, 6H, Me), 1.25 (s, 6H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.1 (C$^7$), 130.9 (C$^8$), 128.7 (C$^9$), 123.8 (C$^{10}$), 105.5 (C$^4$), 82.9 (C$^3$), 77.4 (C$^6$), 25.2 (C$^5$), 24.7 (C$^1$ or C$^2$), 24.6 (C$^1$ or C$^2$), 16.1 (C$^{11}$). MS (EI) m/z 263 ([M-CH$_3$]+).

Reaction of 1,5-Dienes with Pinacol

Same procedure was applied as described above for 2d. The products were obtained as colorless oils.

2-(4-Pentenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (9). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.83–5.72 (m, 1H, H$^e$), 5.01 (t, $J = 4.8$ Hz, 1H, H$^a$), 5.00–4.89 (m, 2H, H$^f$ and H$^g$), 2.09–2.03 (m, 2H, H$^h$), 1.60–1.54 (m, 2H, H$^h$), 1.52–1.43 (m, 2H, H$^h$), 1.16 (s, 12H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.5 (C$^8$), 114.6 (C$^9$), 100.8 (C$^4$), 78.8 (C$^6$), 79.2 (C$^5$), 24.7 (C$^1$ or C$^2$), 24.6 (C$^1$ or C$^2$), 16.1 (C$^{11}$).
81.6 (C^3), 35.8 (C^5), 33.6 (C^7), 24.2 (C^1 or C^2), 23.6 (C^6), 22.0 (C^1 or C^2). MS (EI) m/z 197 ([M-H]^+).

2,2,3,3,6-Pentamethyl-1,4-dioxaspiro[4,4]nonane (10). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.08–1.65 (m, 5H), 1.46–1.39 (m, 1H), 1.22–1.13 (m, 1H), 1.17 (s, 12H, Me), 0.97 (d, \(J = 6.4\) Hz, 3H, Me).

2-(3-Cyclohexenylmethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (12). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.65–5.58 (m, 2H, H^e and H^f), 5.13 (t, \(J = 5.4\) Hz, 1H, H^g), 2.18–2.10 (m, 1H, H^h), 2.05–1.98 (m, 2H, H^i), 1.80–1.66 (m, 3H, H^c, H^d and H^g), 1.54 (t, \(J = 5.8\) Hz, 2H, H^b), 1.33–1.20 (m, 1H, H^b), 1.17 (s, 12H, Me). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 126.9 (C^8 or C^9), 126.2 (C^8 or C^9), 99.5 (C^4), 81.5 (C^3), 43.3 (C^5), 32.0 (C^7), 29.7 (C^6), 29.0 (C^10), 24.9 (C^{11}), 24.2 (C^1 or C^2), 22.0 (C^1 or C^2). MS (EI) m/z 223 ([M-H]^+).
2-Benzyl-4,4,5,5-tetramethyl-1,3-dioxolane (2d)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
2-(p-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2e)

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) \]
2-(o-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2f)

^1^H NMR (400 MHz, CDCl$_3$)

^1^C NMR (100 MHz, CDCl$_3$)
2-\((m\text{-Nitrobenzyl})\)-4,4,5,5-tetramethyl-1,3-dioxolane (2g)

\[\text{\H{\text{H}}{\text{H}}} \ 1H \ 1H \ \text{H}^d \ 1H \ 1H \ 1H \ \text{H}^c \ 1H \ 1H \ \text{H}^e \ 1H \ 1H \]

\[^1\text{H NMR (400 MHz, CDCl}_3\)]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\)]
2-\((m\text{-Trifluoromethylbenzyl})\)-4,4,5,5-tetramethyl-1,3-dioxolane (2h)

\[1^1H\text{ NMR (400 MHz, CDCl}_3\text{)}\]

\[1^3C\text{ NMR (100 MHz, CDCl}_3\text{)}\]
2-(p-Methylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2i)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(o-Methylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2j)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(p-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2k)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(m-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2l)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(o-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2m)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(2-Naphthylmethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2n)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

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2-Naphthyl-4,4,5,5-tetramethyl-1,3-dioxolane

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$) (a mixture with 2n)
2-(Phenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5a)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(Phenoxymethyl)-2,4,4,5,5-pentamethyl-1,3-dioxolane (6a)

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{)}\ (a\ mixture\ with\ 5a) \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{)}\ (a\ mixture\ with\ 5a) \]
2-(p-Methoxycarbonylphenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5b)

\[
\begin{align*}
\text{Me} & \times 4 \\
12\text{H} & \\
\text{OMe} & \\
3\text{H} & \\
\end{align*}
\]

\[\text{H^9} \quad 2\text{H} \quad \text{H^d} \quad 2\text{H} \quad \text{H^g} \quad 1\text{H} \quad \text{H^c} \quad 2\text{H} \quad \text{H^b} \quad 2\text{H} \]

\[^1\text{H NMR (400 MHz, CDCl}	ext{3})\]

\[
\begin{align*}
\text{C}^9 & \\
\text{C}^8 & \\
\text{C}^7 & \\
\text{C}^{10} & \\
\text{C}^{11} & \\
\text{C}^4 & \\
\text{C}^3 & \\
\text{C}^6 & \\
\text{C}^{12} & \\
\text{C}^5 & \\
\text{C}^1 + \text{C}^2 & \\
\end{align*}
\]

\[^{13}\text{C NMR (100 MHz, CDCl}	ext{3})\]
2-(p-Methoxycarbonylphenoxyethyl)-2,4,4,5,5-pentamethyl-1,3-dioxolane (6b)

$^1$H NMR (400 MHz, CDCl₃) (a mixture with 5b)

$^{13}$C NMR (100 MHz, CDCl₃) (a mixture with 5b)
2-(2,6-Dimethylphenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5c)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(2,6-Dimethylphenoxyethyl)-2,4,4,5,5-pentamethyl-1,3-dioxolane (6c)

$^1$H NMR (400 MHz, CDCl$_3$) (a mixture with 5c)

$^{13}$C NMR (100 MHz, CDCl$_3$) (a mixture with 5c)
2-(4-Pentenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (9)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(3-Cyclohexenylmethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (12)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
References