

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, Kitaoyanishi-machi,
Nara 630-8506, Japan*

ura@cc.nara-wu.ac.jp

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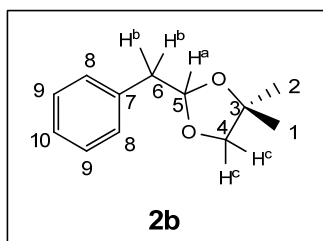
General Information

$\text{PdCl}_2(\text{MeCN})_2$,¹ 2-methyl-1,2-propanediol,² methyl 4-(allyloxy)benzoate³ and allyl 2,6-dimethylphenyl ether⁴ 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 MgSO_4 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 (^{13}C)) or a Bruker AV-300N (300 MHz (^1H), 75 MHz (^{13}C)) spectrometer. Chemical shift values (δ) were expressed relative to SiMe_4 . 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. \times 25 m). Mass spectra were recorded on a SHIMADZU GCMS-QP5050 spectrometer.

Reaction of Styrene with Several 1,2-Diols

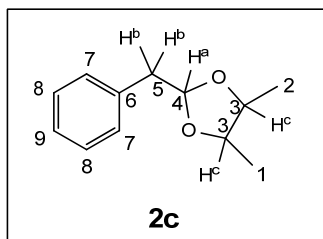
A procedure for 2-benzyl-4,4,5,5-tetramethyl-1,3-dioxolane (**2d**) is representative. To a reaction vessel, $\text{PdCl}_2(\text{MeCN})_2$ (31 mg, 0.12 mmol), *p*-benzoquinone (259 mg, 2.39 mmol), styrene (137 μL , 1.20 mmol) and dehydrated DMF (1.2 mL) were added. Pinacol (1.42 g, 12.0 mmol) was then added, and the reaction mixture was stirred at 60 $^\circ\text{C}$ 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 CDCl_3 . 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**⁵, **3a**^{5,6}, **3b**⁷ and **3c**⁶ were in accordance with those reported in the literature. The compound data for **2b**, **2c** and **2d** are listed below.



2-Benzyl-4,4-dimethyl-1,3-dioxolane (2b). ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.13 (m, 5H, arom.), 5.20 (t, $J = 4.5$ Hz, 1H, H^a), 3.59 (d, $J = 7.8$ Hz, 1H, H^c), 3.54 (d, $J = 7.8$ Hz, 1H, H^c), 2.97 (dd, $J = 14.1, 4.2$ Hz, 1H,

H^b), 2.90 (dd, $J = 14.1, 5.1$ Hz, 1H, H^b), 1.26 (s, 3H, Me), 1.24 (s, 3H, Me). ¹³C NMR (75 MHz, CDCl₃) δ 136.2 (C⁷), 129.8 (C⁸ or C⁹), 128.1 (C⁸ or C⁹), 126.4 (C¹⁰), 103.9 (C⁵), 78.6 (C³), 76.0 (C⁴), 41.5 (C⁶), 26.6 (Me), 25.0 (Me).

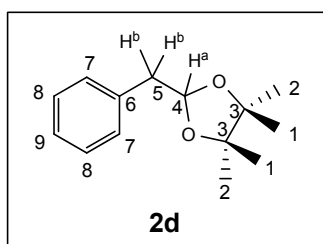


2-Benzyl-4,5-dimethyl-1,3-dioxolane (2c). Compound **2c** was isolated as a mixture of three diastereomers.

For isomer I: ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.14 (m, 5H, arom.), 5.05 (t, $J = 4.8$ Hz, 1H, H^a), 4.13–4.04 (m, 2H, H^c), 2.95 (d, $J = 4.8$ Hz, 2H, H^b), 1.13–1.05 (m, 6H, Me). ¹³C NMR (75 MHz, CDCl₃) δ 136.3 (C⁶), 129.8 (C⁷ or C⁸), 128.2 (C⁷ or C⁸), 126.5 (C⁹), 103.2 (C⁴), 74.6 (C³ and C^{3'}), 41.7 (C⁵), 15.4 (Me).

For isomer II: ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.14 (m, 5H, arom.), 5.23 (t, $J = 4.6$ Hz, 1H, H^a), 3.63–3.45 (m, 2H, H^c), 2.93 (d, $J = 4.6$ Hz, 2H, H^b), 1.23 (d, $J = 6.0$ Hz, 3H, Me), 1.18 (d, $J = 6.0$ Hz, 3H, Me). ¹³C NMR (CDCl₃, 75 MHz) δ 136.3 (C⁶), 129.8 (C⁷ or C⁸), 128.2 (C⁷ or C⁸), 126.4 (C⁹), 103.4 (C⁴), 79.7 (C³), 78.1 (C^{3'}), 41.6 (C⁵), 17.1 (Me), 16.9 (Me).

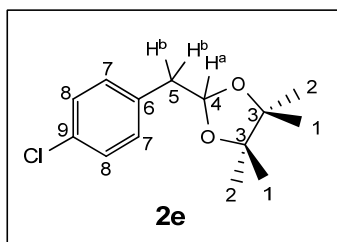
For isomer III: ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.14 (m, 5H, arom.), 5.37 (t, $J = 4.4$ Hz, 1H, H^a), 4.19–4.10 (m, 2H, H^c), 2.87 (d, $J = 4.4$ Hz, 2H, H^b), 1.13–1.05 (m, 6H, Me). ¹³C NMR (CDCl₃, 75 MHz) δ 136.3 (C⁶), 129.8 (C⁷ or C⁸), 128.2 (C⁷ or C⁸), 126.4 (C⁹), 102.7 (C⁴), 74.3 (C³ and C^{3'}), 41.9 (C⁵), 14.2 (Me).



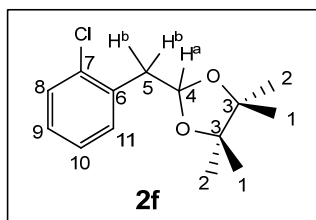
2-Benzyl-4,4,5,5-tetramethyl-1,3-dioxolane (2d). ¹H NMR (300 MHz, CDCl₃) δ 7.30–7.15 (m, 5H, arom.), 5.21 (t, $J = 4.9$ Hz, 1H, H^a), 2.89 (d, $J = 4.9$ Hz, 2H, H^b), 1.16 (s, 6H, Me), 1.15 (s, 6H, Me). ¹³C NMR (75 MHz, CDCl₃) δ 136.6 (C⁶), 129.8 (C⁷ or C⁸), 128.1 (C⁷ or C⁸), 126.3 (C⁹), 101.1 (C⁴), 81.9 (C³), 43.1 (C⁵), 24.1 (C¹ or C²), 22.0 (C¹ or C²). MS (EI) m/z 219 ([M-H]⁺).

Reaction of Vinylarenes with Pinacol

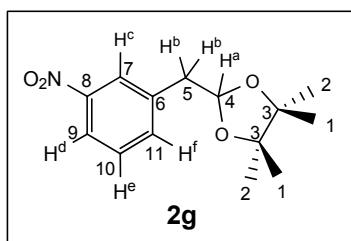
Same procedure was applied as described above for **2d**. The products were obtained as colorless oils.



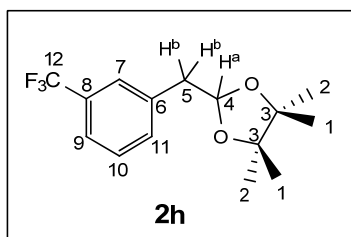
2-(*p*-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2e). ^1H NMR (400 MHz, CDCl_3) δ 7.23 (d, $J = 8.3$ Hz, 2H, arom.), 7.16 (d, $J = 8.3$ Hz, 2H, arom.), 5.17 (t, $J = 4.9$ Hz, 1H, H^a), 2.85 (d, $J = 4.9$ Hz, 2H, H^b), 1.16 (s, 6H, Me), 1.13 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 135.0 (C^6 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 ($[\text{M}-\text{H}]^+$).



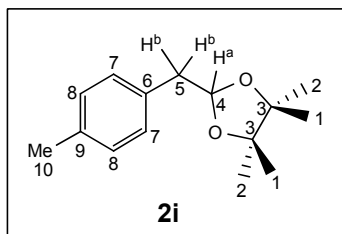
2-(*o*-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2f). ^1H NMR (400 MHz, CDCl_3) δ 7.34–7.30 (m, 2H, arom.), 7.20–7.11 (m, 2H, arom.), 5.23 (t, $J = 5.1$ Hz, 1H, H^a), 3.06 (d, $J = 5.1$ Hz, 2H, H^b), 1.20 (s, 6H, Me), 1.17 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 134.5 (C^6), 134.5 (C^7), 132.1 (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 ($[\text{M}-\text{H}]^+$).



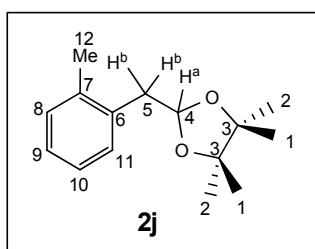
2-(*m*-Nitrobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2g). ^1H NMR (400 MHz, CDCl_3) δ 8.11 (s, 1H, H^c), 8.07 (dt, $J = 8.0, 1.1$ Hz, 1H, H^d), 7.57 (dd, $J = 7.6, 0.4$ Hz, 1H, H^f), 7.43 (t, $J = 7.9$ Hz, 1H, H^e), 5.23 (t, $J = 4.7$ Hz, 1H, H^a), 2.98 (d, $J = 4.7$ Hz, 2H, H^b), 1.16 (s, 6H, Me), 1.10 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 148.1 (C^8), 138.4 (C^6), 136.4 (C^{11}), 128.9 (C^{10}), 124.9 (C^7), 121.6 (C^9), 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 ($[\text{M}-\text{H}]^+$).



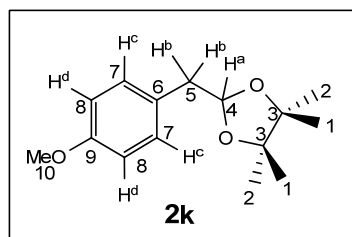
2-(*m*-Trifluoromethylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2h). ^1H NMR (400 MHz, CDCl_3) δ 7.50–7.34 (m, 4H, arom.), 5.22 (t, $J = 4.7$ Hz, 1H, H^a), 2.94 (d, $J = 4.7$ Hz, 2H, H^b), 1.16 (s, 6H, Me), 1.11 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 137.3 (C^6), 133.5 (q, $J_{\text{CF}} = 1.3$ Hz, C^{10}), 130.3 (q, $J_{\text{CF}} = 31.8$ Hz, C^8), 128.5 (C^{11}), 126.8 (q, $J_{\text{CF}} = 3.8$ Hz, C^7 or C^9), 124.2 (q, $J_{\text{CF}} = 272$ Hz, C^{12}), 123.3 (q, $J_{\text{CF}} = 3.8$ 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 ($[\text{M}-\text{H}]^+$).



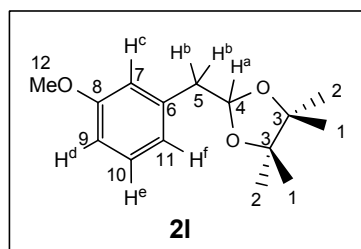
2-(*p*-Methylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2i). ^1H NMR (400 MHz, CDCl_3) δ 7.15 (d, $J = 8.0$ Hz, 2H, arom.), 7.09 (d, $J = 8.0$ Hz, 2H, arom.), 5.20 (t, $J = 5.0$ Hz, 1H, H^a), 2.86 (d, $J = 5.0$ Hz, 2H, H^b), 2.31 (s, 3H, Me), 1.19 (s, 6H, Me), 1.17 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 135.8 (C^6 or C^9), 133.5 (C^6 or C^9), 129.7 (C^7 or C^8), 128.9 (C^7 or C^8), 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 ($[\text{M}-\text{H}]^+$).



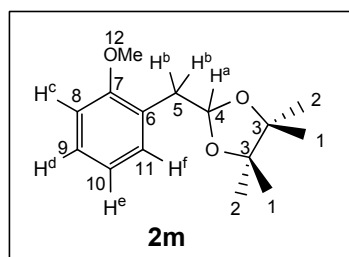
2-(*o*-Methylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2j). ^1H NMR (400 MHz, CDCl_3) δ 7.21–7.18 (m, 1H, arom.), 7.14–7.09 (m, 3H, arom.), 5.23 (t, $J = 5.0$ Hz, 1H, H^a), 2.91 (d, $J = 5.0$ Hz, 2H, H^b), 2.33 (s, 3H, Me), 1.16 (s, 6H, Me), 1.15 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 136.9 (C^6 or C^7), 135.0 (C^6 or C^7), 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 ($[\text{M}-\text{H}]^+$).



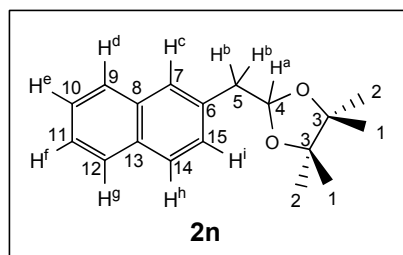
2-(*p*-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2k). ^1H NMR (400 MHz, CDCl_3) δ 7.16 (d, $J = 8.4$ Hz, 2H, H^c), 6.82 (d, $J = 8.4$ Hz, 2H, H^d), 5.17 (t, $J = 5.0$ Hz, 1H, H^a), 3.76 (s, 3H, OMe), 2.78 (d, $J = 5.0$ Hz, 2H, H^b), 1.16 (s, 6H, Me), 1.16 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 158.2 (C^9), 130.8 (C^7), 128.7 (C^6), 113.6 (C^8), 101.2 (C^4), 81.9 (C^3), 55.2 (C^{10}), 42.1 (C^5), 24.1 (C^1 or C^2), 22.1 (C^1 or C^2). MS (EI) m/z 249 ($[\text{M}-\text{H}]^+$).



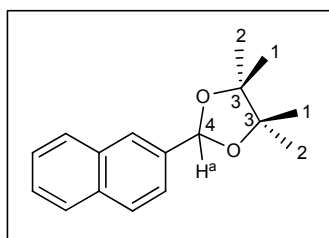
2-(*m*-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2l). ^1H NMR (400 MHz, CDCl_3) δ 7.19 (t, $J = 7.9$ Hz, 1H, H^e), 6.84 (dd, $J = 7.5, 0.4$ Hz, 1H, H^d or H^f), 6.81 (s, 1H, H^c), 6.75 (dd, $J = 8.2, 2.6$ Hz, 1H, H^d or H^f), 5.22 (t, $J = 5.0$ Hz, 1H, H^a), 3.78 (s, 3H, OMe), 2.87 (d, $J = 5.0$ Hz, 2H, H^b), 1.17 (s, 12H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 159.4 (C^8), 138.1 (C^6), 129.1 (C^{10}), 122.2 (C^9 or C^{11}), 115.6 (C^7), 111.7 (C^9 or C^{11}), 100.0 (C^4), 81.9 (C^3), 55.1 (C^{12}), 43.2 (C^5), 24.1 (C^1 or C^2), 22.0 (C^1 or C^2). MS (EI) m/z 249 ($[\text{M}-\text{H}]^+$).



2-(*o*-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2m). ^1H NMR (400 MHz, CDCl_3) δ 7.24–7.20 (m, 1H, H^f), 7.21–7.16 (dt, $J = 1.7, 7.8$ Hz, 1H, H^d), 6.88 (dt, $J = 0.8, 7.4$ Hz, 1H, H^e), 6.82 (d, $J = 8.2$ Hz, 1H, H^c), 5.26 (t, $J = 5.2$ Hz, 1H, H^a), 3.79 (s, 3H, OMe), 2.93 (d, $J = 5.2$ Hz, 2H, H^b), 1.20 (s, 6H, Me), 1.16 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 157.6 (C^7), 131.5 (C^{11}), 127.7 (C^9), 125.2 (C^6), 120.4 (C^{10}), 110.3 (C^8), 100.1 (C^4), 81.7 (C^3), 55.3 (C^{12}), 37.5 (C^5), 24.1 (C^1 or C^2), 22.1 (C^1 or C^2). MS (EI) m/z 249 ($[\text{M}-\text{H}]^+$).



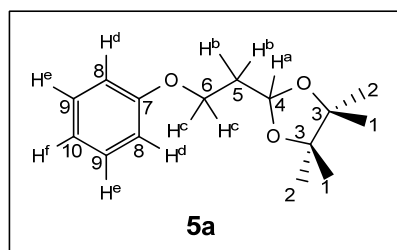
2-(2-Naphthylmethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2n). ^1H NMR (400 MHz, CDCl_3) δ 7.81–7.75 (m, 3H, H^d , H^e and H^h), 7.70 (s, 1H, H^c), 7.47–7.39 (m, 3H, H^e , H^f and H^i), 5.33 (t, $J = 4.9$ Hz, 1H, H^a), 3.08 (d, $J = 4.9$ Hz, 2H, H^b), 1.19 (s, 12H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 134.2 (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}), 127.6 (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^+).



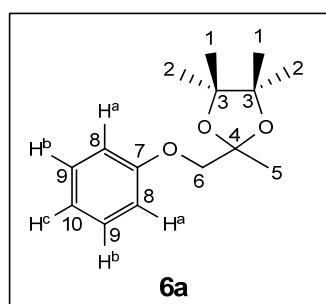
2-Naphthyl-4,4,5,5-tetramethyl-1,3-dioxolane. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (s, 1H, arom.), 7.87–7.79 (m, 3H, arom.), 7.60 (d, $J = 8.6$ Hz, 1H, arom.), 7.50–7.43 (m, 2H, arom.), 6.14 (s, 1H, H^a), 1.36 (s, 6H, Me), 1.30 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 137.2 (arom.), 133.5 (arom.), 133.0 (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

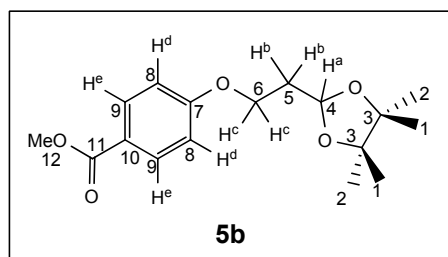
Same procedure was applied as described above for **2d**. The products were obtained as colorless oils.



