Supplementary Information

Ketalization of Ketones to 1,3-Dioxolanes and Concurring Self-Aldolization Catalyzed by an Amorphous, Hydrophilic SiO_2-SO_3H Catalyst under Microwave Irradiation

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1,4-Dioxaspiro[4.5]decane (**1**)

GC, t_R = 11.56 min; bp (purified by fractional distillation) 87-89 °C/30 mmHg; IR (KBr) ν / cm^{-1} 2937, 2863, 1163, 1104; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (2H, br s, CH_2), 1.60 (8H, s, 4 × CH_2), 3.85 (4H, s, OCH_2CH_2O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.9, 64.1, 35.1, 25.1, 23.9; MS *m/z* 142 (38.97) $[M]^+$ $C_8H_{14}O_2^+$, 141 (2.56) $[M - H]^+$ $C_8H_{13}O_2^+$, 99 (100.00) $[M - C_2H_3O]^+$ $C_6H_{11}O^+$, 55 (98.07) $[M - C_5H_{11}O]^+$ $C_3H_3O^+$.

3,3-Dimethyl-1,5-dioxaspiro[5.5]-undecane or cyclohexanone, 2,2-dimethyl-1,3-propanediol ketal (**2**)

GC, t_R = 19.29 min; IR (KBr) ν / cm^{-1} 2919, 2849, 1723, 1454, 1244, 1108, 1038; MS *m/z* 184 (16.88) $[M]^+$ $C_{11}H_{20}O_2^+$, 183 (2.56) $[M - H]^+$ $C_{11}H_{19}O_2^+$, 141 (100.0) $[M - C_3H_7O_2]^+$ $C_8H_{13}O_2^+$.

3-Ethyl-1,5-dioxaspiro[5.5]undec-3-yl) metanol (**3**)

GC, t_R = 34.96 min; MS *m/z* 214 (17.88) $[M]^+$ $C_{12}H_{22}O_3^+$, 185 (18.56) $[M - C_2H_5]^+$ $C_{10}H_{17}O_3^+$, 171 (100.0) $[M - C_3H_7]^+$ $C_9H_{15}O_3^+$.

1,4-Dioxaspiro[4.5]dec-2-yl metanol (**4**)

GC, t_R = 21.96 min; IR (KBr) ν / cm^{-1} 3443 (br), 2935, 2862, 1161, 1103, 1043, 932; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.23-4.13 (m, 1H), 4.04-3.96 (m, 1H), 3.78-3.64 (m, 2H), 3.58-3.45 (m, 1H), 2.10 (br s, 1H), 1.66-1.20 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.93 (C2), 75.71 (C4), 65.33 (C5), 63.08 (CH_2OH), 36.35, 34.72, 25.06, 23.94, 23.71 (cyclohexyl); MS *m/z* 172 (8.89) $[M]^+$ $C_9H_{16}O_3^+$, 141 (9.13) $[M - CH_3O]^+$ $C_8H_{13}O_2$, 129 (100.00) $[M - C_2H_3O]^+$ $C_7H_{13}O_2^+$, 55 (90.11) $[M - C_5H_9O_3]^+$ $C_4H_7^+$.

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2-Methyl-2-phenyl-1,3-dioxolane (**5**)

GC, t_R = 17.32 min; mp (white crystals) 61-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (3H, s, CH_3), 3.73-3.83 (2H, m, CH_2–O), 3.99-4.09 (2H, m, CH_2–O), 7.29 (1H, t, *J* 7.6 Hz, ArH), 7.35 (2H, t, *J* 7.6 Hz, 2 × ArH), 7.48 (2H, d, *J* 7.6 Hz, 2 × ArH); MS *m/z* 149 (100.00) $[M - CH_3]^+$ $C_9H_9O_2^+$, 105 (76.56) $[M - C_3H_7O]^+$ $C_7H_5O^+$, 87 (100.0) $[M - C_6H_5]^+$ $C_4H_7O_2^+$, 77 (59.15) $[M - C_4H_7O_2]^+$ $C_6H_5^+$.

2,5,5-Trimethyl-2-phenyl-1,3-dioxane (**6**)

GC, t_R = 23.75 min; IR (KBr) ν / cm^{-1} 2991, 2855, 2363, 1688, 1260, 757; MS *m/z* 191 (66.78) $[M - CH_3]^+$ $C_{13}H_{18}O_2^+$, 129 (92.56) $[M - C_6H_5]^+$ $C_7H_{13}O_2^+$, 105 (100.0) $[M - C_5H_{13}O]^+$ $C_7H_5O^+$, 77 (42.40) $[M - C_7H_{13}O_2]^+$ $C_6H_5^+$.

5-Ethyl-2-methyl-2-phenyl-1,3-dioxan-5-yl) methanol (**7**)

GC, t_R = 38.27 min; IR (KBr) ν / cm^{-1} 3382, 2967, 2867, 2363, 2187, 2017, 1659, 1454, 1278, 1026, 698; MS *m/z* 236 (0.00) $[M]^+$ $C_{14}H_{20}O_3^+$, 221 (65.16) $[M - CH_3]^+$ $C_{13}H_{17}O_3^+$, 159 (92. 21) $[M - C_6H_5]^+$ $C_8H_{15}O_3^+$, 105 (89.09) $[M - C_7H_{15}O_2]^+$ $C_7H_5O^+$, 77 (46.40) $[M - C_8H_{15}O_3]^+$ $C_6H_5^+$, 43 (100.0) $[M - C_{12}H_{15}O_2]^+$ $C_2H_5O^+$.

2-Methyl-2-phenyl-1,3-dioxolan-4-yl) methanol (**8**)

GC, t_R = 38.35 min; IR (KBr) ν / cm^{-1} 3358 (br), 2925, 2855, 2363, 1448, 1273, 920, 698; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.22 (m, 5H), 4.39-4.29 (m, 1H), 4.20-4.01 (m, 1H), 3.90-3.55 (m, 3H), 1.80 (br s, 1H), 1.60 and 1.65 (2 s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.98, 128.20, 127.88, 125.21 (CPh), 109.63 (C2), 75.96 (C4), 66.19 and 65.69 (C5), 63.35 and 62.82 (CH_2OH), 28.09 and 27.95 (CH_3); MS *m/z* 194 (16.88) $[M]^+$ $C_{11}H_{14}O_3^+$, 105 (100.00) $[M - C_4H_9O_2]^+$ $C_7H_5O^+$, 77 (95.08) $[M - C_4H_7O_3]^+$ $C_7H_7^+$.