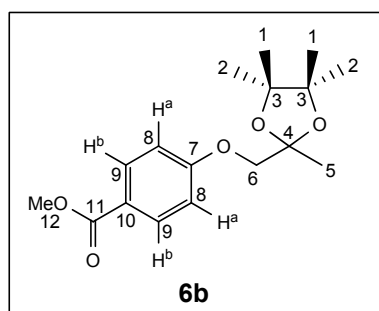
2-(Phenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5a). ^1H NMR (400 MHz, CDCl_3) δ 7.27–7.22 (m, 2H, H^e), 6.92–6.86 (m, 3H, H^d and H^f), 5.25 (t, $J = 5.3$ Hz, 1H, H^a), 4.08 (t, $J = 6.7$ Hz, 2H, H^c), 2.10–2.05 (m, 2H, H^b), 1.19 (s, 6H, Me), 1.19 (s, 6H, Me). ^{13}C NMR (400 MHz, CDCl_3) δ 158.8 (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^+).



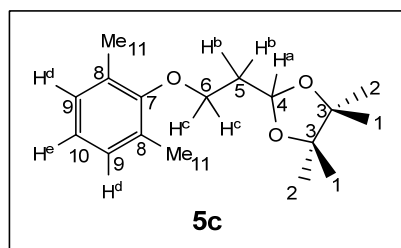
2-(Phenoxymethyl)-2,4,4,5,5-pentamethyl-1,3-dioxolane (6a). Compound **6a** was obtained as a mixture with **5a**. ^1H NMR (400 MHz, CDCl_3) δ 7.27–7.22 (m, 2H, H^b), 6.92–6.86 (m, 3H, H^a and H^c), 3.86 (s, 2H, CH_2), 1.56 (s, 3H, Me), 1.30 (s, 6H, Me), 1.25 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 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 ($[\text{M}-\text{CH}_3]^+$).



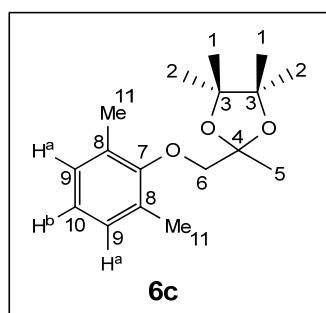
2-(p-Methoxycarbonylphenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5b). ^1H NMR (400 MHz, CDCl_3) δ 7.93 (dd, $J = 9.0, 1.0$ Hz, 2H, H^e), 6.87 (dd, $J = 8.9, 0.9$ Hz, 2H, H^d), 5.22 (t, $J = 5.2$ Hz, 1H, H^a), 4.11 (t, $J = 6.6$ Hz, 2H, H^c), 3.82 (s, 3H, OMe), 2.10–2.04 (m, 2H, H^b), 1.18 (s, 6H, Me), 1.17 (s, 6H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 166.8 (C^{11}), 162.6 (C^7), 131.5 (C^9), 122.4 (C^{10}), 114.0 (C^8), 97.8 (C^4), 82.0 (C^3), 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**. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (dd, $J = 9.0, 1.0$ Hz, 2H, H^b), 6.91 (d, $J = 9.0$ Hz, 2H, H^a), 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) δ 166.7 (C^{11}), 162.5 (C^7), 131.5 (C^9), 122.7 (C^{10}), 114.2 (C^8), 105.2 (C^4), 83.2 (C^3), 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 ($[\text{M}-\text{CH}_3]^+$).



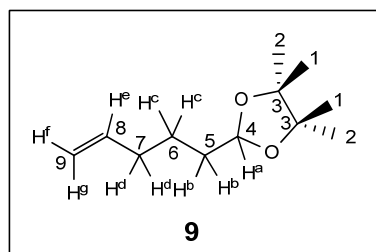
2-(2,6-Dimethylphenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5c). ^1H NMR (400 MHz, CDCl_3) δ 6.98 (d, $J = 7.3$ Hz, 2H, H^d), 6.89 (t, $J = 7.4$ Hz, 1H, H^e), 5.33 (t, $J = 5.0$ Hz, 1H, H^a), 3.84 (dt, $J = 0.8, 6.7$ Hz, 2H, H^c), 2.27 (s, 6H, Me), 2.13–2.07 (m, 2H, H^b), 1.20 (s, 12H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 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**. ^1H NMR (400 MHz, CDCl_3) δ 6.98 (d, $J = 7.3$ Hz, 2H, H^a), 6.89 (t, $J = 7.4$ Hz, 1H, H^b), 3.67 (s, 2H, CH_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) δ 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 ($[\text{M}-\text{CH}_3]^+$).

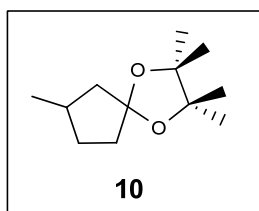
Reaction of 1,5-Dienes with Pinacol

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

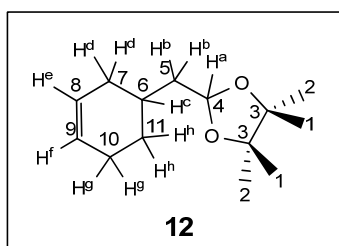


2-(4-Pentenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (9). ^1H NMR (400 MHz, CDCl_3) δ 5.83–5.72 (m, 1H, H^e), 5.01 (t, $J = 4.8$ Hz, 1H, H^a), 5.00–4.89 (m, 2H, H^f and H^g), 2.09–2.03 (m, 2H, H^d), 1.60–1.54 (m, 2H, H^b), 1.52–1.43 (m, 2H, H^c), 1.16 (s, 12H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ 138.5 (C^8), 114.6 (C^9), 100.8 (C^4),

81.6 (C³), 35.8 (C⁵), 33.6 (C⁷), 24.2 (C¹ or C²), 23.6 (C⁶), 22.0 (C¹ or C²). MS (EI) m/z 197 ([M-H]⁺).

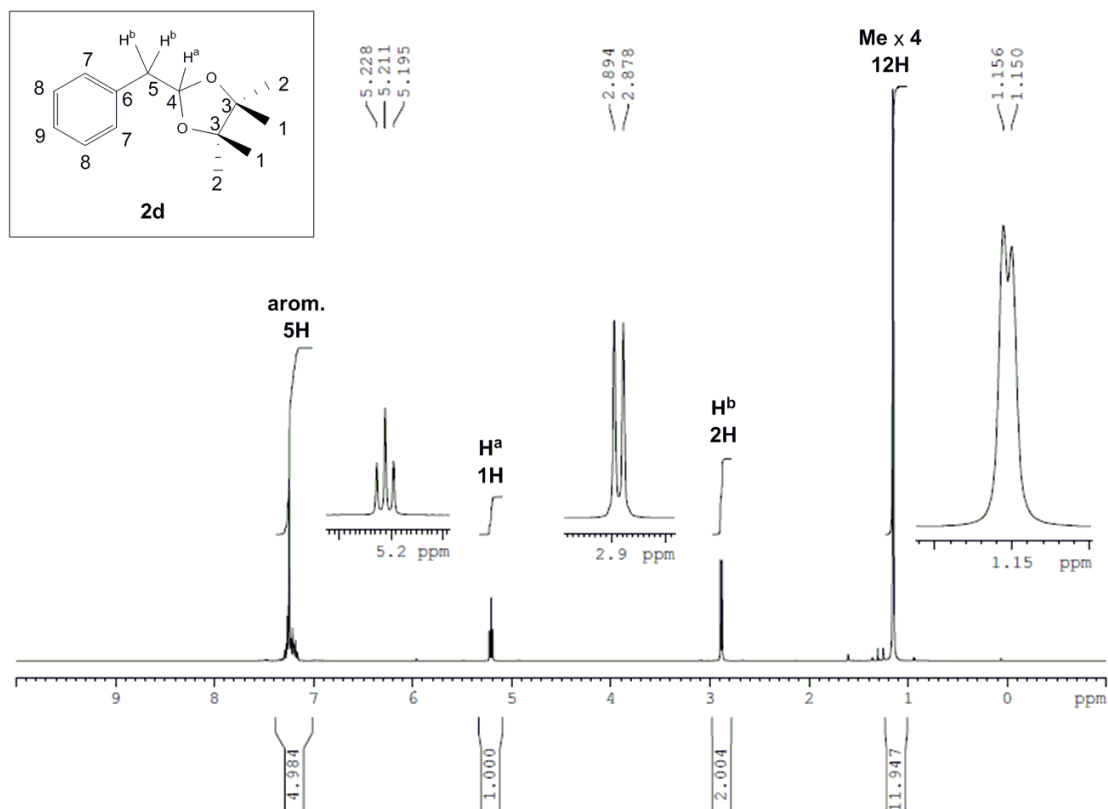


2,2,3,3,6-Pentamethyl-1,4-dioxaspiro[4.4]nonane (10). ¹H NMR (400 MHz, CDCl₃) δ 2.08–1.65 (m, 5H), 1.46–1.39 (m, 1H), 1.22–1.13 (m, 1H), 1.17 (s, 12H, Me), 0.97 (d, J = 6.4 Hz, 3H, Me).

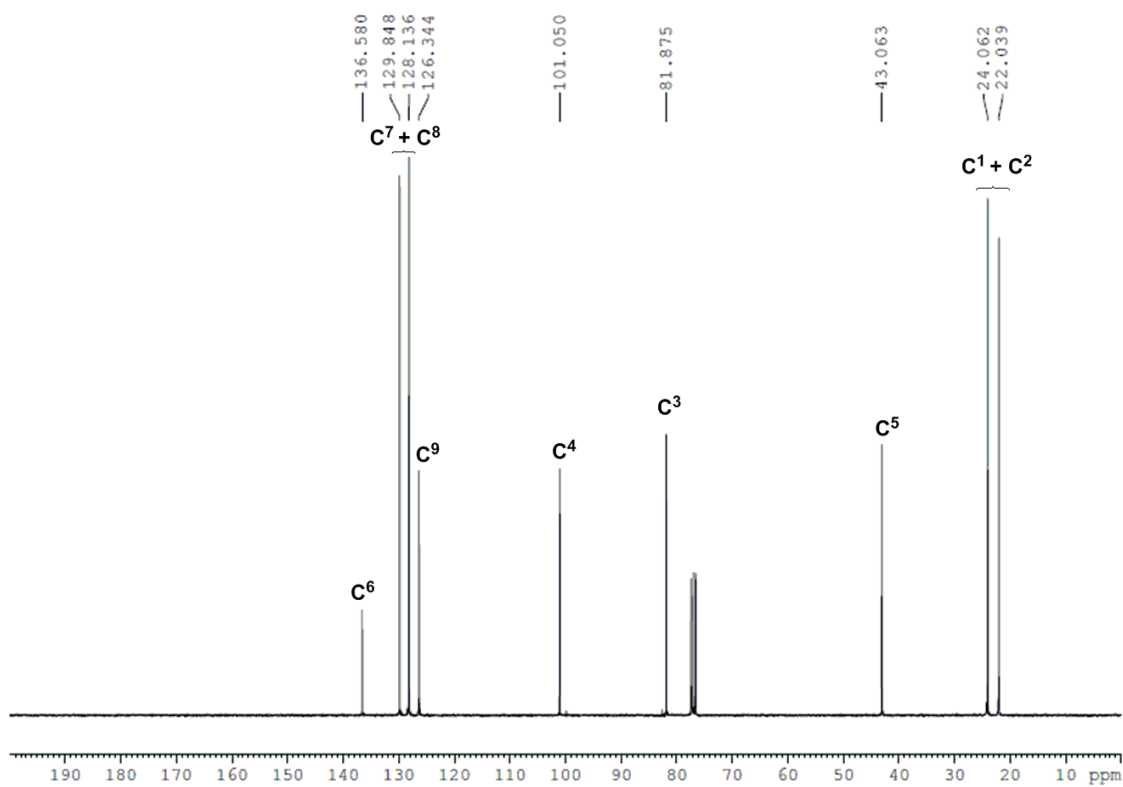


2-(3-Cyclohexenylmethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (12). ¹H NMR (400 MHz, CDCl₃) δ 5.65–5.58 (m, 2H, H^e and H^f), 5.13 (t, J = 5.4 Hz, 1H, H^a), 2.18–2.10 (m, 1H, H^d), 2.05–1.98 (m, 2H, H^h), 1.80–1.66 (m, 3H, H^c, H^d and H^e), 1.54 (t, J = 5.8 Hz, 2H, H^b), 1.33–1.20 (m, 1H, H^g), 1.17 (s, 12H, Me). ¹³C NMR (100 MHz, CDCl₃) δ 126.9 (C⁸ or C⁹), 126.2 (C⁸ or C⁹), 99.5 (C⁴), 81.5 (C³), 43.3 (C⁵), 32.0 (C⁷), 29.7 (C⁶), 29.0 (C¹⁰), 24.9 (C¹¹), 24.2 (C¹ or C²), 22.0 (C¹ or C²). MS (EI) m/z 223 ([M-H]⁺).

2-Benzyl-4,4,5,5-tetramethyl-1,3-dioxolane (2d)

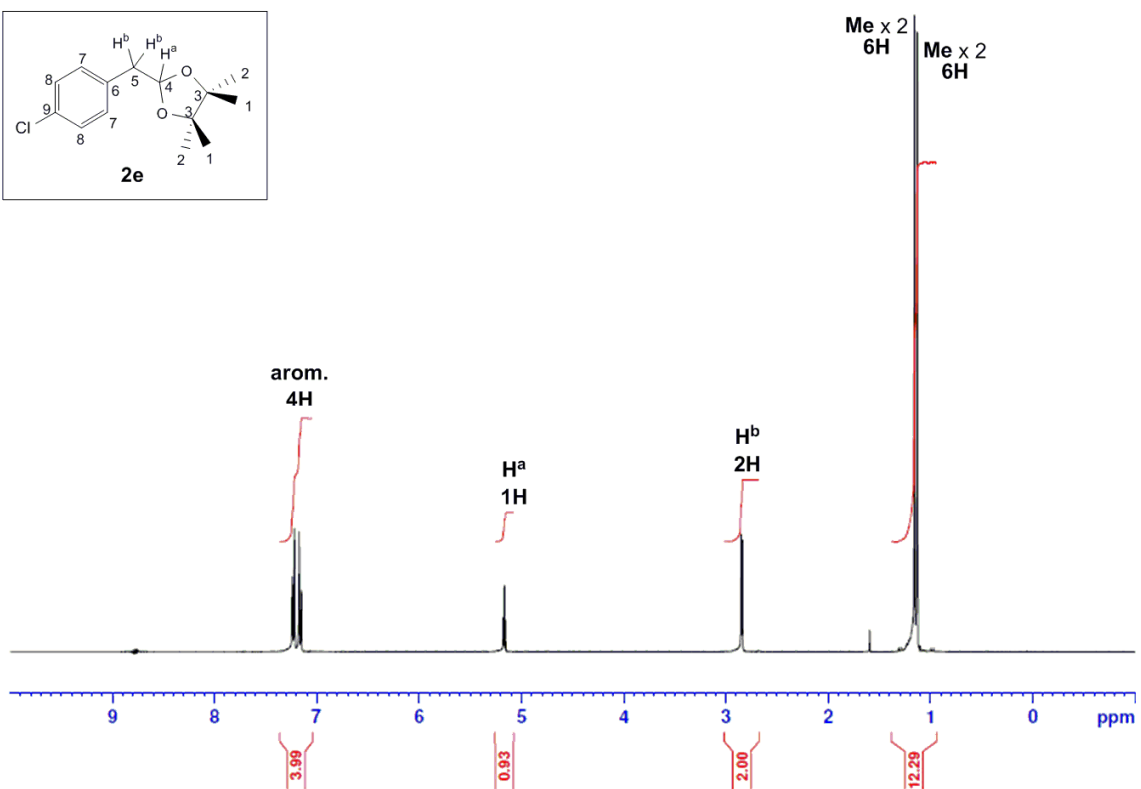
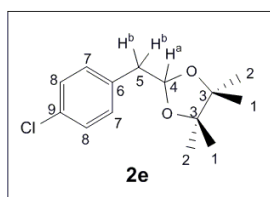


¹H NMR (300 MHz, CDCl₃)

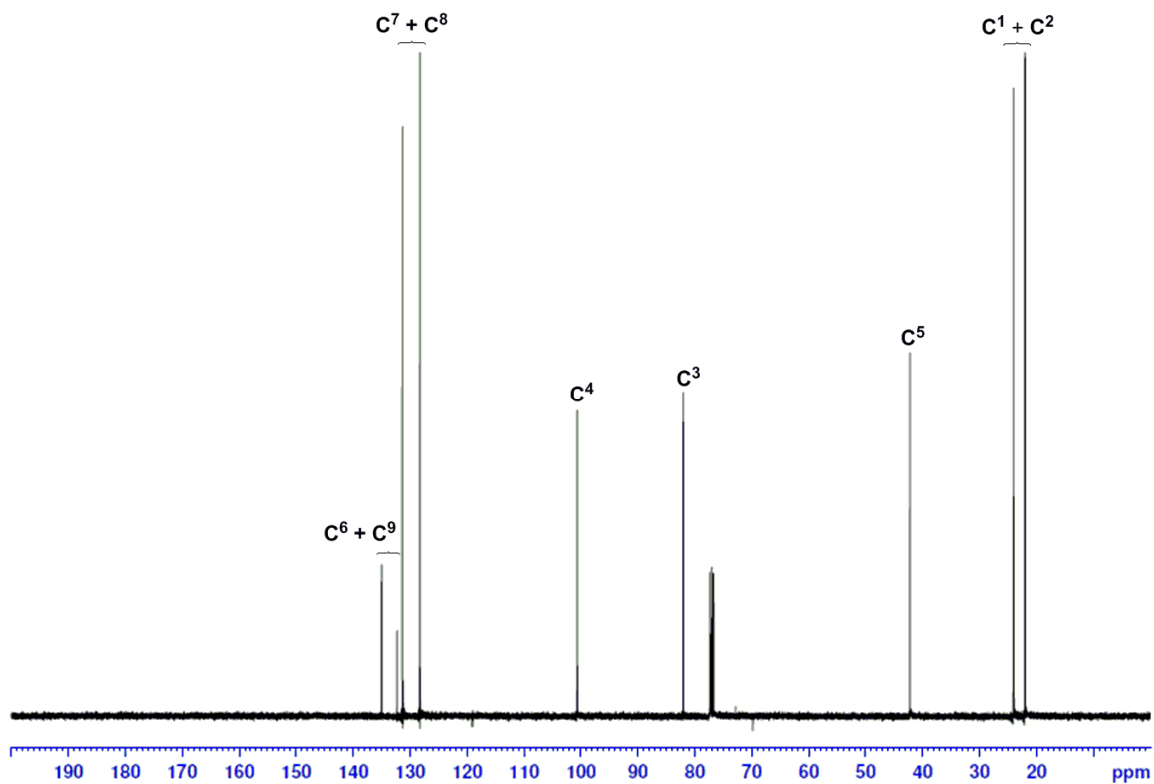


¹³C NMR (75 MHz, CDCl₃)

2-(*p*-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2e)

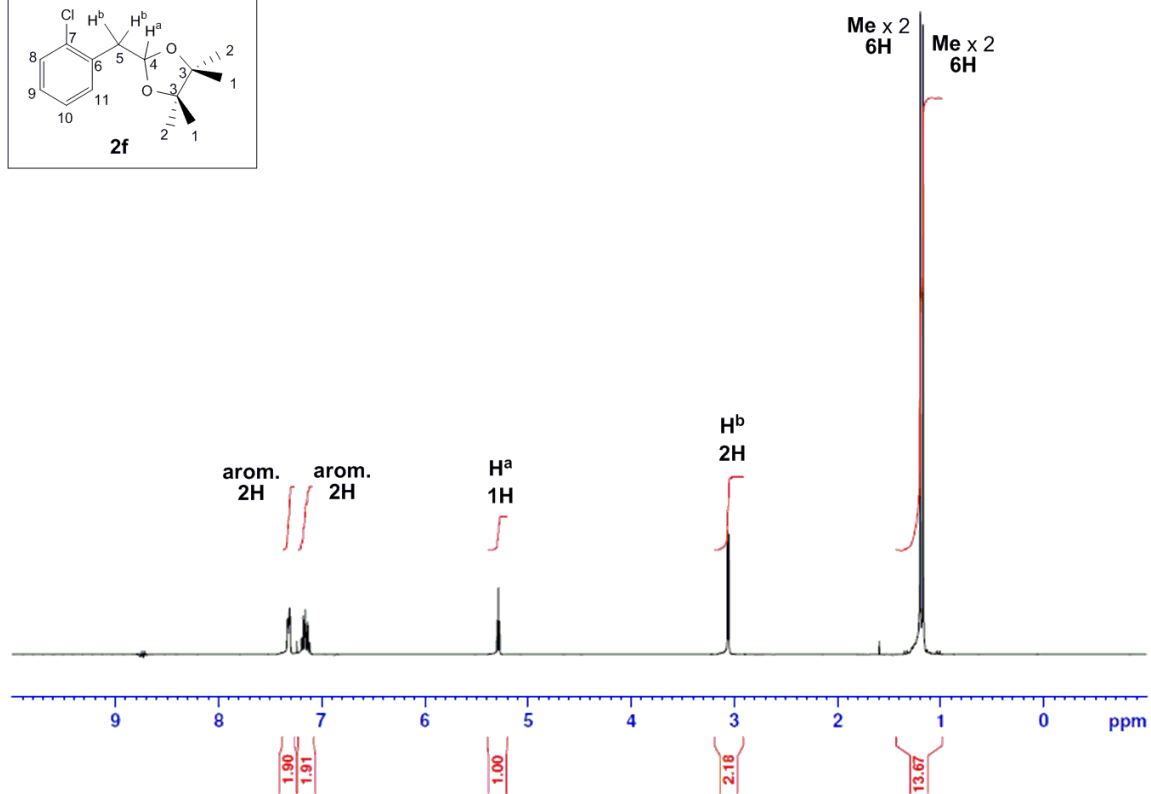
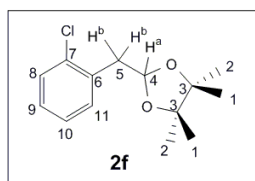


¹H NMR (400 MHz, CDCl₃)

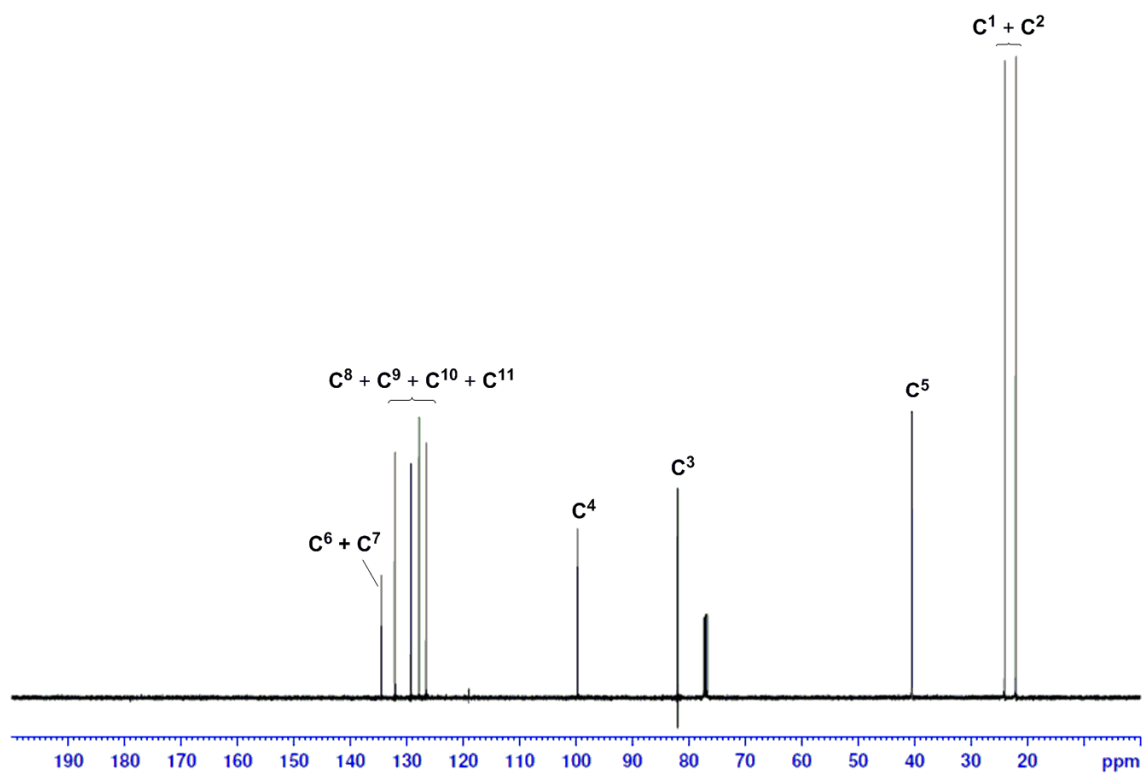


¹³C NMR (100 MHz, CDCl₃)

2-(*o*-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (**2f**)

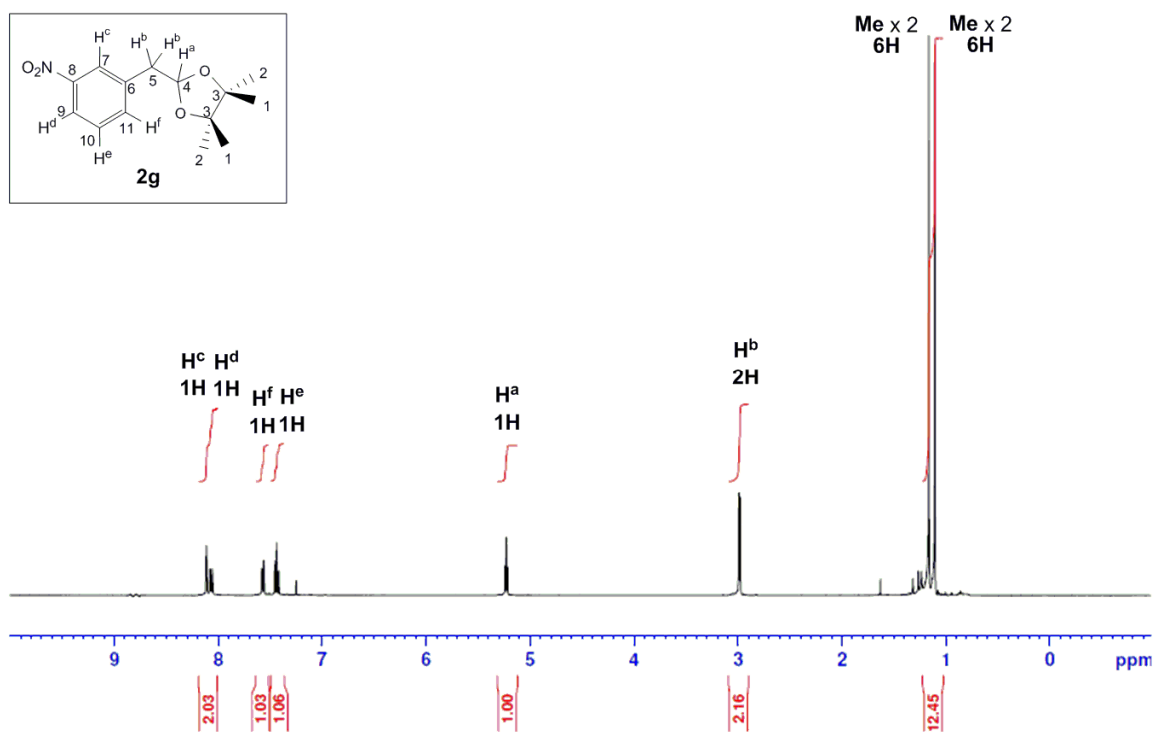
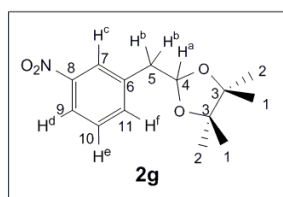


^1H NMR (400 MHz, CDCl_3)

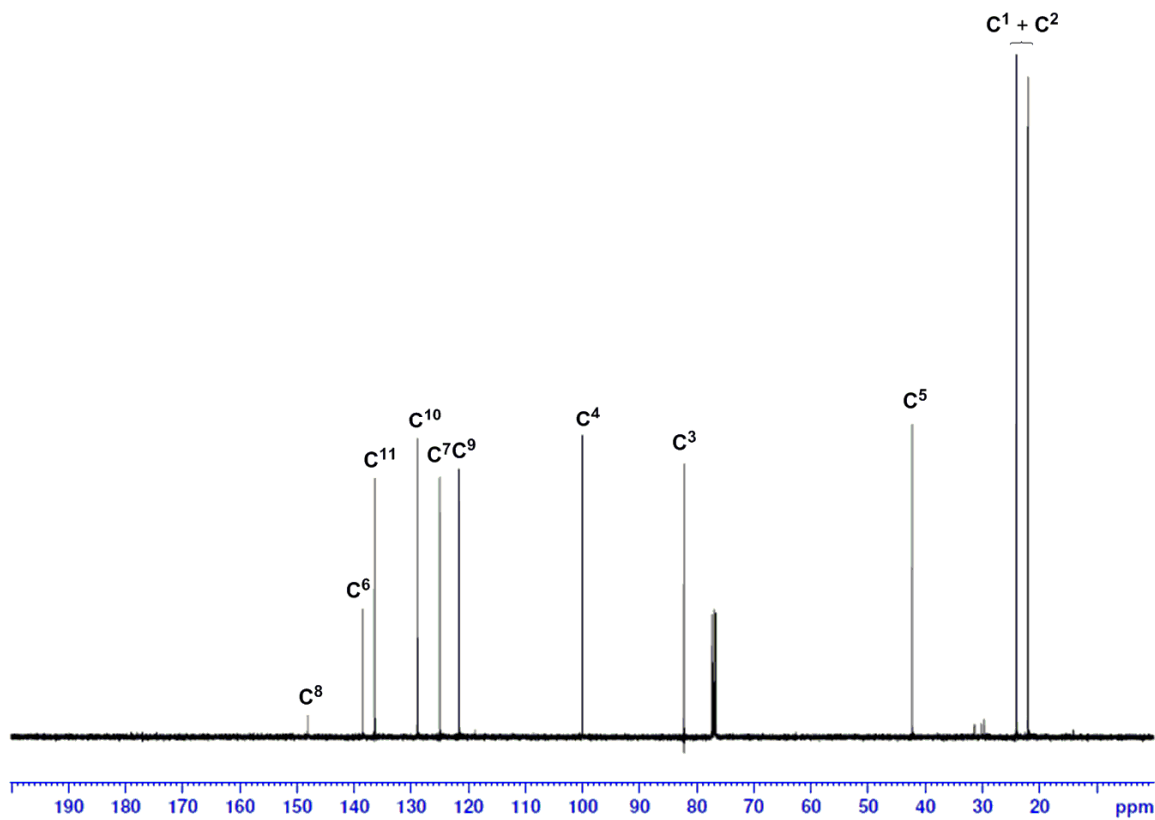


^{13}C NMR (100 MHz, CDCl_3)

2-(*m*-Nitrobenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2g)

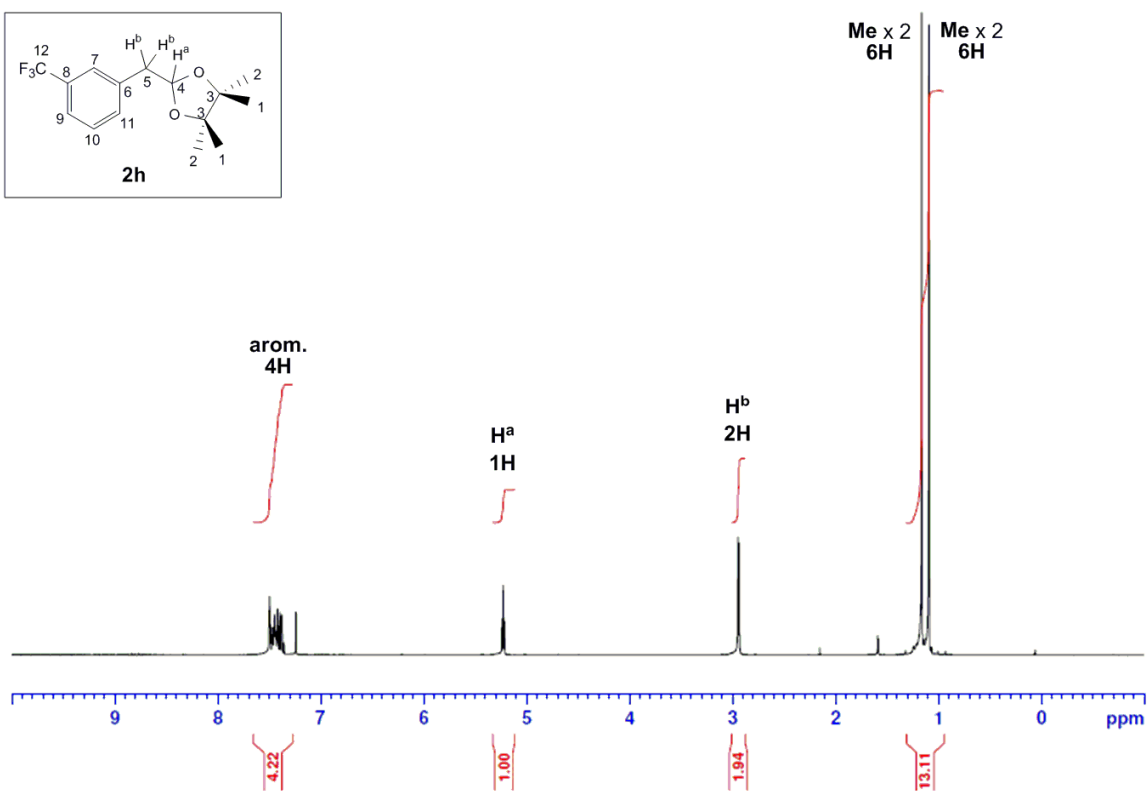
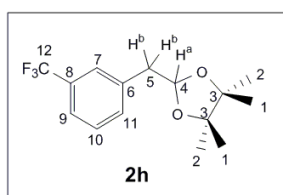


¹H NMR (400 MHz, CDCl₃)

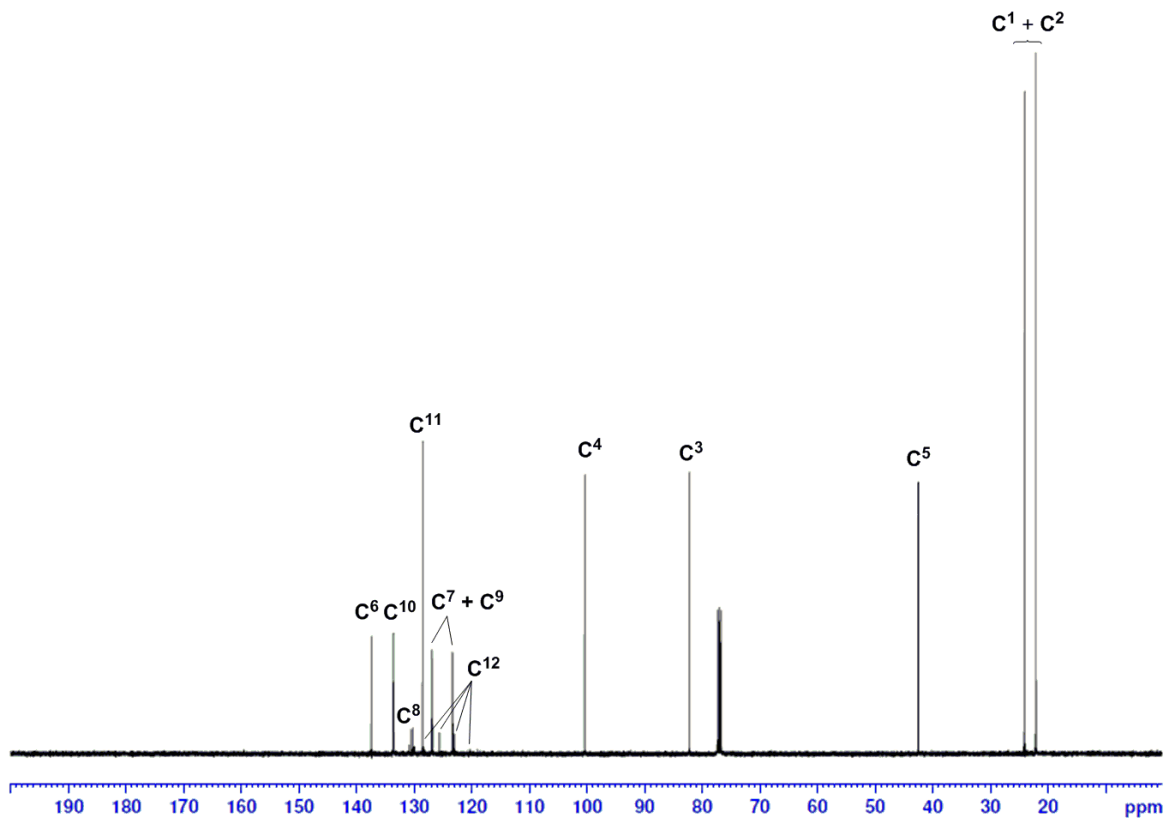


¹³C NMR (100 MHz, CDCl₃)