2,2-Diphenyl-1,3-dioxolane (**13**)

GC, t_R = 39.98 min; MS *m/z* 226 (8.98) $[M]^+$ $C_{15}H_{14}O_2^+$, 149 (87.56) $[M - C_6H_5]^+$ $C_9H_9O_2^+$, 105 (100.00) $[M - C_8H_9O]^+$ $C_7H_5O^+$, 77 (71.20) $[M - C_9H_9O_2]^+$ $C_6H_5^+$.

5,5-Dimethyl-2,2-diphenyl-1,3-dioxane (**14**)

GC, t_R = 45.02 min; IR (KBr) ν / cm^{-1} 2949, 2867, 2371, 2169, 2019, 1659, 1454, 1196, 1020, 920, 698; MS *m/z* 268 (1.88) $[M]^+$ $C_{18}H_{20}O_2^+$, 191 (84.56) $[M - C_6H_5]^+$ $C_{12}H_{15}O_2^+$, 105 (100.0) $[M - C_{11}H_{15}O]^+$ $C_7H_5O^+$, 77 (42.40) $[M - C_{12}H_{15}O_2]^+$ $C_6H_5^+$.

(5-Ethyl-2,2-diphenyl-1,3-dioxan-5-yl) methanol (**15**)

GC, t_R = 56.37 min; IR (KBr) ν / cm^{-1} 3441, 2961, 2861, 2351, 2187, 2029, 1659, 1448, 1096, 1020, 1026, 698; MS *m/z* 298 (2.18) $[M]^+$ $C_{19}H_{22}O_3^+$, 221 (51.16) $[M - H]^+$ $C_{13}H_{17}O_3^+$, 105 (100.0) $[M - C_{12}H_{17}O_2]^+$ $C_7H_5O^+$, 77 (46.40) $[M - C_{13}H_{17}O_3]^+$ $C_6H_5^+$.

2,2'-Oxybis(ethan-1-ol) (**12**)

GC, t_R = 7.70 min; MS *m/z* 105 (1.08) $[M - H]^+$ $C_4H_9O_3^+$, 88 (1.56) $[M - H_2O]^+$ $C_4H_8O_2^+$, 45 (100.0) $[M - C_2H_4O_2]^+$ $C_2H_5O^+$.

(*E*)-1,3-Diphenylbut-2-en-1-one (**18**)

Colorless oil; GC, t_R = 47.21 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 3H), 7.17 (s, 1H), 7.40-7.43 (m, 3H), 7.47 (dd, *J* 8.0, 7.2 Hz, 2H), 7.53-7.58 (m, 3H), 7.99 (d, *J* 7.2 Hz, 2H); MS *m/z* 222 (16.88) $[M]^+$ $C_{16}H_{14}O^+$, 145 (22.56) $[M - C_6H_5]^+$ $C_{10}H_9O^+$, 115 (57.88) $[M - C_9H_9]^+$ $C_7H_5O^+$, 105 (43.78) $[M - C_9H_9]^+$ $C_7H_5O^+$, 91 (31.10) $[M - C_9H_7O]^+$ $C_7H_7^+$, 40 (100) $[M - C_{13}H_{10}O]^+$ $C_3H_4^+$.

[1,1'-Bi(cyclohexylidene)]-2-one (**19**)

Colorless oil; GC, t_R = 30.50 min; IR (KBr) ν / cm^{-1} 2922, 2851, 1675, 1639, 1444, 729; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (t, *J* 10 Hz, 1H), 2.88 (dd, *J* 11.2 and 5.0 Hz, 1H), 2.42-2.36 (m, 1H), 2.34-2.26 (m, 1H), 2.06-1.96 (m, 4H), 1.96-1.80 (m, 4H), 1.74-1.52 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.82, 136.07, 123.88, 58.98, 42.33, 31.05, 27.88, 27.49, 25.50, 25.06, 23.06, 22.62; MS *m/z* 178 (40.08) $[M]^+$ $C_{12}H_{18}O^+$, 149 (2.56) $[M - H]^+$ $C_8H_{13}O_2^+$, 149 (100.0) $[M - C_2H_5]^+$ $C_6H_8O_2^+$, 81 (51.80) $[M - C_2H_4O_2]^+$ $C_6H_9^+$, 70 (4.12) $[M - C_8H_{12}]^+$ $C_4H_6O^+$, 55 (4.12) $[M - C_9H_{15}]^+$ $C_3H_3O^+$.

(2*E*)-1,3-bis(4-Methylphenyl)but-2-en-1-one (**20**)

Colorless oil; GC, t_R = 54.80 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* 5.0 Hz, 2H), 7.59 (d, *J* 5.0 Hz, 2H), 7.37 (d, *J* 8.0 Hz, 2H), 7.33 (d, *J* 8.0 Hz, 2H), 2.69 (s, 3H), 2.52 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6, 163.8, 154.5, 143.2, 139.9, 139.3, 136.9, 129.4, 129.3, 128.5, 126.5, 121.5, 21.9, 21.5, 19.0; MS *m/z* 250 (11.88) $[M]^+$ $C_{18}H_{18}O^+$, 249 (29.56) $[M - H]^+$ $C_{18}H_{17}O^+$, 119 (25.61) $[M - C_7H_7]^+$ $C_{11}H_{11}O^+$, 115 (40.10) $[M - C_{10}H_{11}]^+$ $C_8H_7O^+$, 91 (100.00) $[M - C_{11}H_{11}O]^+$ $C_7H_7^+$, 77 (11.08) $[M - C_{12}H_{13}]^+$ $C_6H_5^+$.

1,4-Dioxaspiro[4.5]decane (**1**)