2-(*m*-Trifluoromethylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2h)

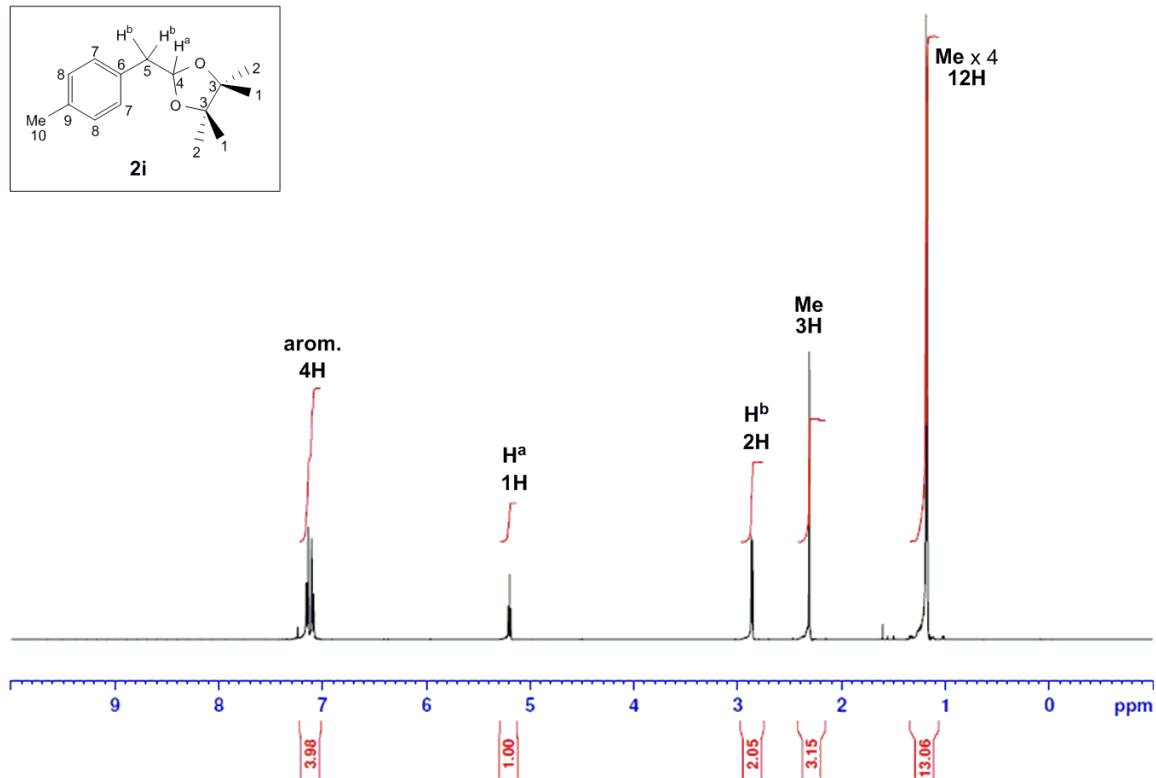
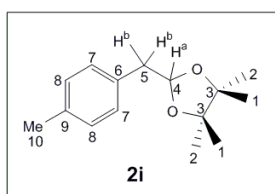


¹H NMR (400 MHz, CDCl₃)

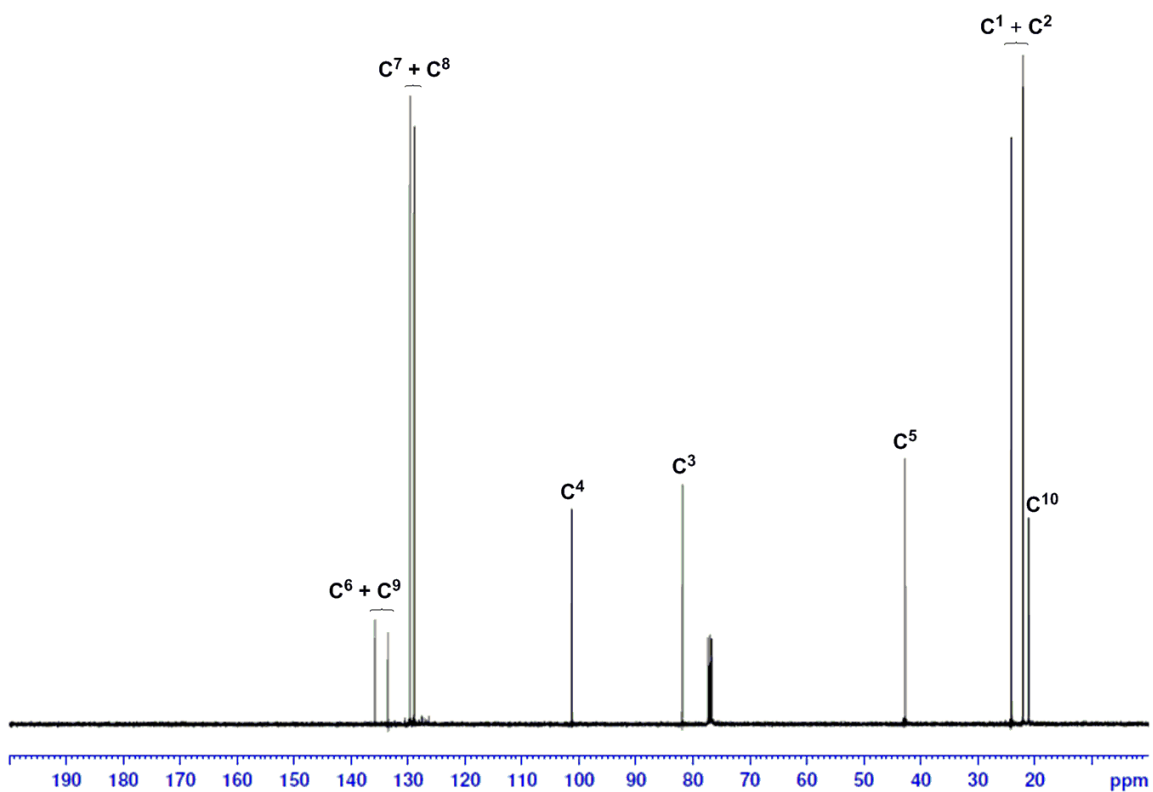


¹³C NMR (100 MHz, CDCl₃)

2-(*p*-Methylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (**2i**)

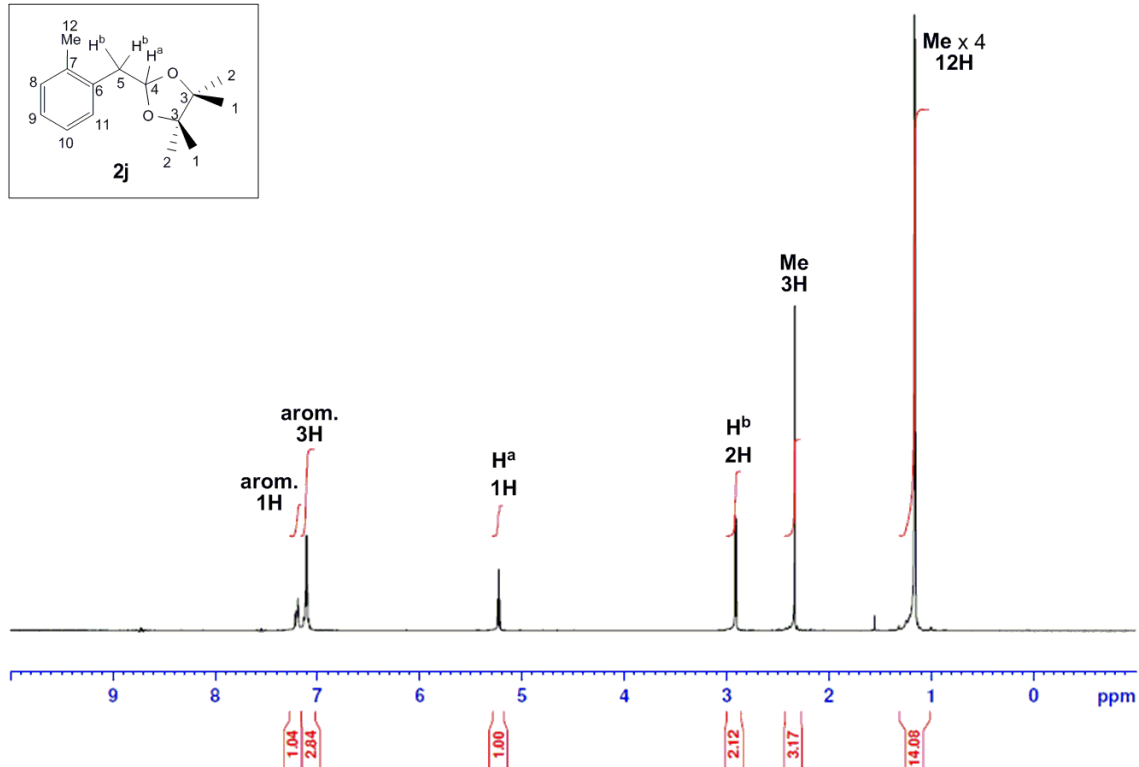
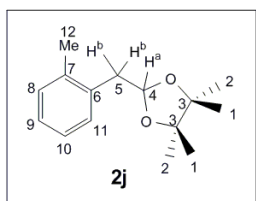


$^1\text{H NMR}$ (400 MHz, CDCl_3)

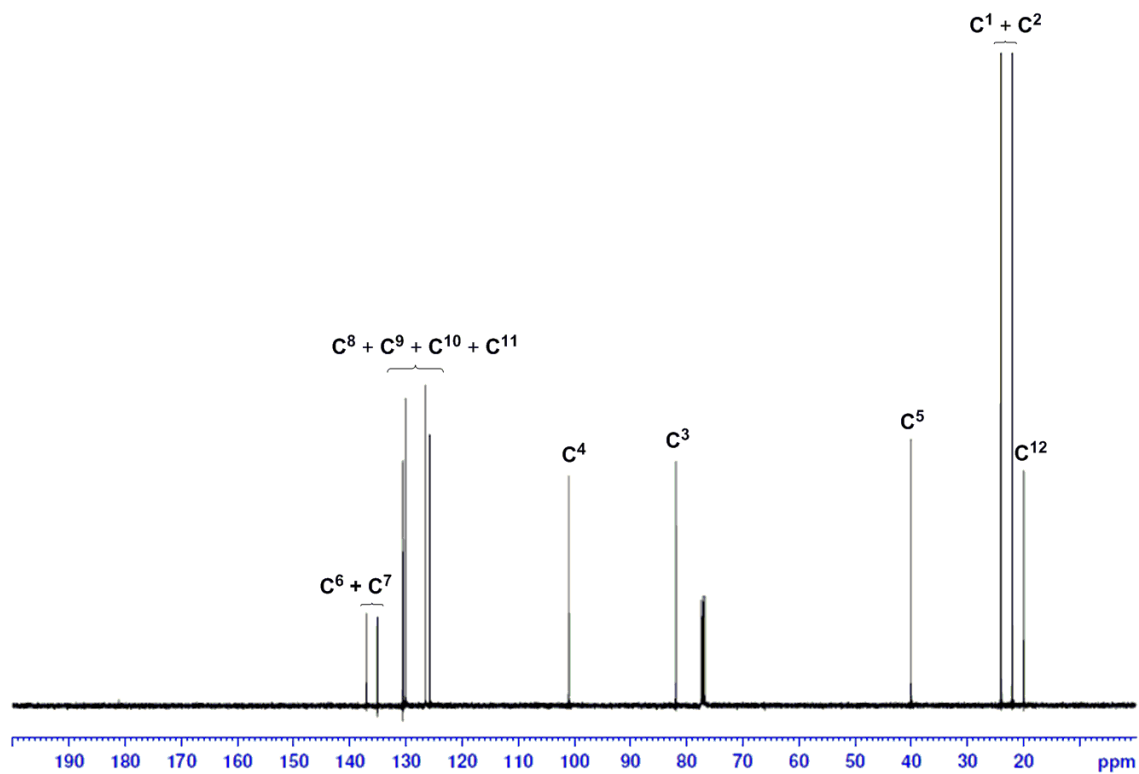


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

2-(*o*-Methylbenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (**2j**)

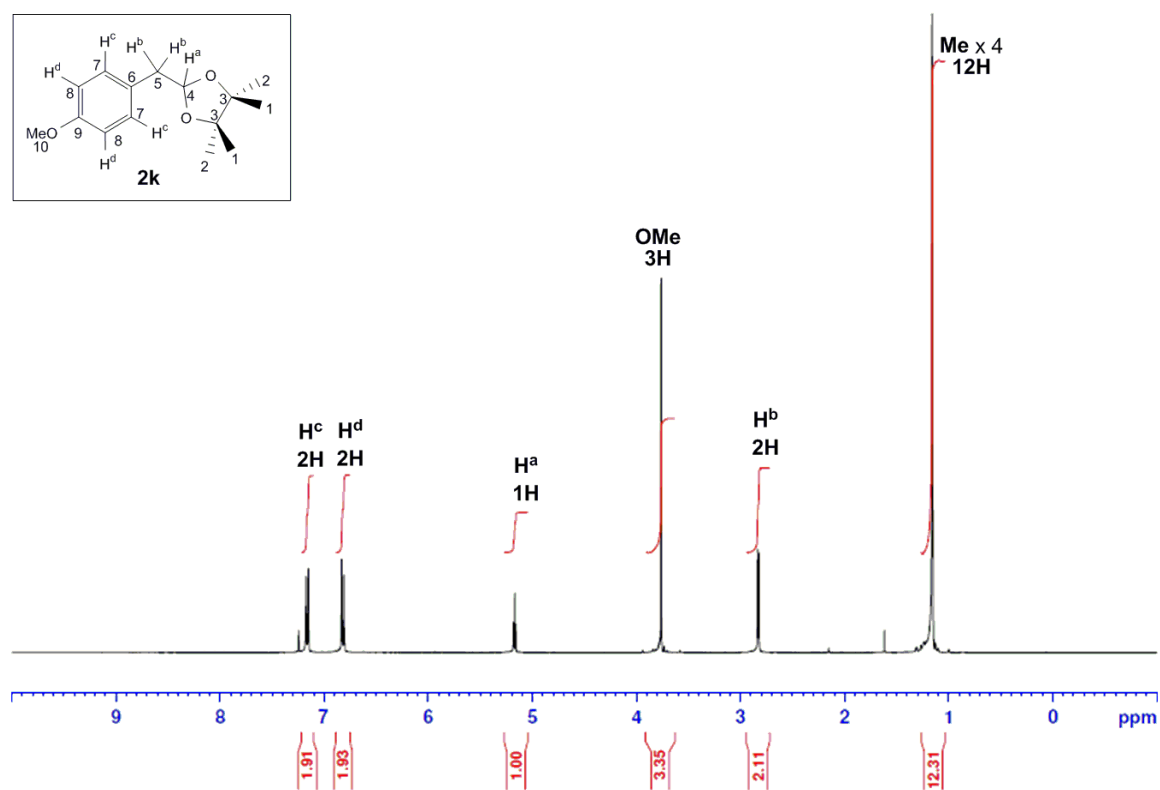
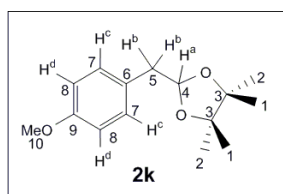


¹H NMR (400 MHz, CDCl₃)

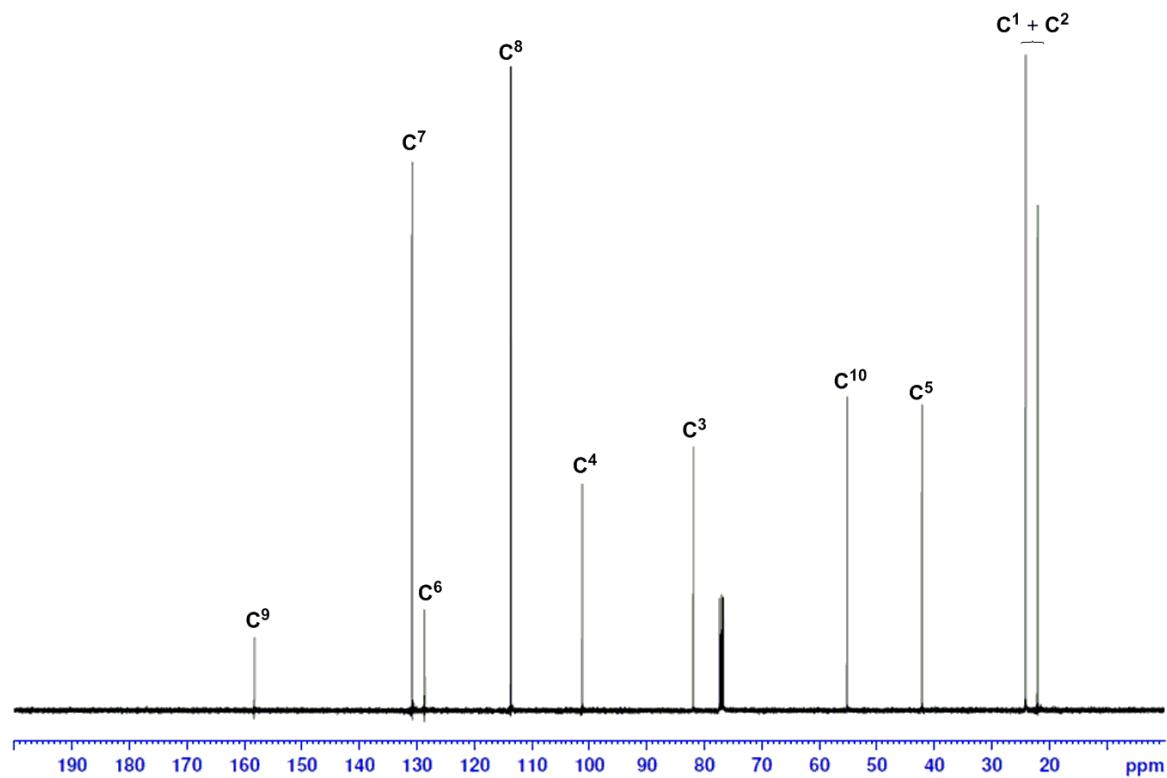


¹³C NMR (100 MHz, CDCl₃)

2-(*p*-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2k)

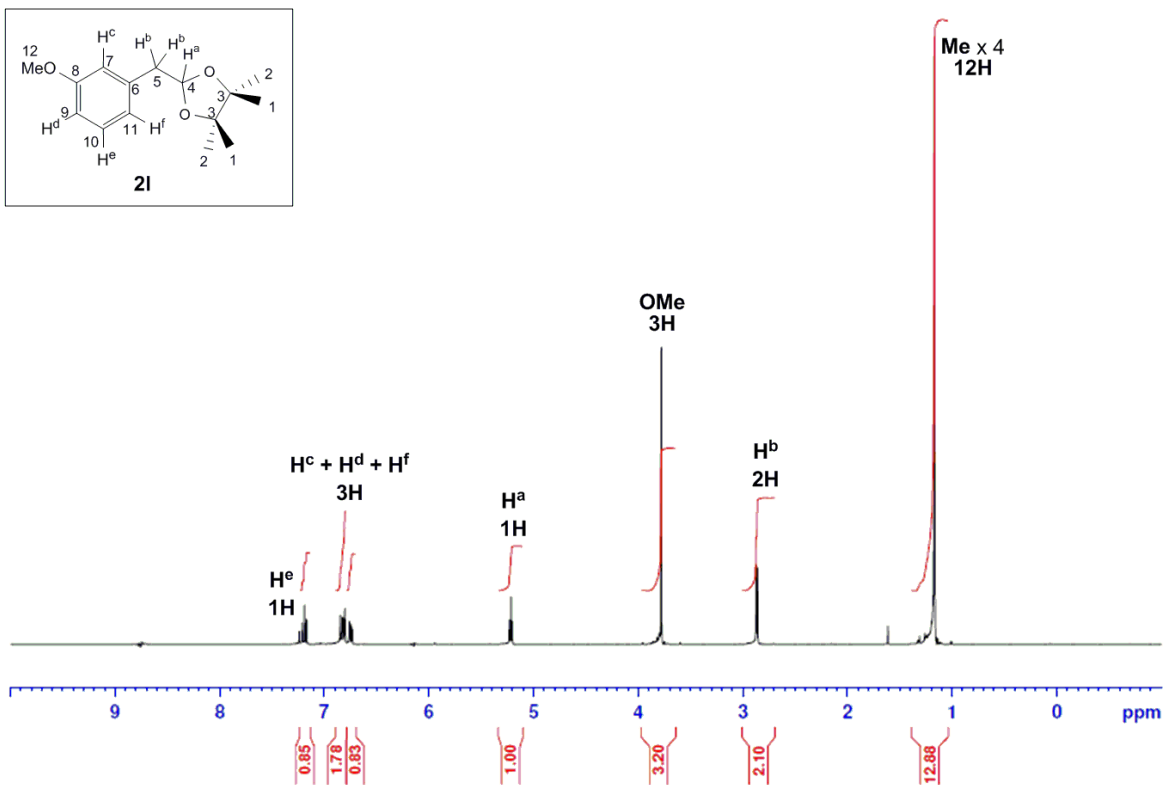
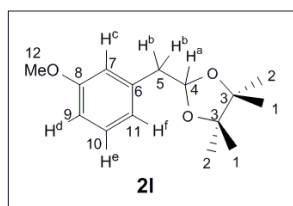


¹H NMR (400 MHz, CDCl₃)

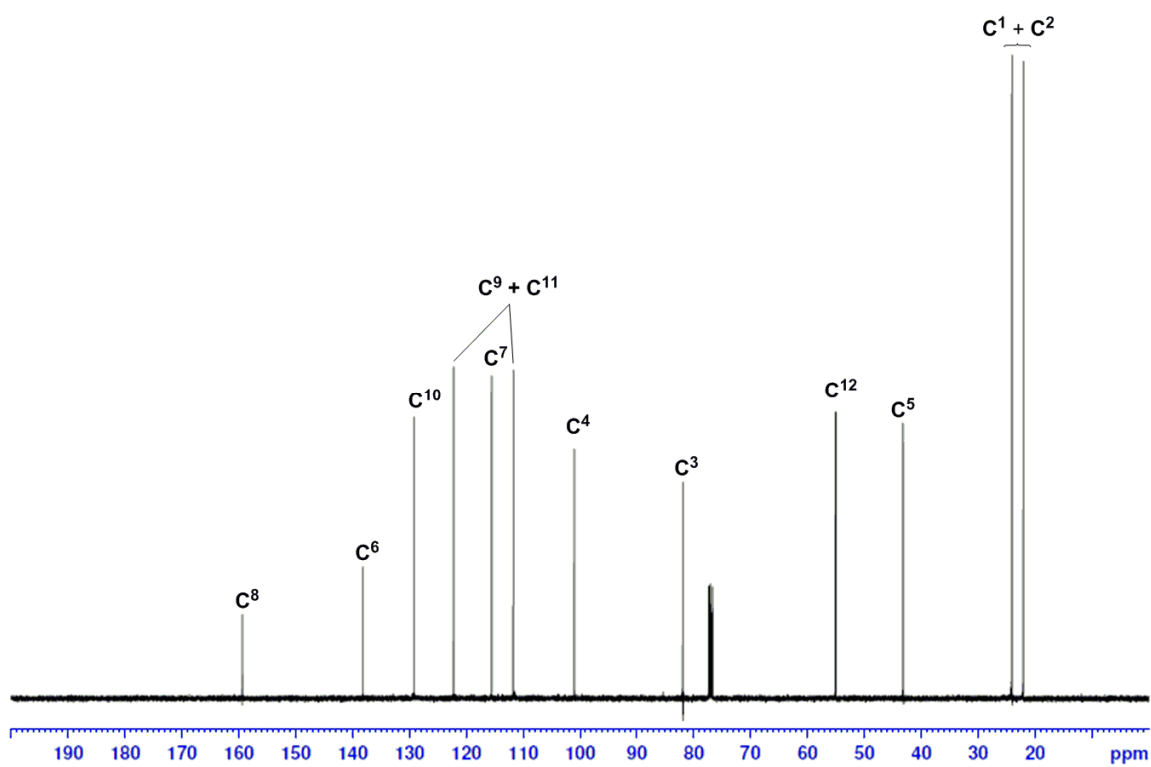


¹³C NMR (100 MHz, CDCl₃)

2-(*m*-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (**21**)

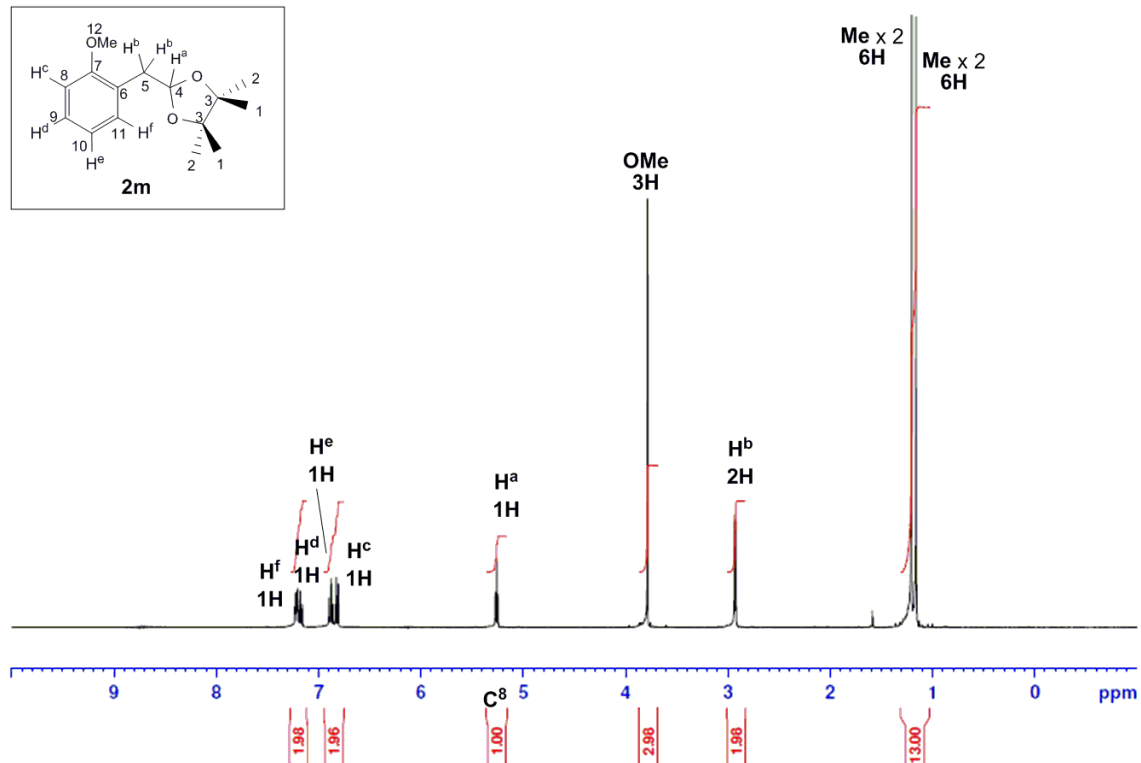
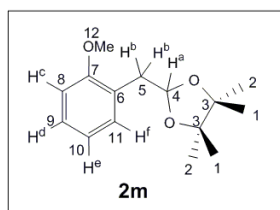


¹H NMR (400 MHz, CDCl₃)

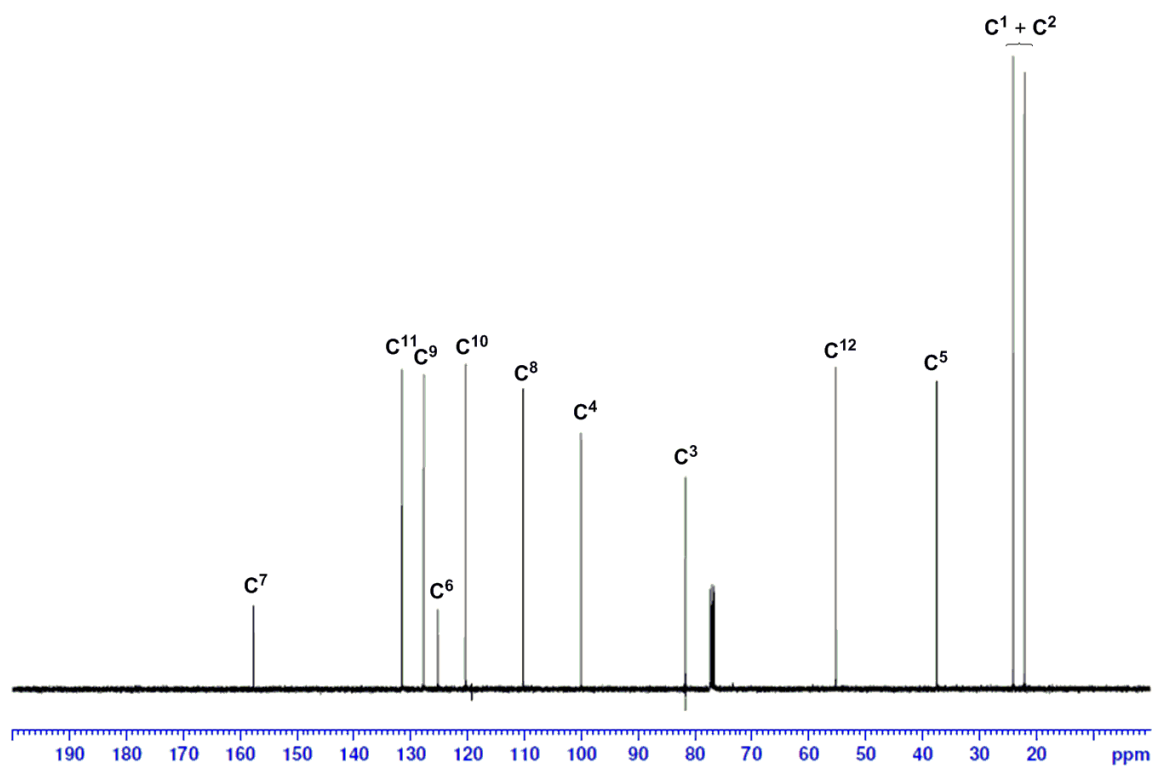


¹³C NMR (100 MHz, CDCl₃)

2-(*o*-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2m)

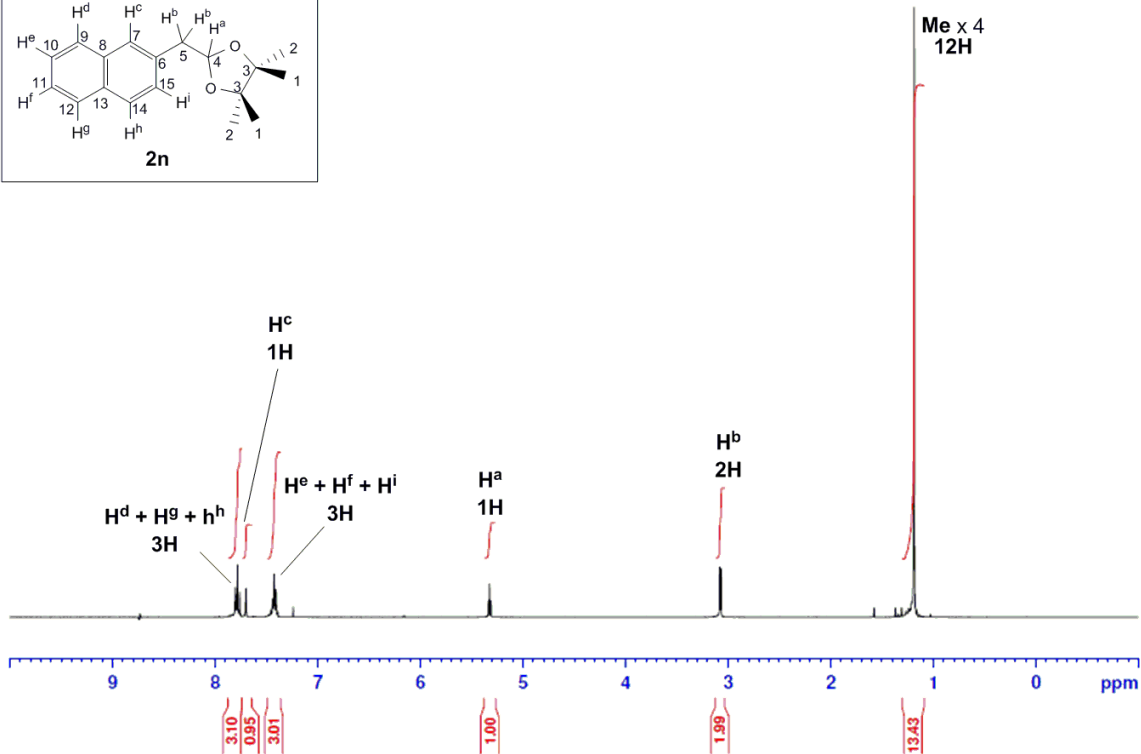
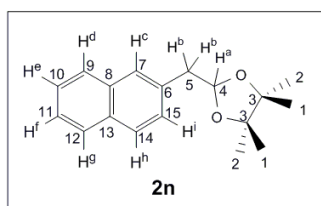


¹H NMR (400 MHz, CDCl₃)