GC t_R = 11.55 min

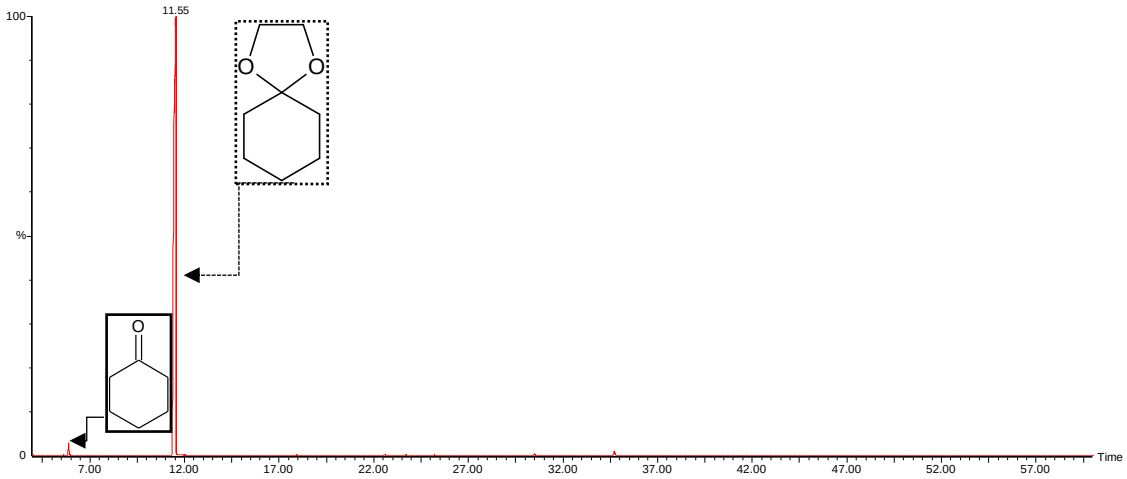


Figure S1. GC chromatogram of 1,4-dioxaspiro[4.5]decane (**1**).

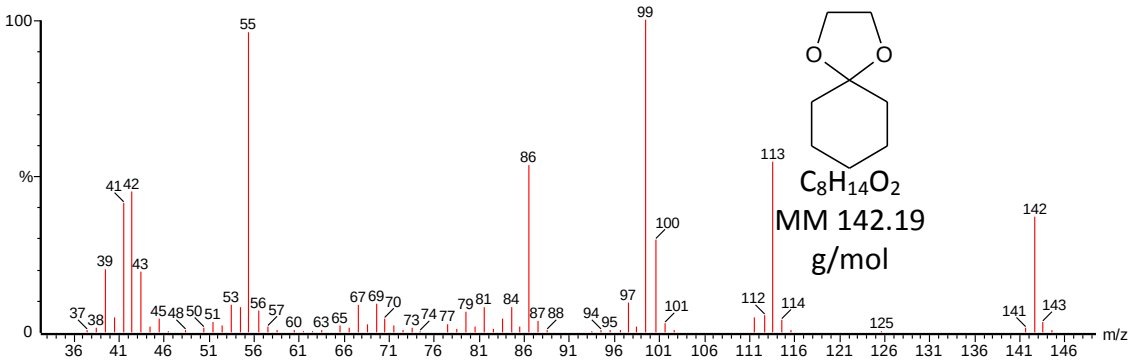


Figure S2. Mass spectrum of 1,4-dioxaspiro[4.5]decane (**1**).

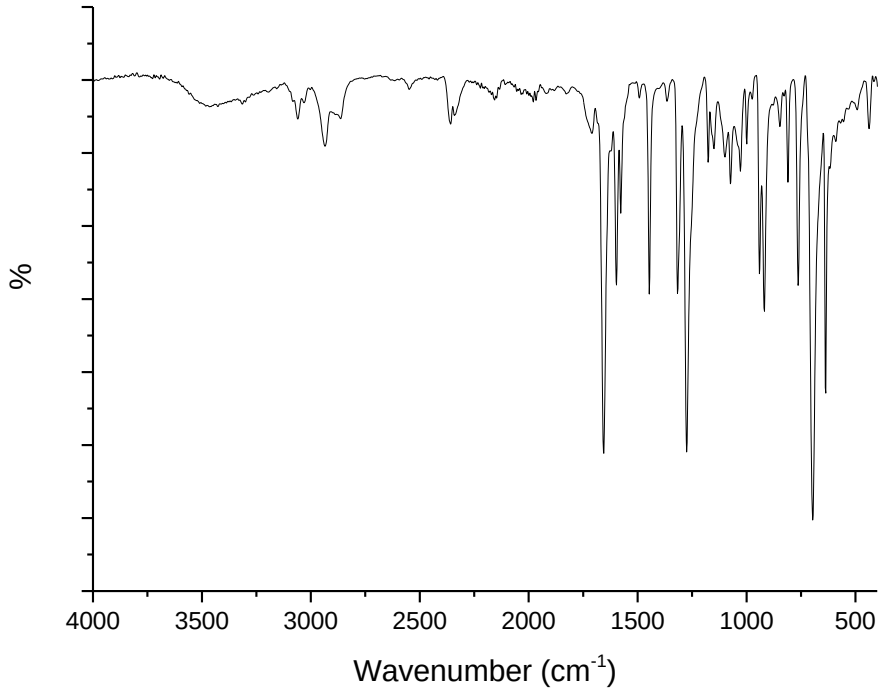


Figure S3. IR spectrum (KBr) of 1,4-dioxaspiro[4.5]decane (**1**).

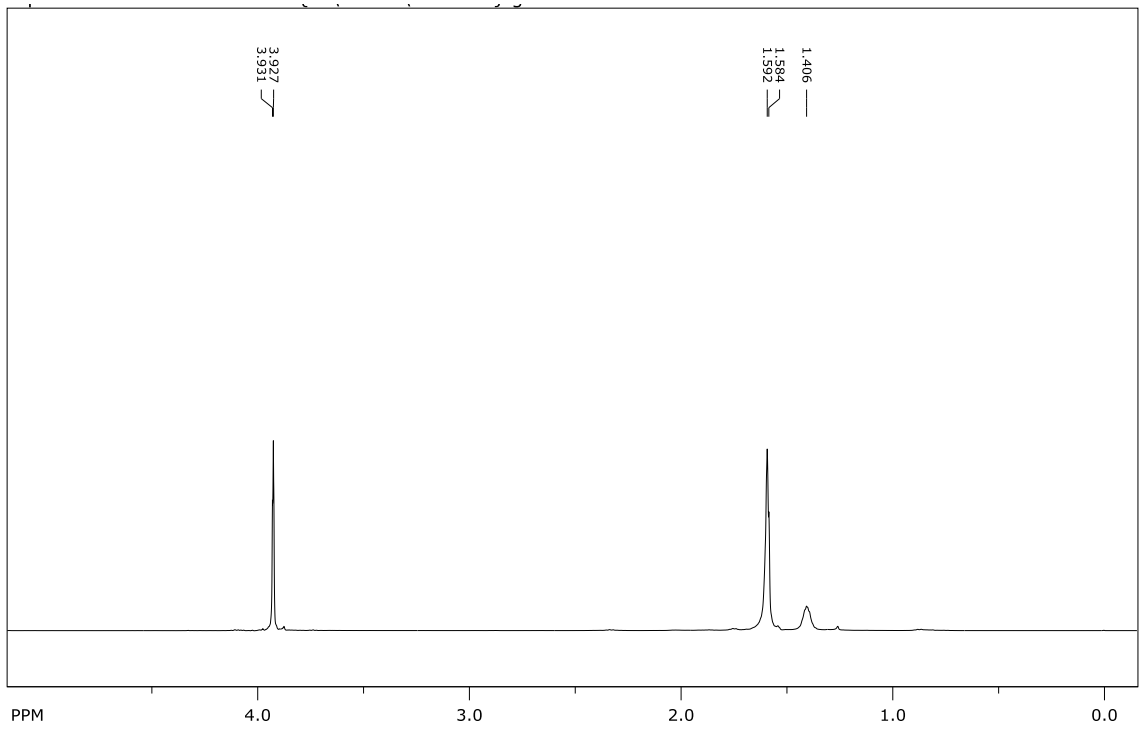


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1,4-dioxaspiro[4.5]decane (**1**).

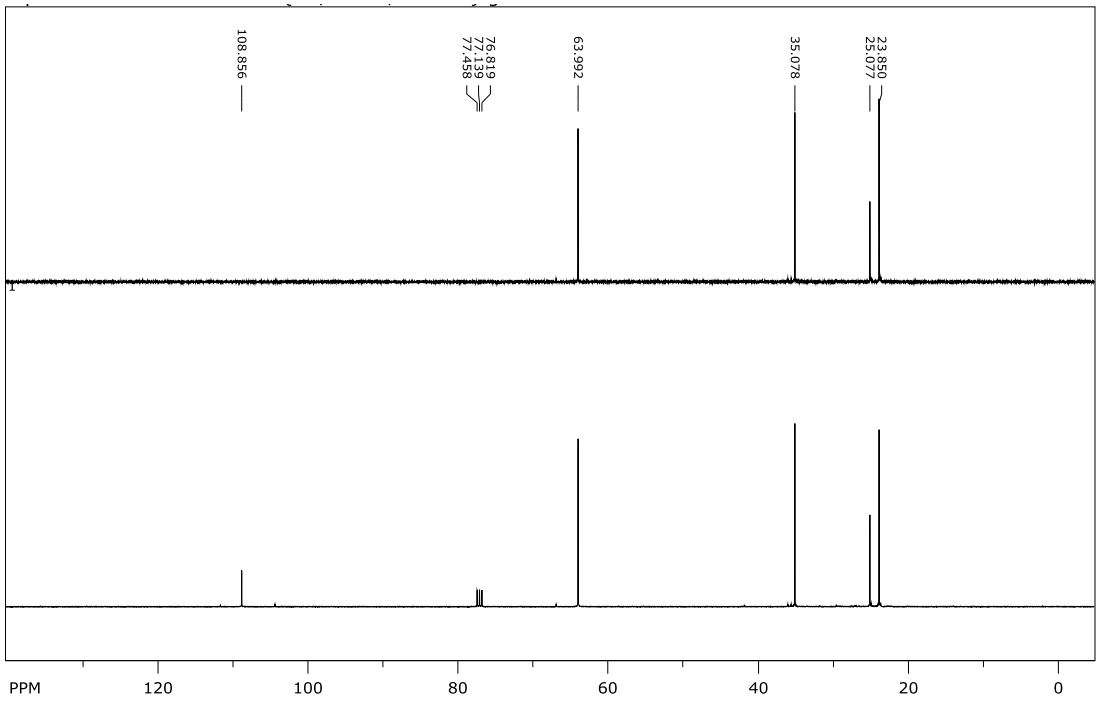


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1,4-dioxaspiro[4.5]decane (**1**).

3,3-Dimethyl-1,5-dioxaspiro[5.5]-undecane or cyclohexanone, 2,2-dimethyl-1,3-propanediol ketal (**2**)

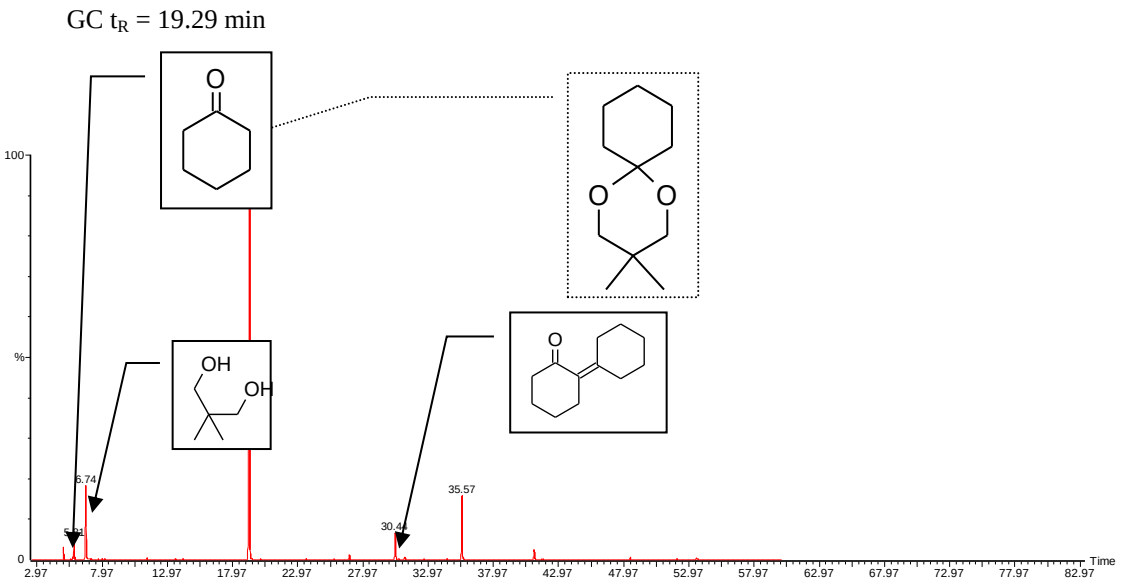


Figure S6. GC chromatogram of 3,3-dimethyl-1,5-dioxaspiro[5.5]-undecane or cyclohexanone, 2,2-dimethyl-1,3-propanediol ketal (**2**).