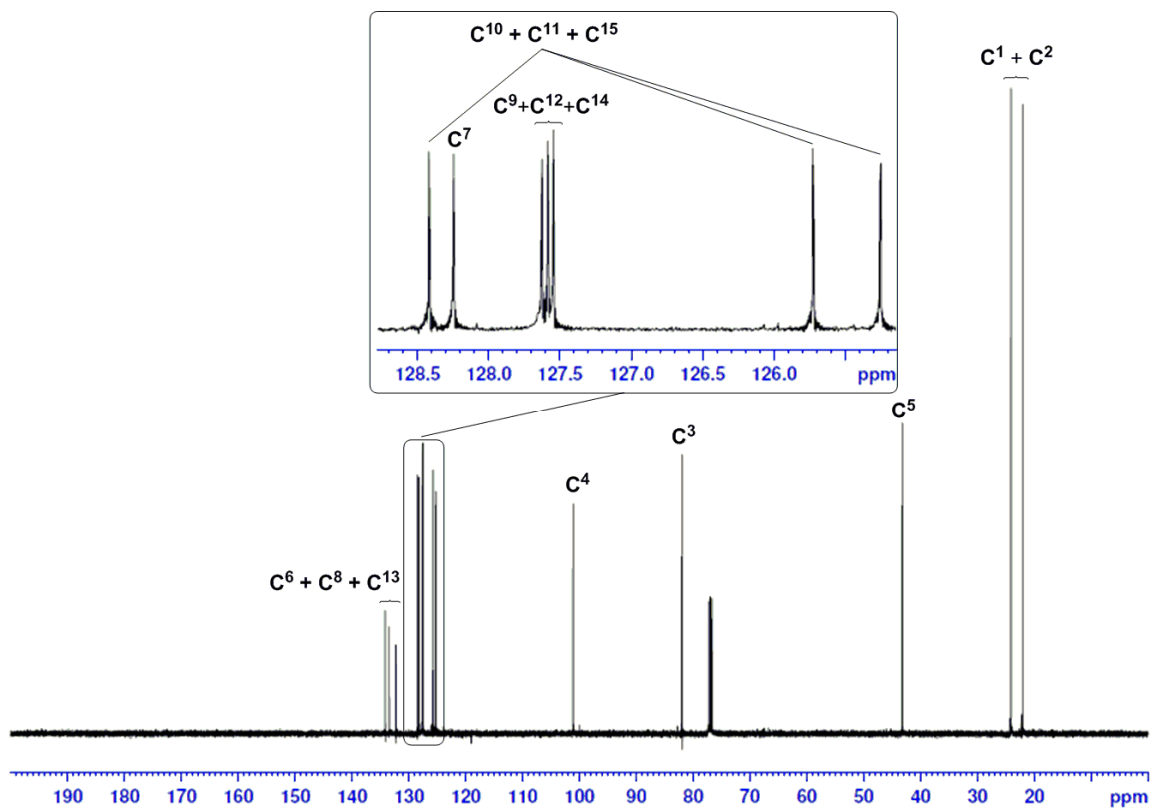


¹³C NMR (100 MHz, CDCl₃)

2-(2-Naphthylmethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2n)

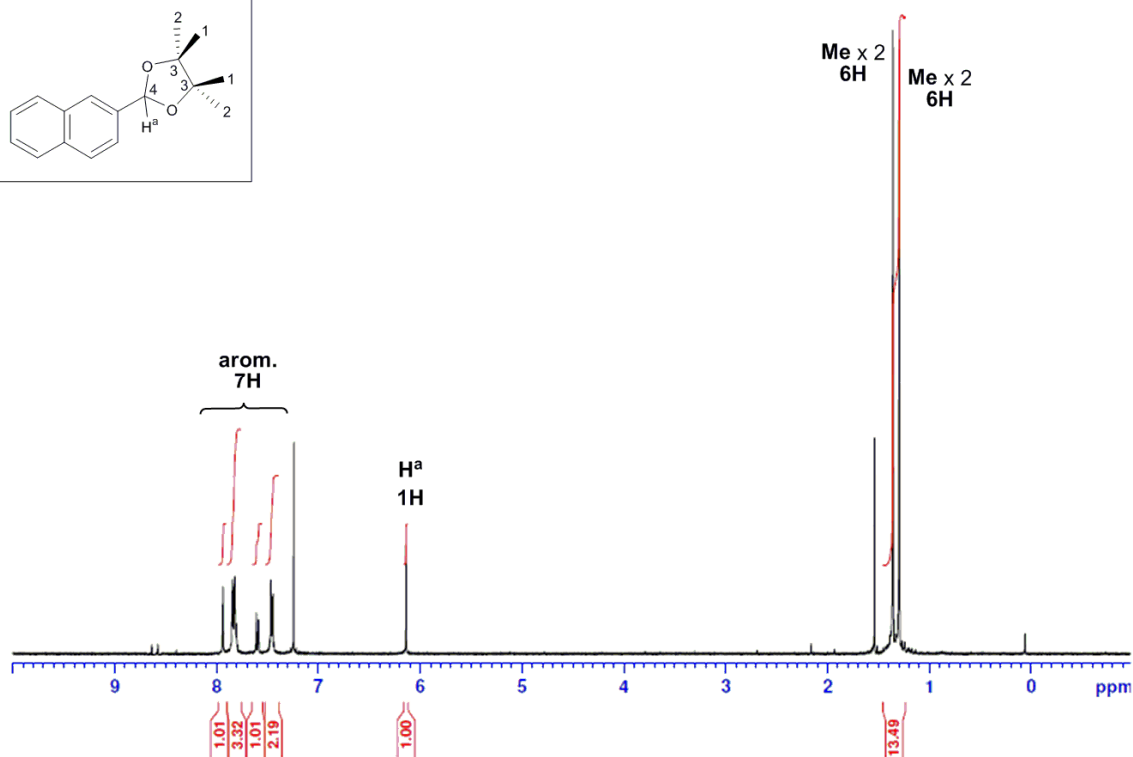
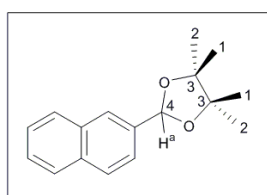


¹H NMR (400 MHz, CDCl₃)

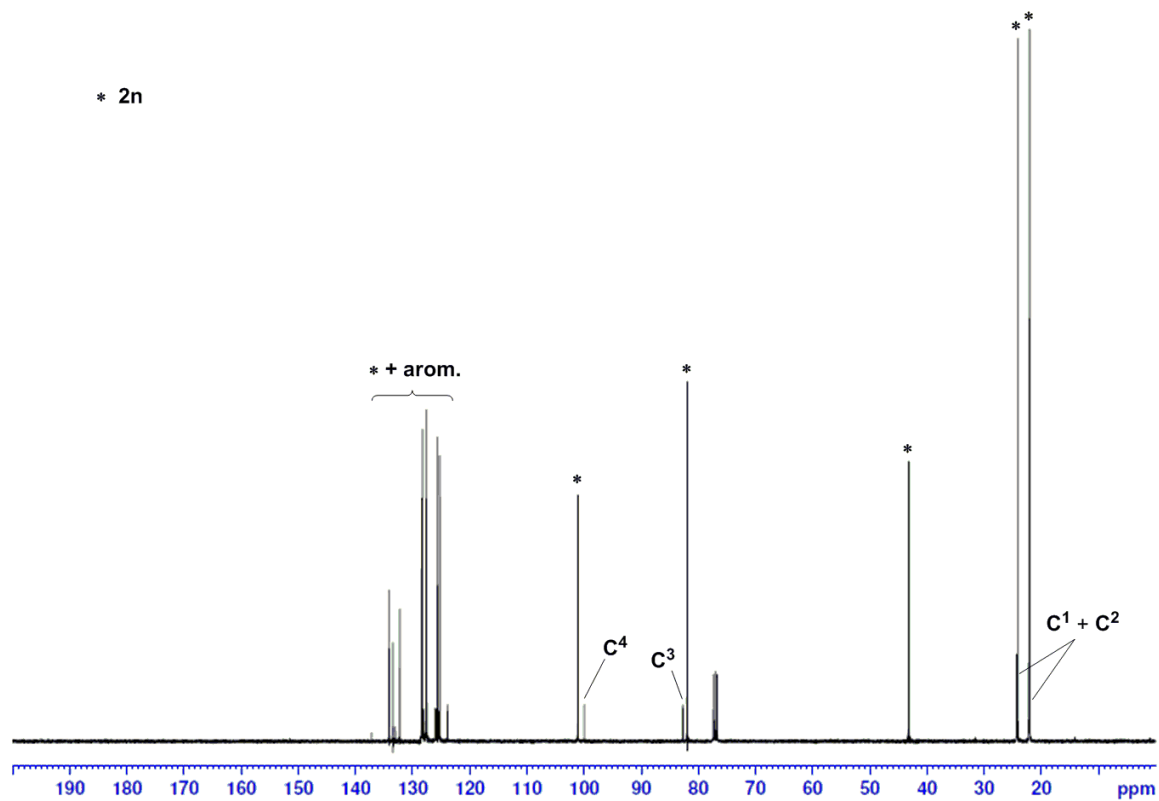


¹³C NMR (100 MHz, CDCl₃)

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

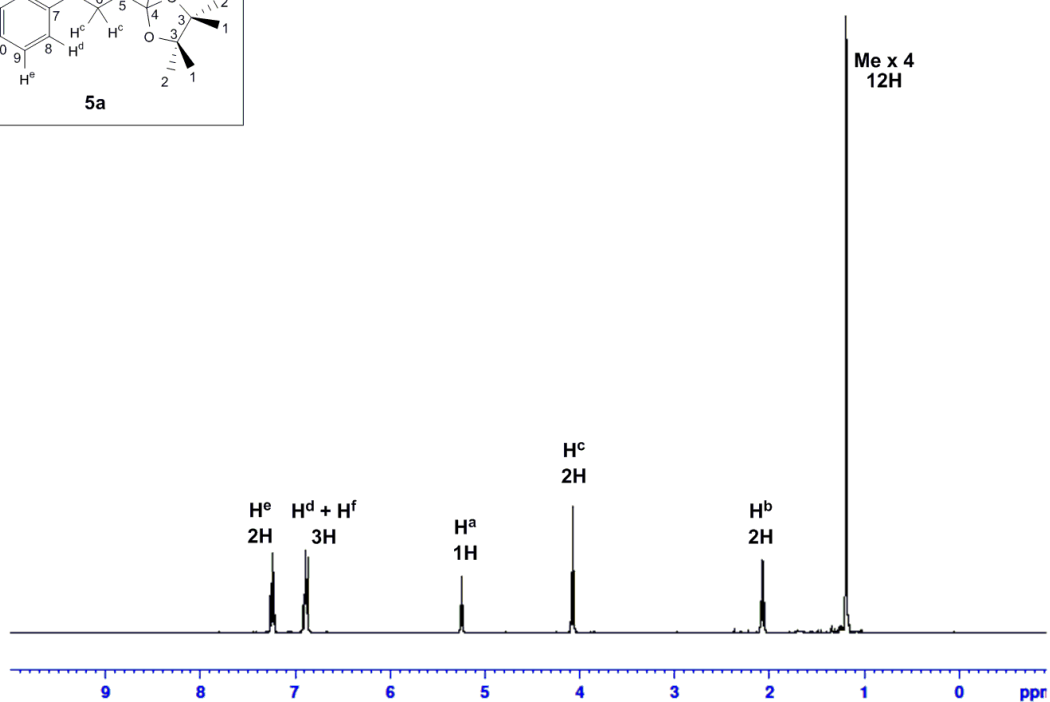
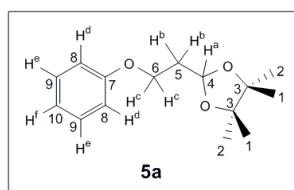


^1H NMR (400 MHz, CDCl_3)

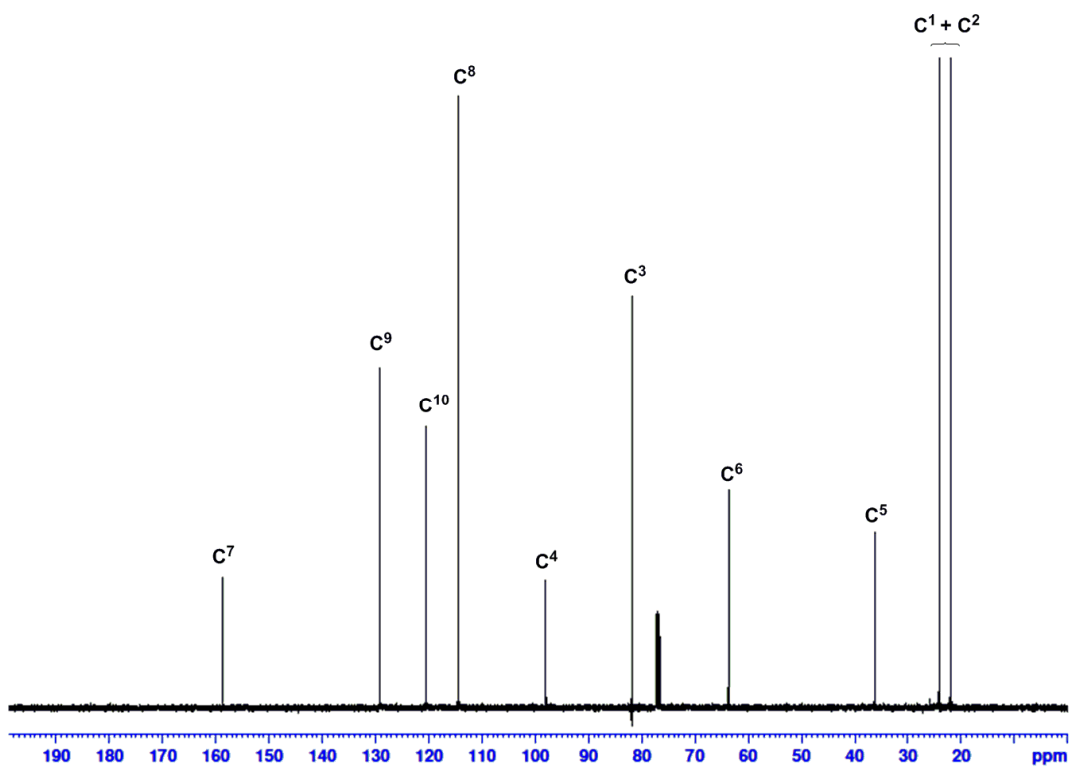


^{13}C NMR (100 MHz, CDCl_3) (a mixture with **2n**)

2-(Phenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5a)

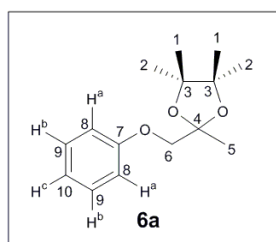


¹H NMR (400 MHz, CDCl₃)

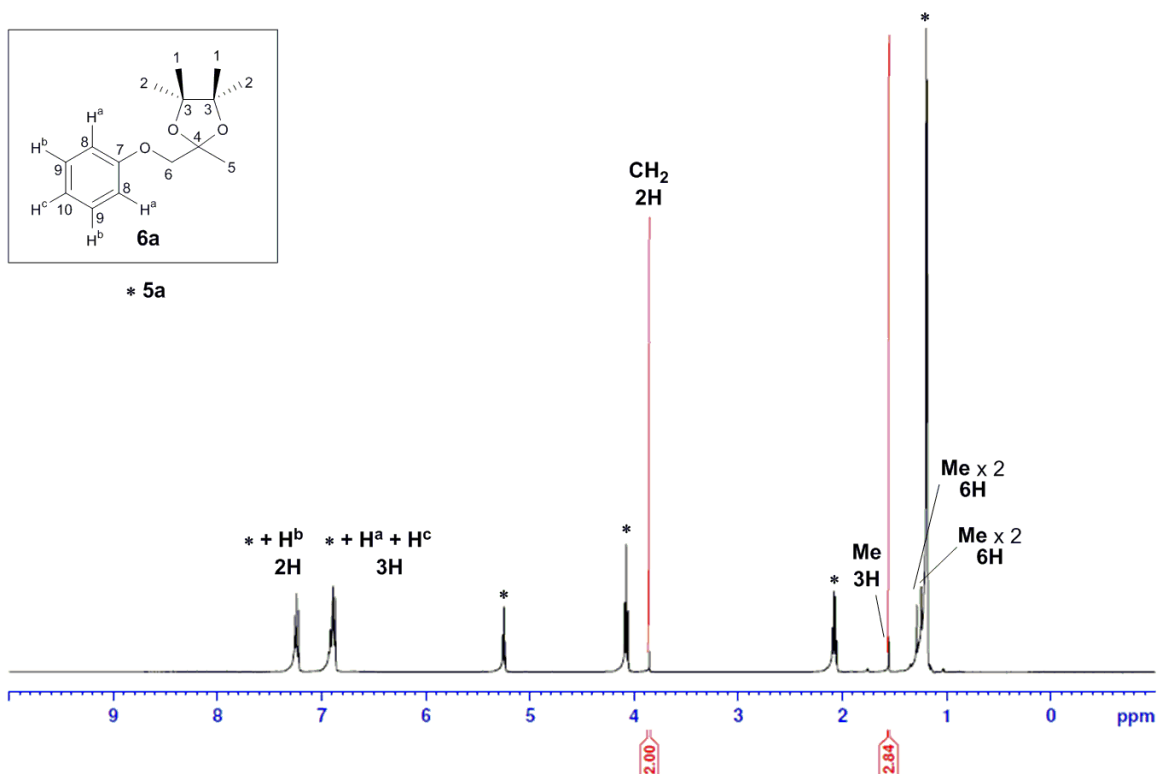


¹³C NMR (100 MHz, CDCl₃)

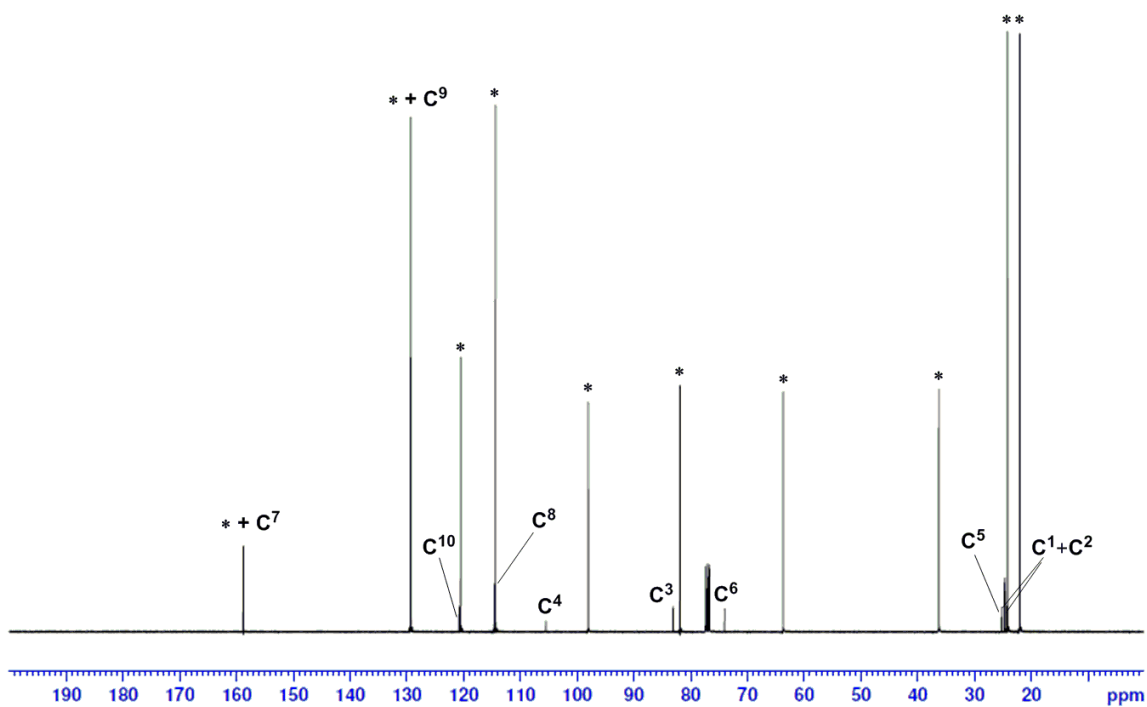
2-(Phenoxymethyl)-2,4,4,5,5-pentamethyl-1,3-dioxolane (6a)