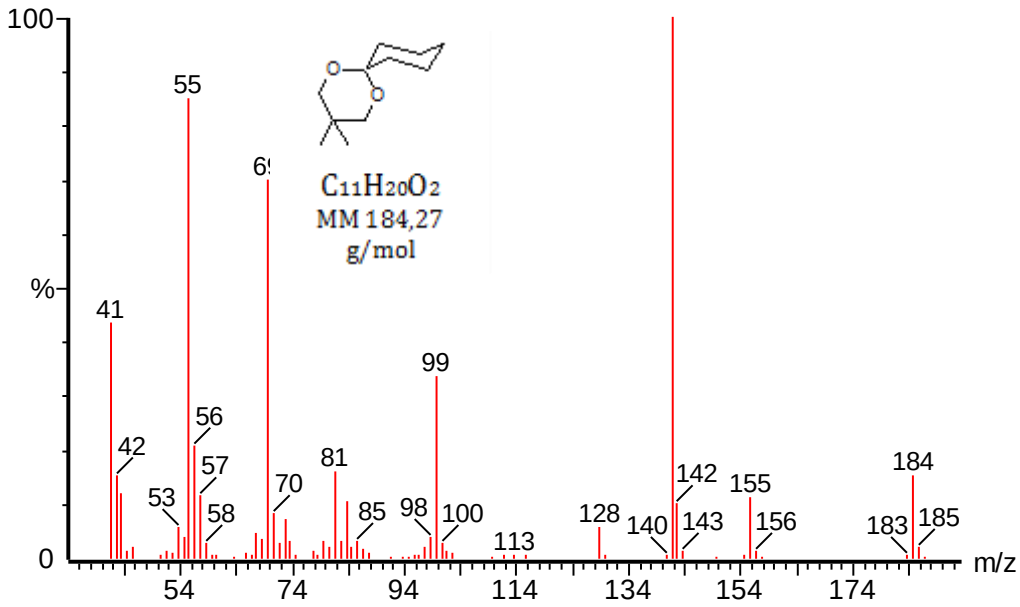


Figure S7. Mass spectrum of 3,3-dimethyl-1,5-dioxaspiro[5.5]-undecane or cyclohexanone, 2,2-dimethyl-1,3-propanediol ketal (**2**).

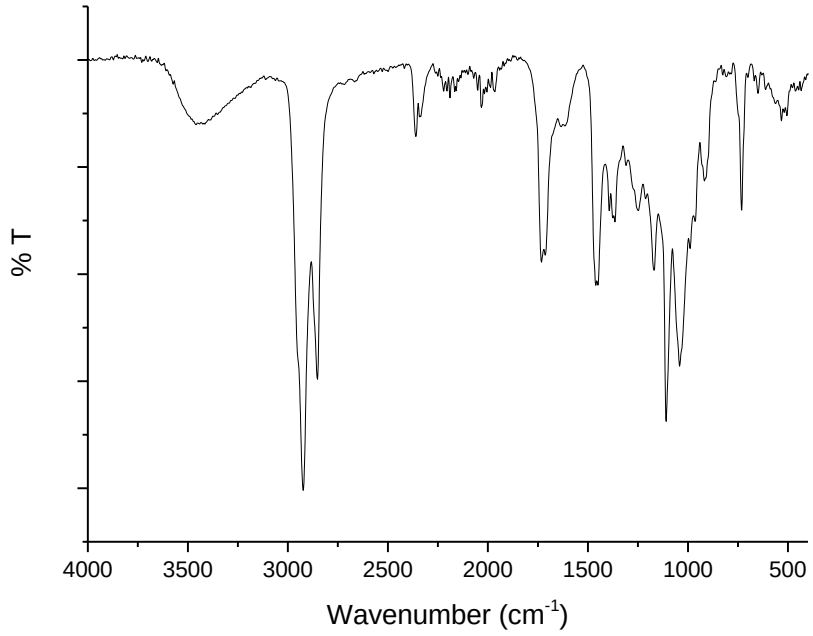


Figure S8. IR spectrum (KBr) of 3,3-dimethyl-1,5-dioxaspiro[5.5]-undecane or cyclohexanone, 2,2-dimethyl-1,3-propanediol ketal (**2**).

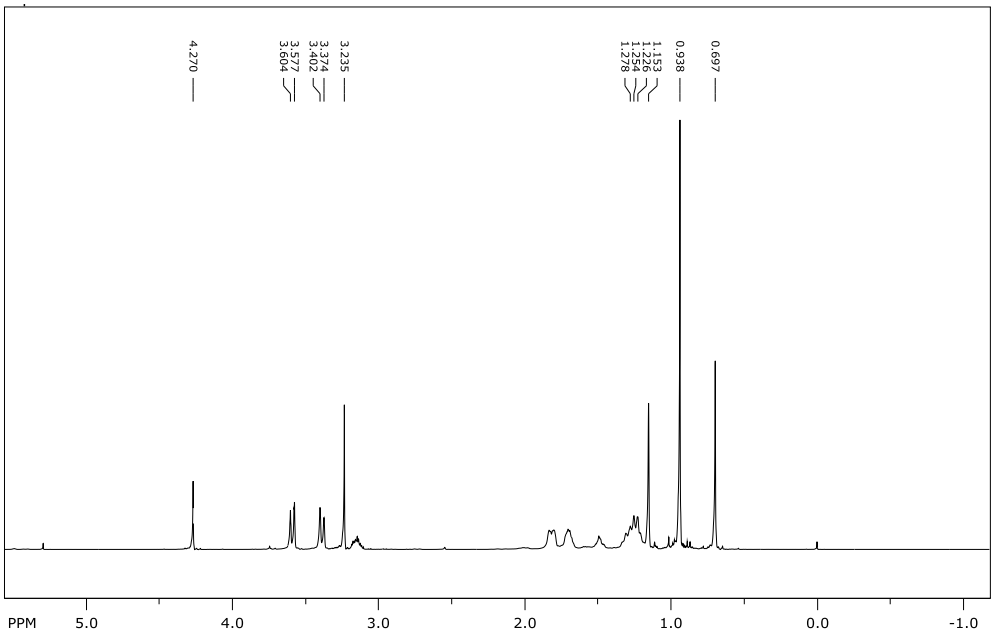


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3,3-dimethyl-1,5-dioxaspiro[5.5]-undecane or cyclohexanone, 2,2-dimethyl-1,3-propanediol ketal (**2**).