* 5a

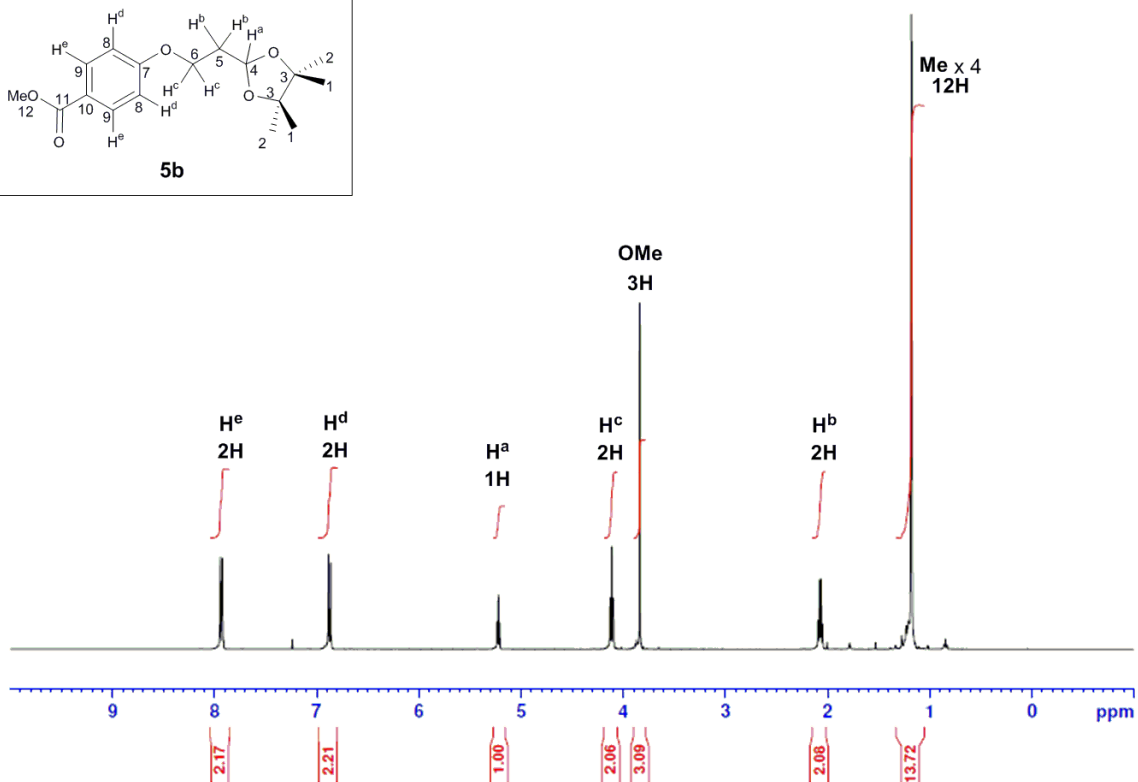
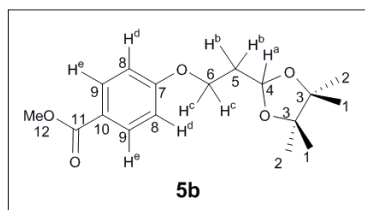


¹H NMR (400 MHz, CDCl₃) (a mixture with 5a)

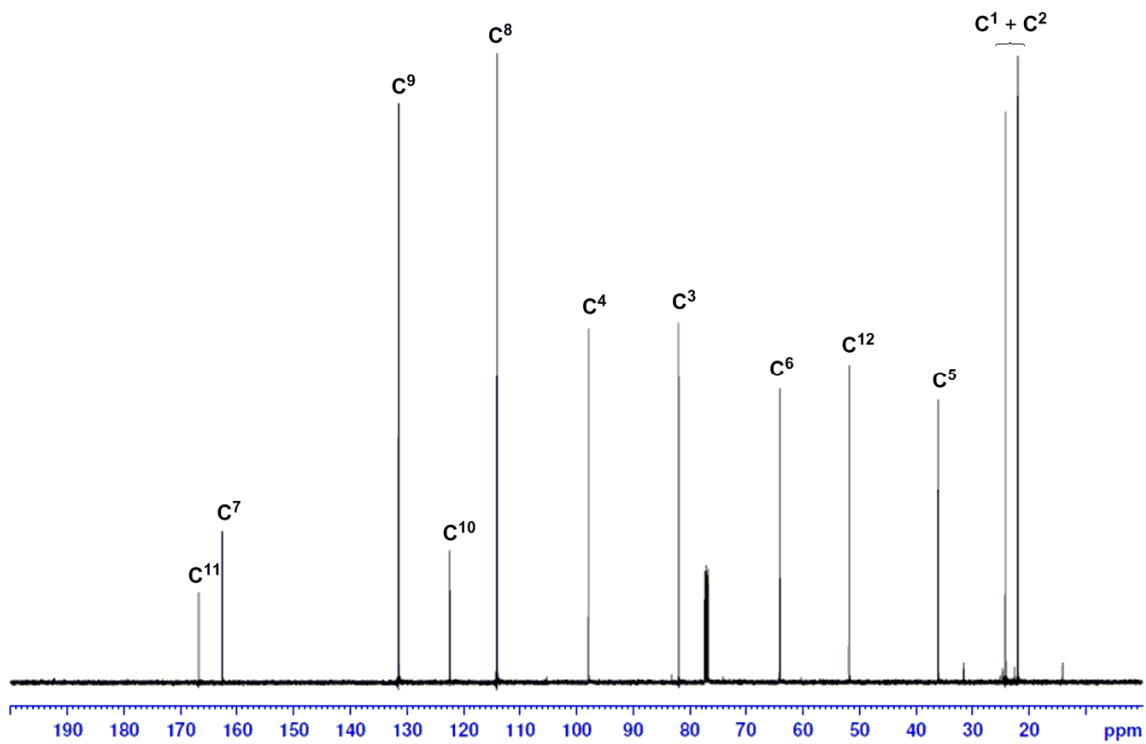


¹³C NMR (100 MHz, CDCl₃) (a mixture with 5a)

2-(*p*-Methoxycarbonylphenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (**5b**)

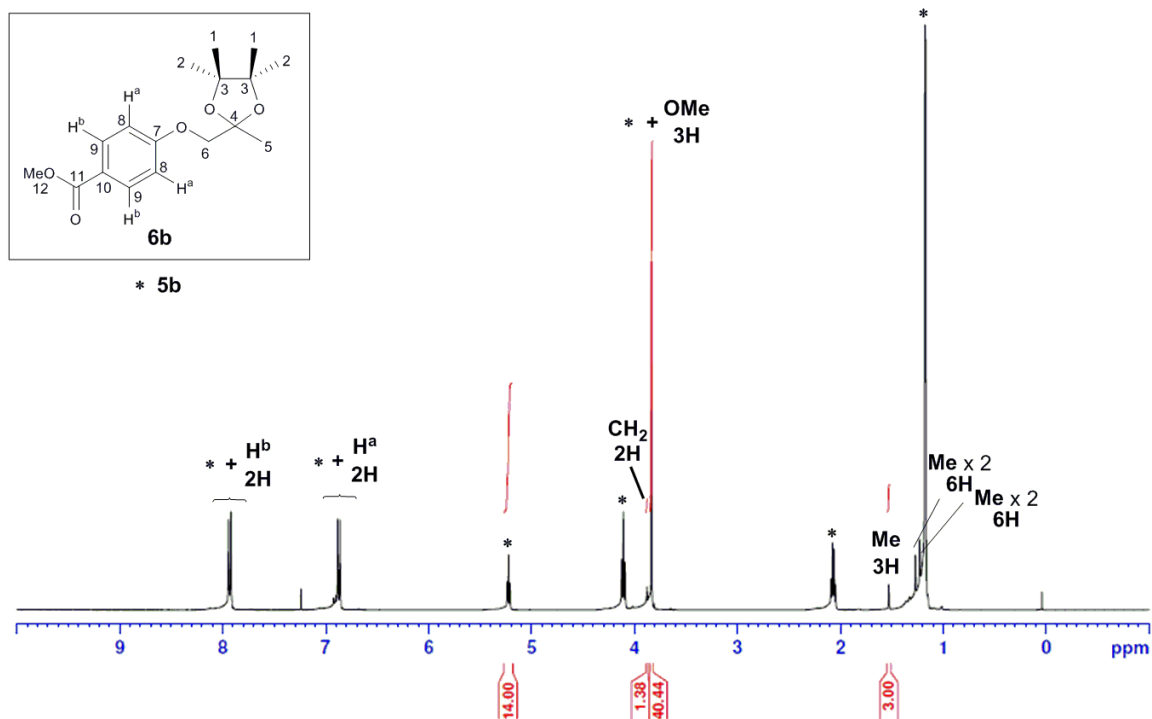


¹H NMR (400 MHz, CDCl₃)

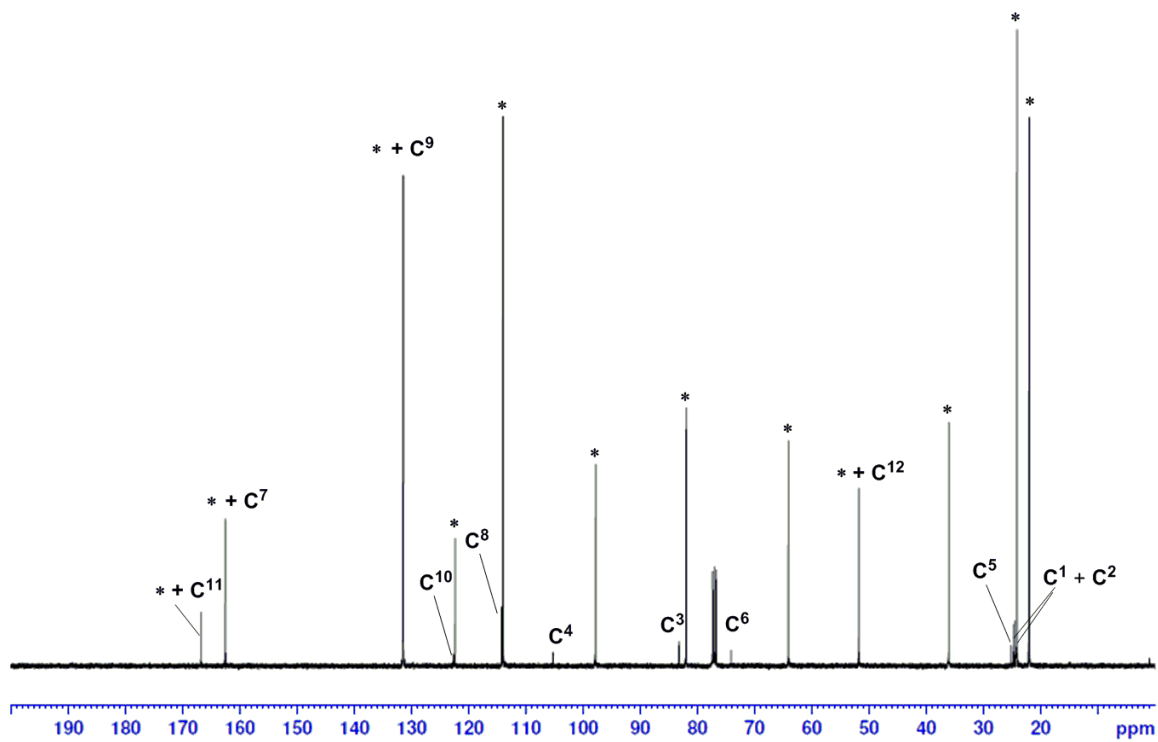


¹³C NMR (100 MHz, CDCl₃)

2-(*p*-Methoxycarbonylphenoxy)methyl)-2,4,4,5,5-pentamethyl-1,3-dioxolane (6b**)**

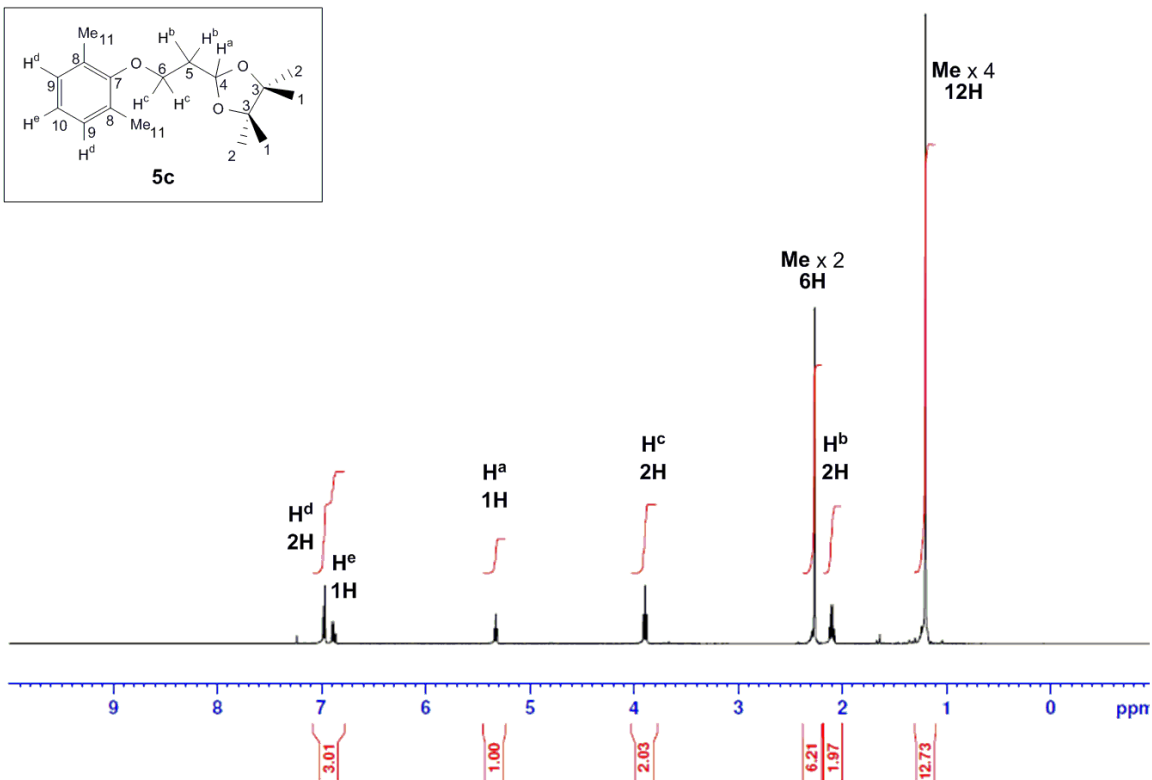
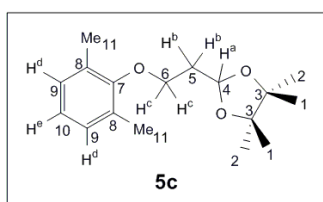


¹H NMR (400 MHz, CDCl₃) (a mixture with **5b**)

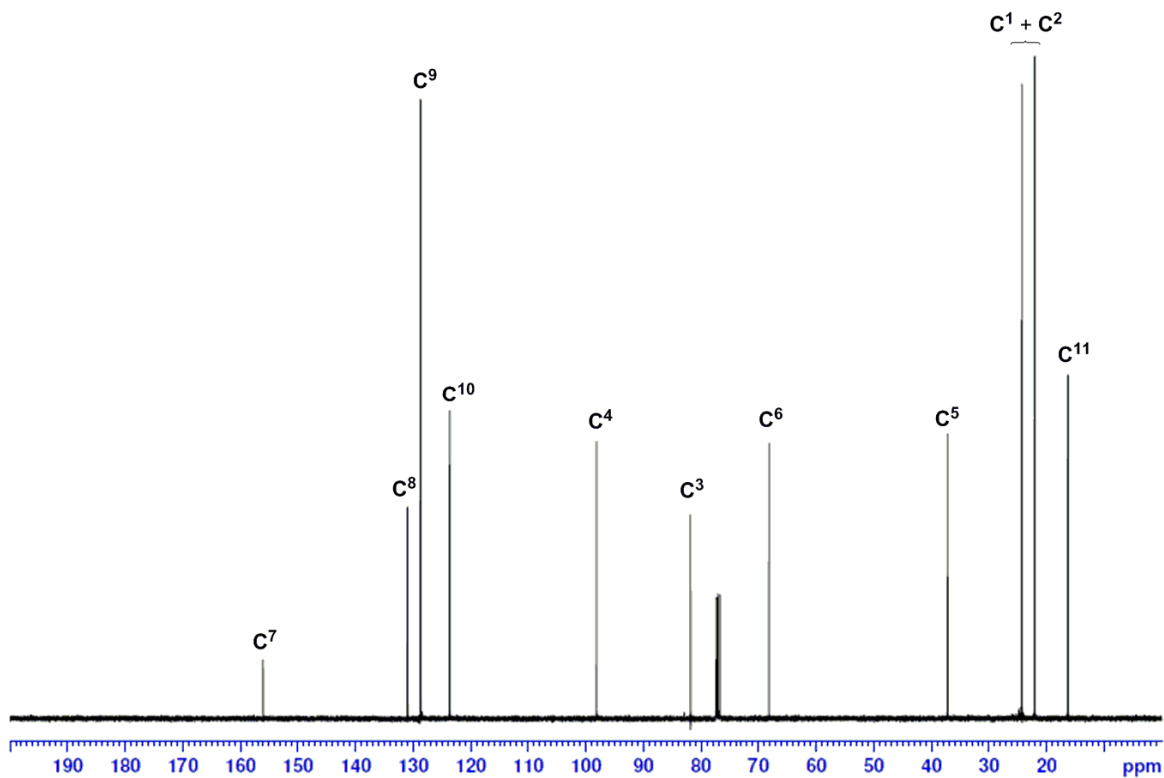


¹³C NMR (100 MHz, CDCl₃) (a mixture with **5b**)