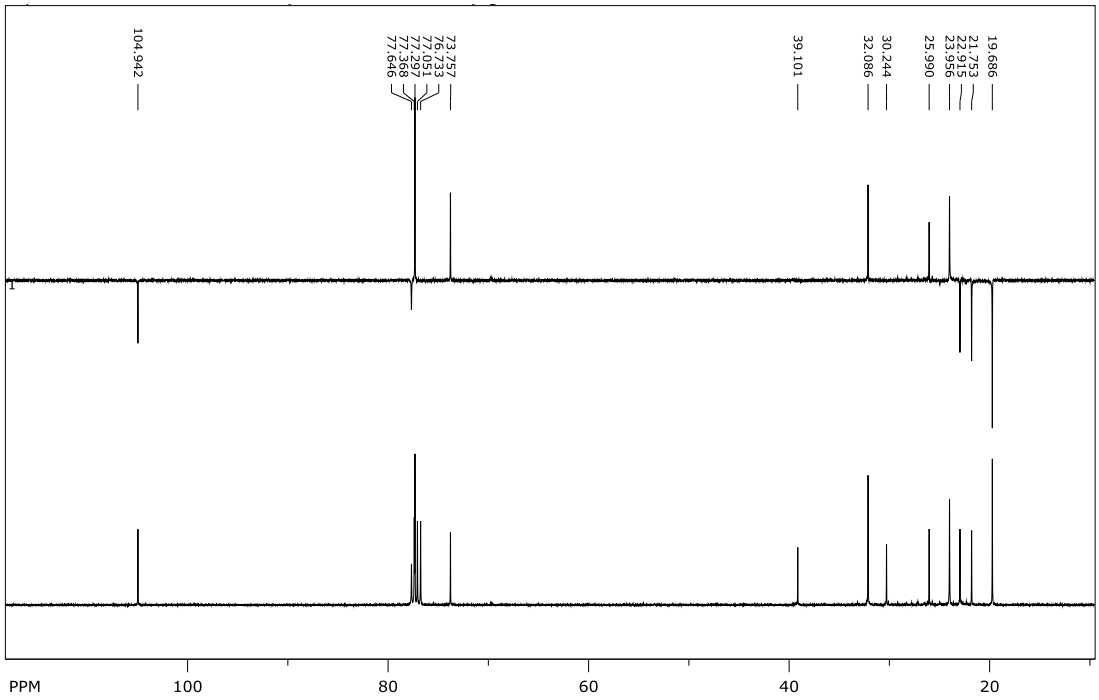


Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3,3-dimethyl-1,5-dioxaspiro[5.5]-undecane or cyclohexanone, 2,2-dimethyl-1,3-propanediol ketal (**2**).

3-Ethyl-1,5-dioxaspiro[5.5]undec-3-yl) metanol (**3**)

GC t_R = 34.96 min

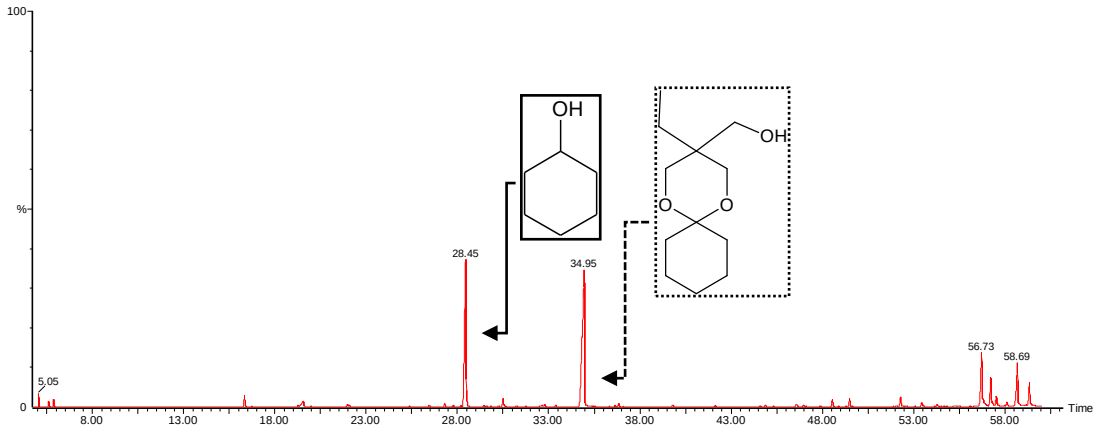


Figure S11. GC chromatogram of 3-ethyl-1,5-dioxaspiro[5.5]undec-3-yl) metanol (**3**).

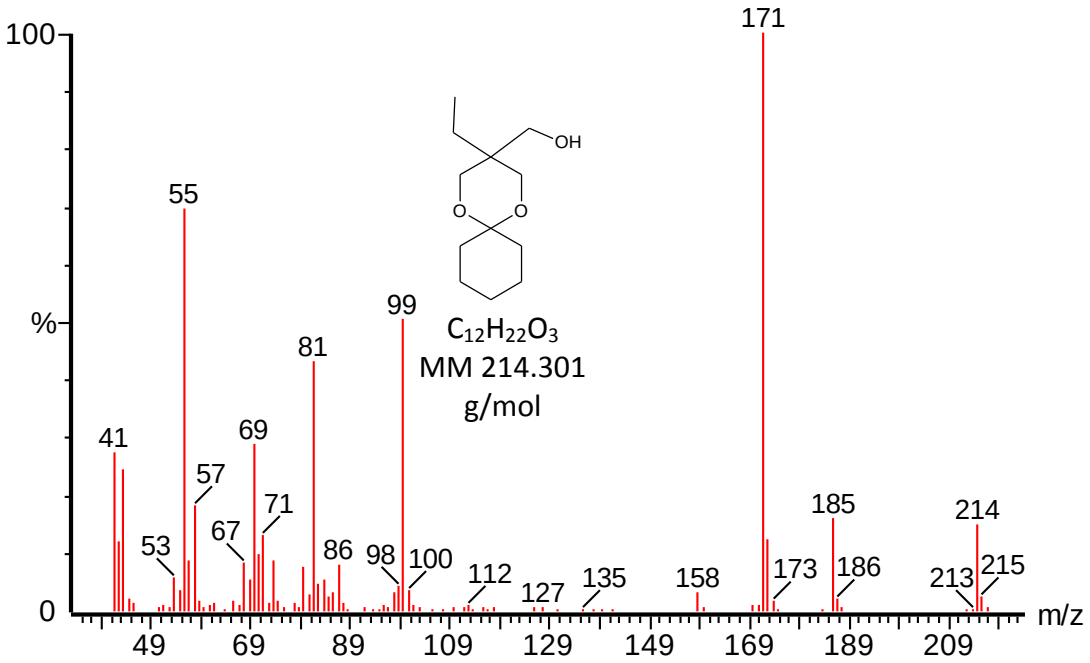


Figure S12. Mass spectrum of 3-ethyl-1,5-dioxaspiro[5.5]undec-3-yl) metanol (**3**).

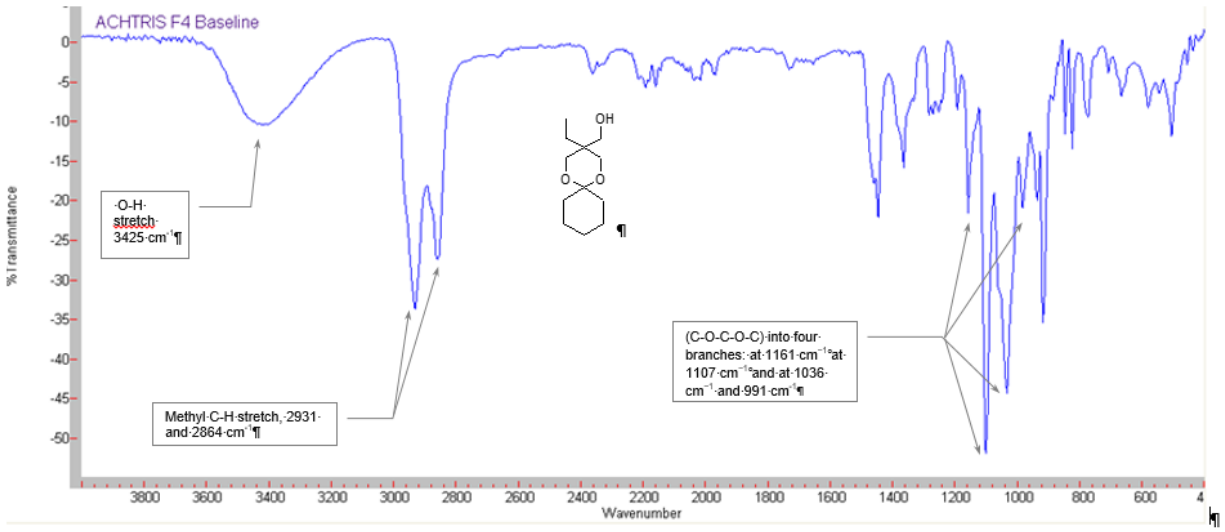


Figure S13. IR spectrum (KBr) of 3-ethyl-1,5-dioxaspiro[5.5]undec-3-yl) metanol (**3**).

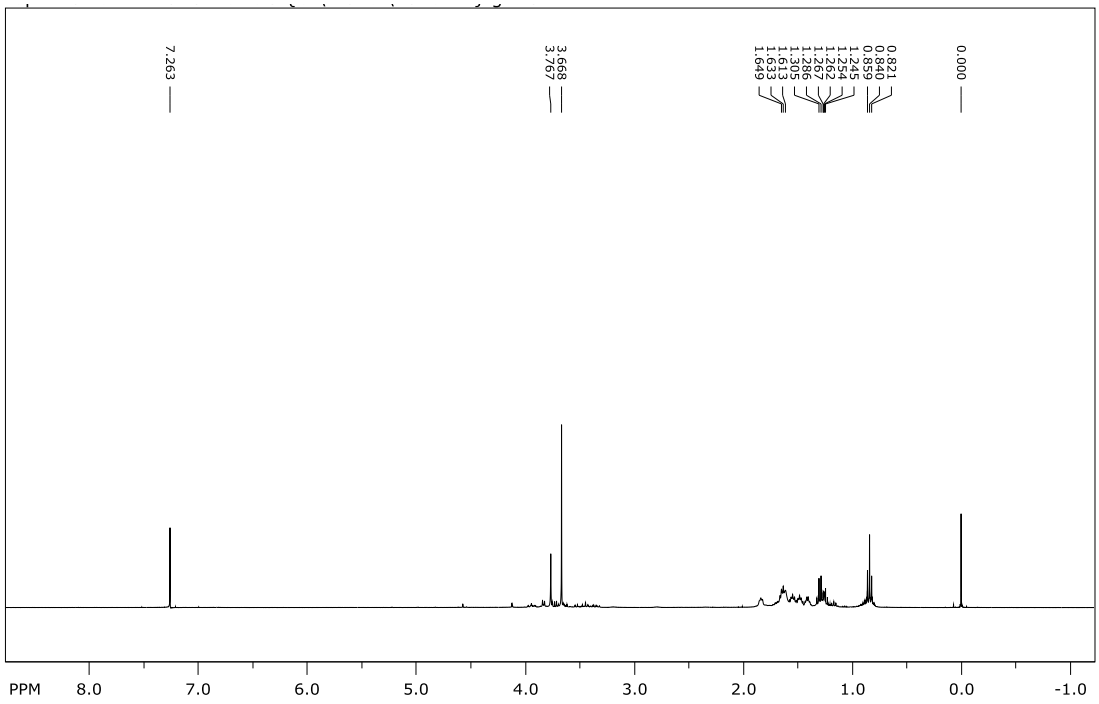


Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-ethyl-1,5-dioxaspiro[5.5]undec-3-yl) metanol (**3**).