2-(2,6-Dimethylphenoxyethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (5c)

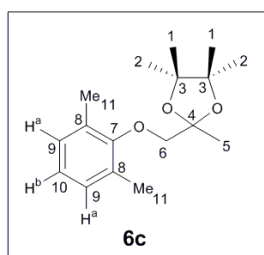


¹H NMR (400 MHz, CDCl₃)

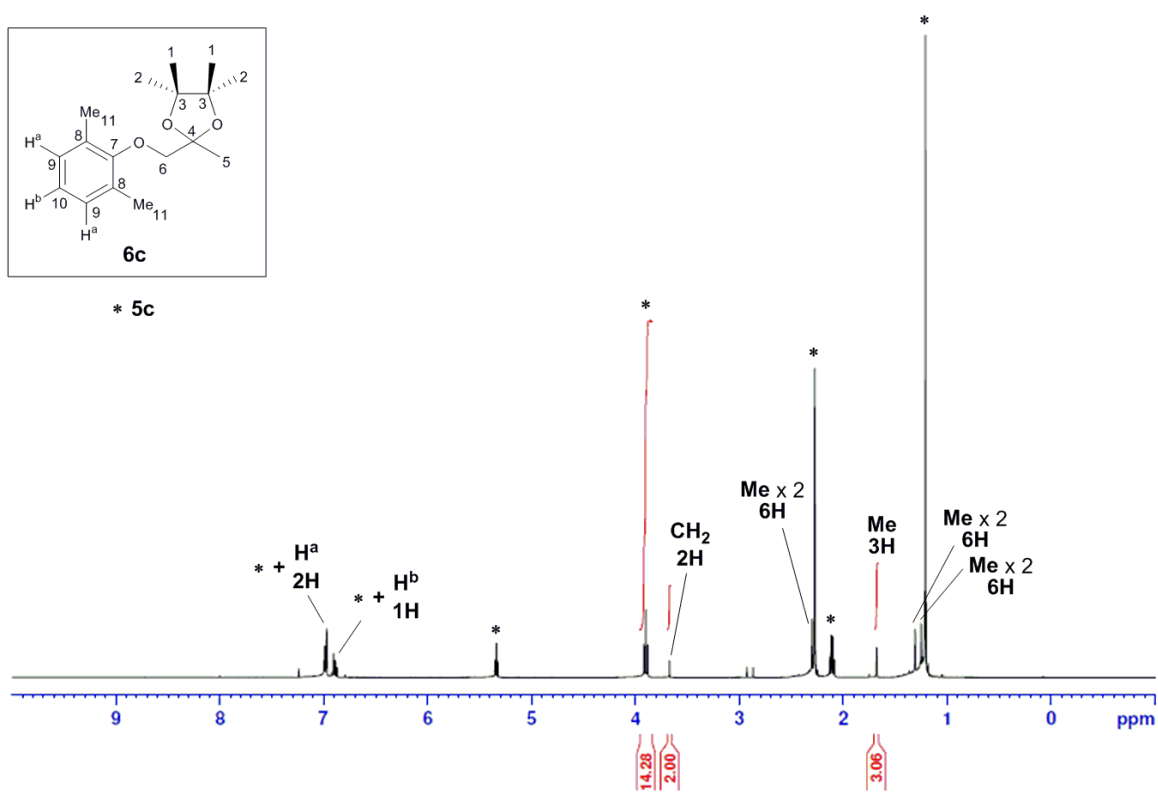


¹³C NMR (100 MHz, CDCl₃)

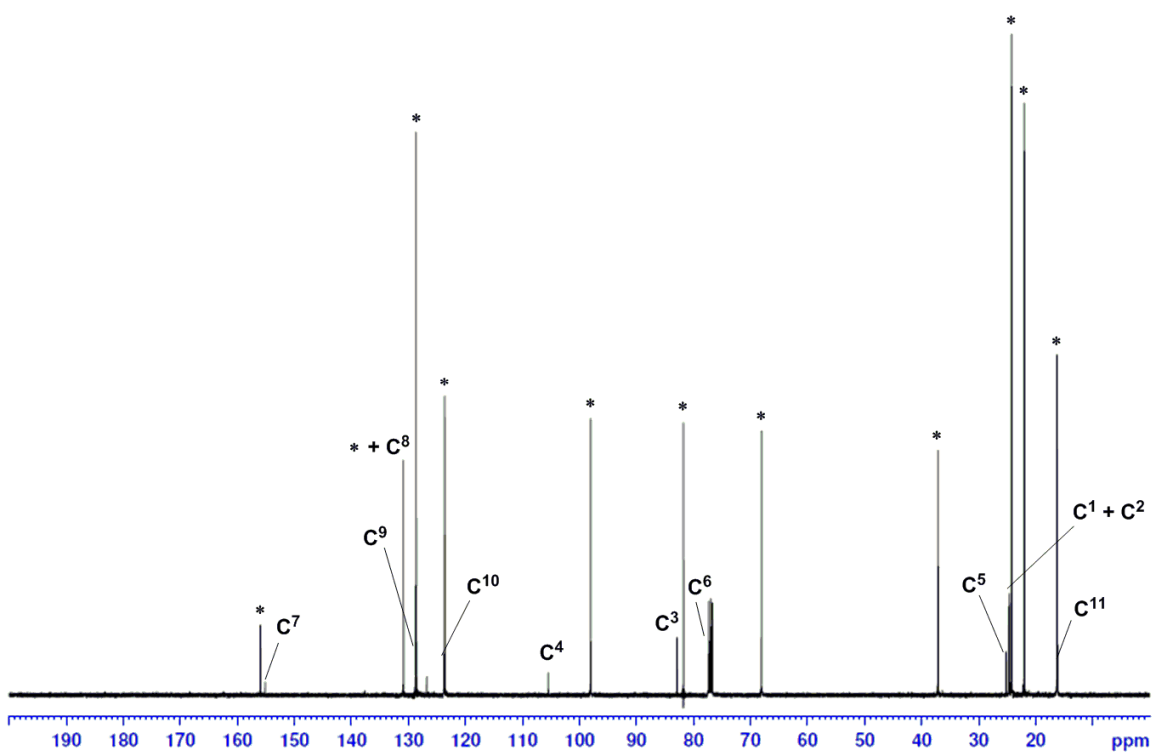
2-(2,6-Dimethylphenoxyethyl)-2,4,4,5,5-pentamethyl-1,3-dioxolane (6c)



* 5c

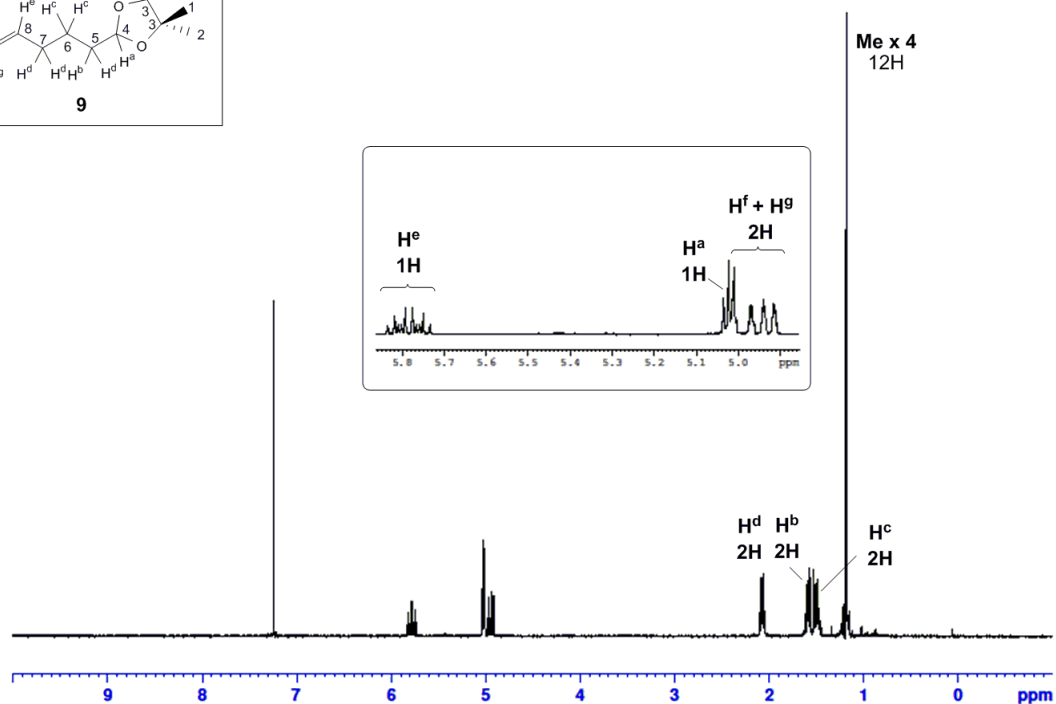
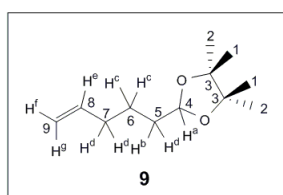


¹H NMR (400 MHz, CDCl₃) (a mixture with 5c)

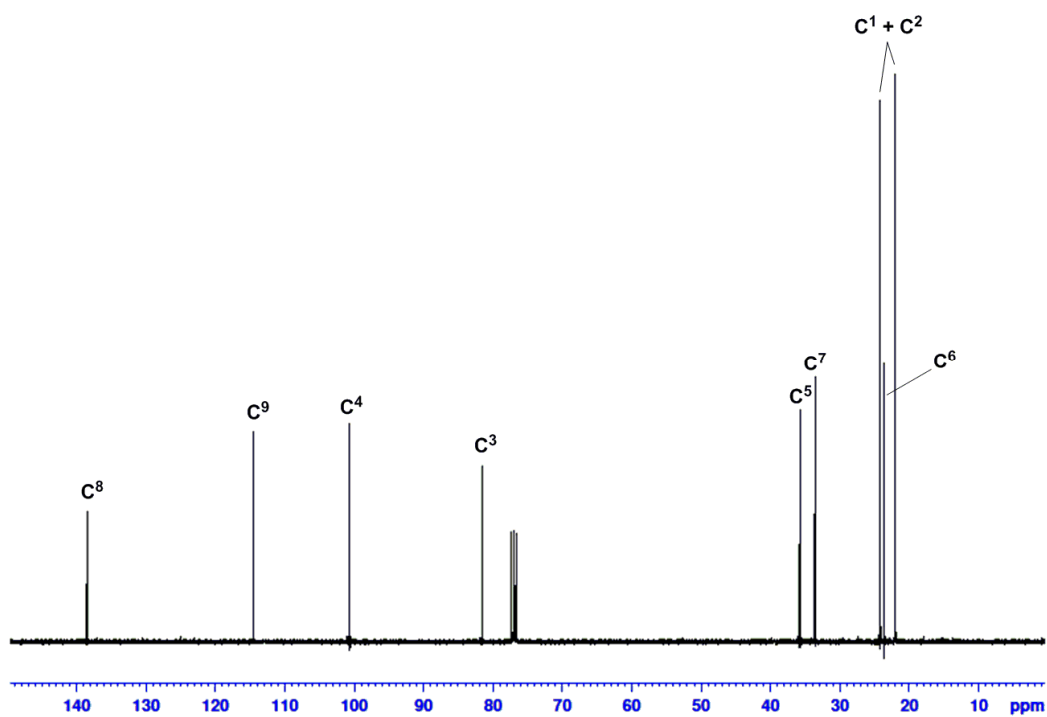


¹³C NMR (100 MHz, CDCl₃) (a mixture with 5c)

2-(4-Pentenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (9)

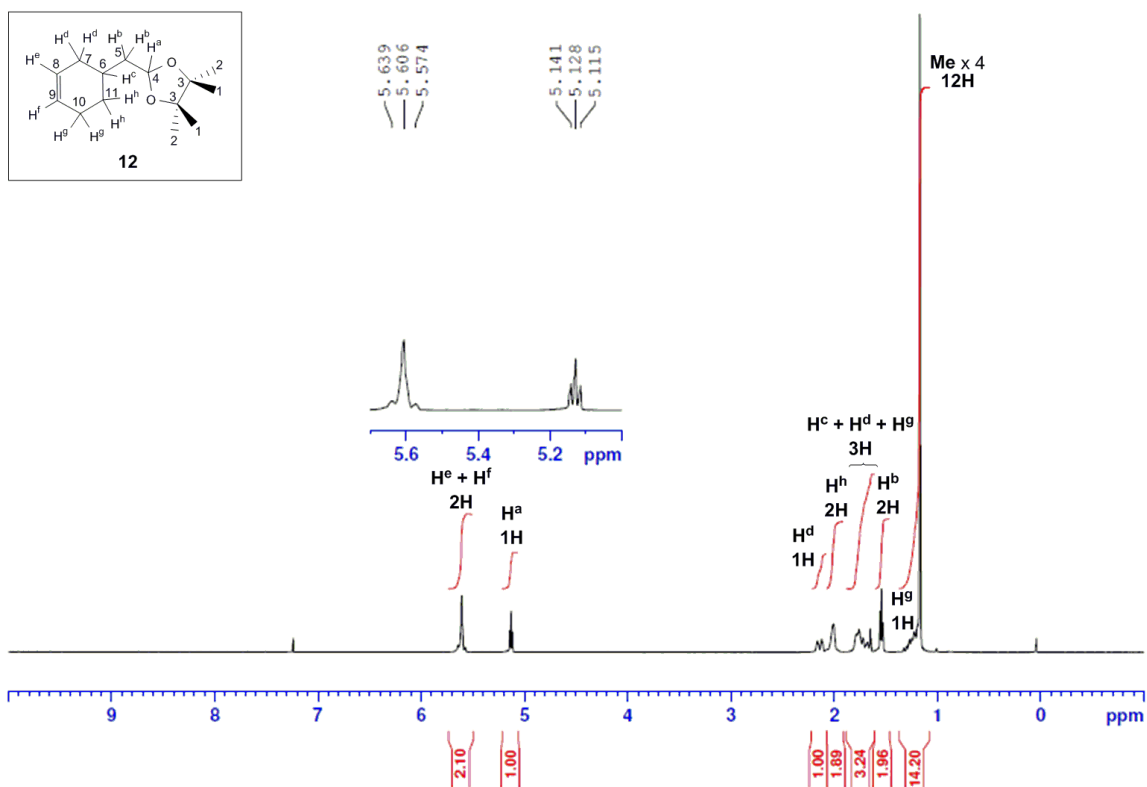


¹H NMR (400 MHz, CDCl₃)

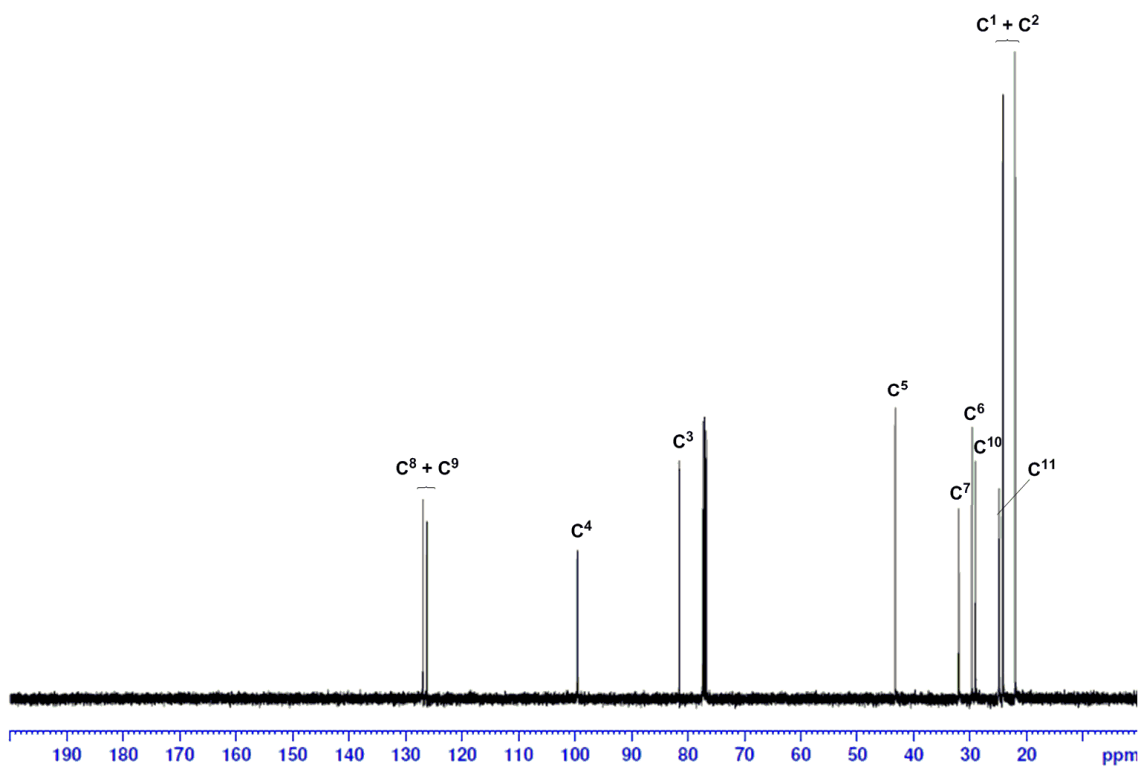


¹³C NMR (100 MHz, CDCl₃)

2-(3-Cyclohexenylmethyl)-4,4,5,5-tetramethyl-1,3-dioxolane (12)



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

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