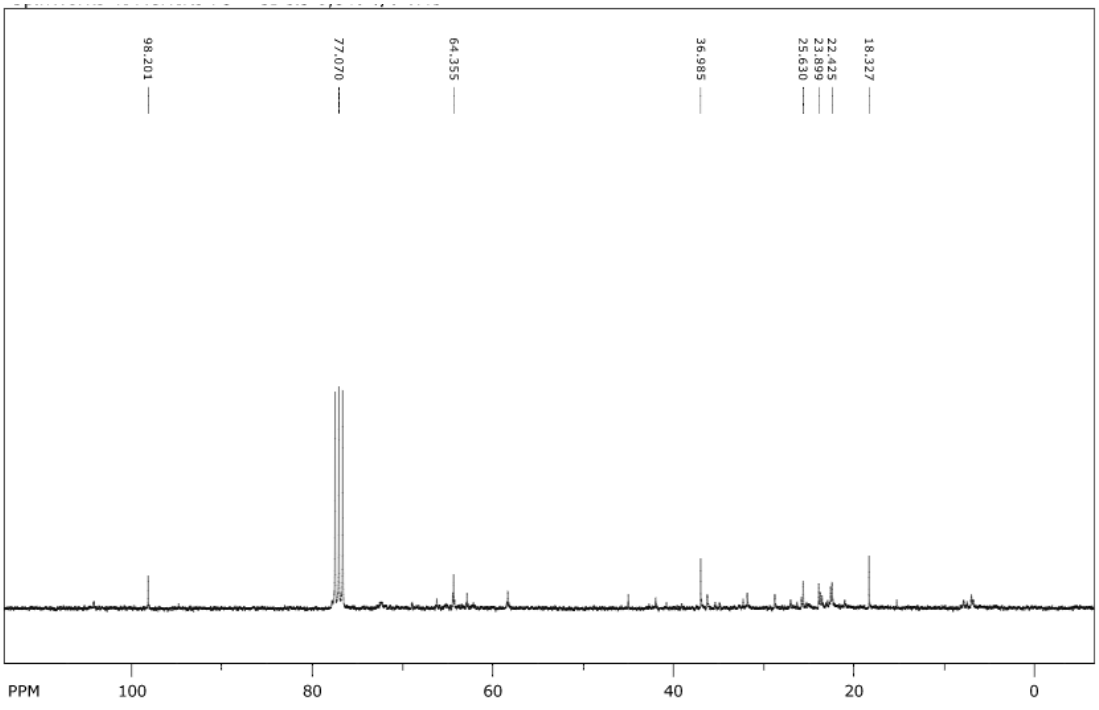


Figure S15. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3-ethyl-1,5-dioxaspiro[5.5]undec-3-yl) metanol (**3**).

1,4-Dioxaspiro[4.5]dec-2-yl methanol (**4**)

GC t_R = 21.96 min

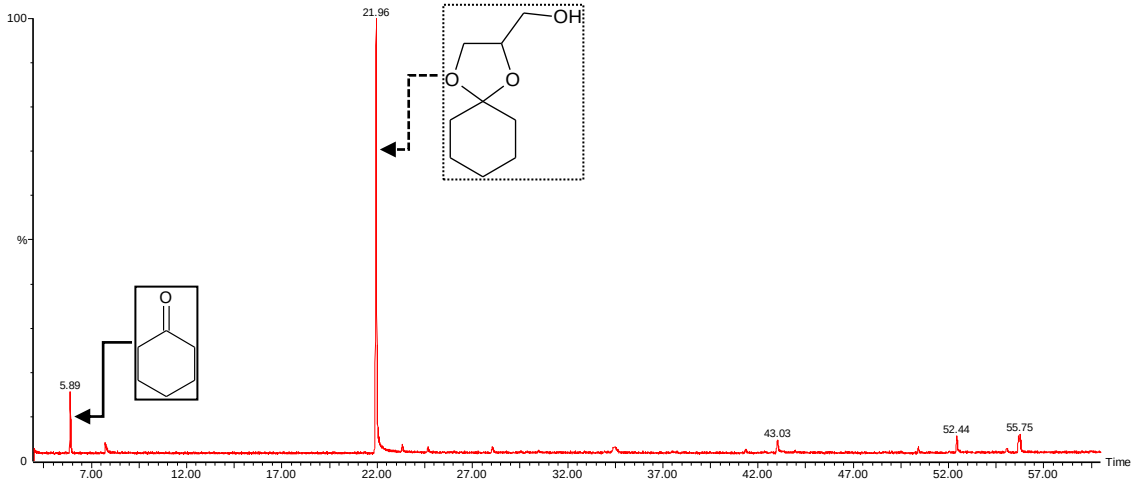


Figure S16. GC chromatogram of 1,4-dioxaspiro[4.5]dec-2-yl methanol (**4**).

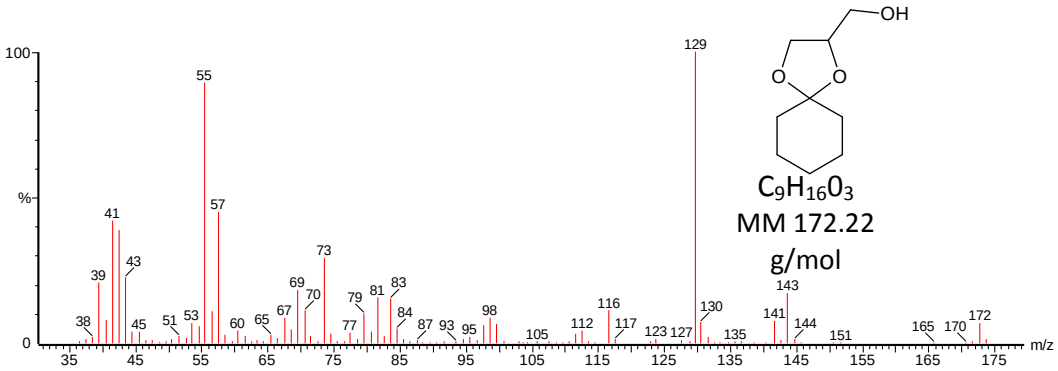


Figure S17. Mass spectrum of 1,4-dioxaspiro[4.5]dec-2-yl methanol (**4**).

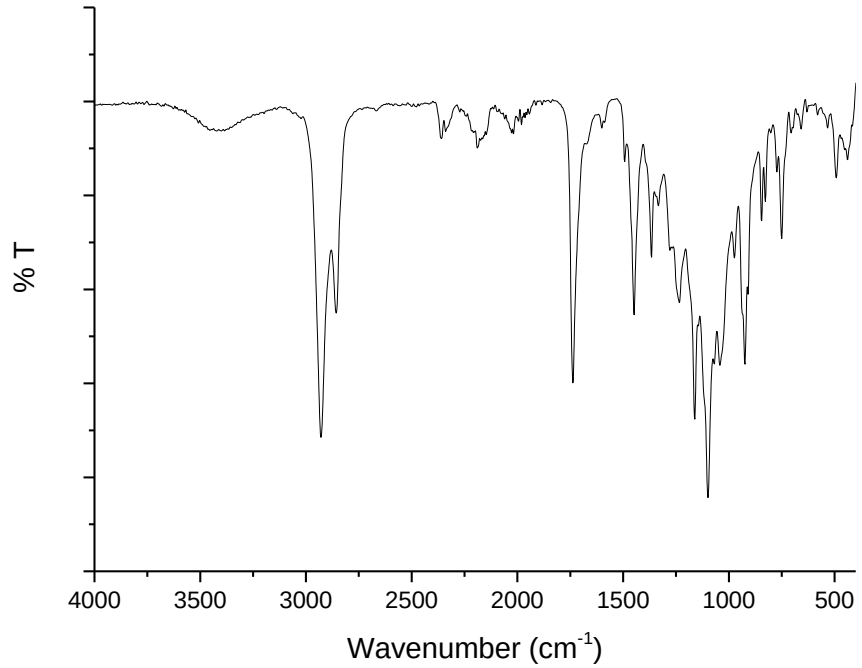


Figure S18. IR spectrum (KBr) of 1,4-dioxaspiro[4.5]dec-2-yl methanol (**4**).

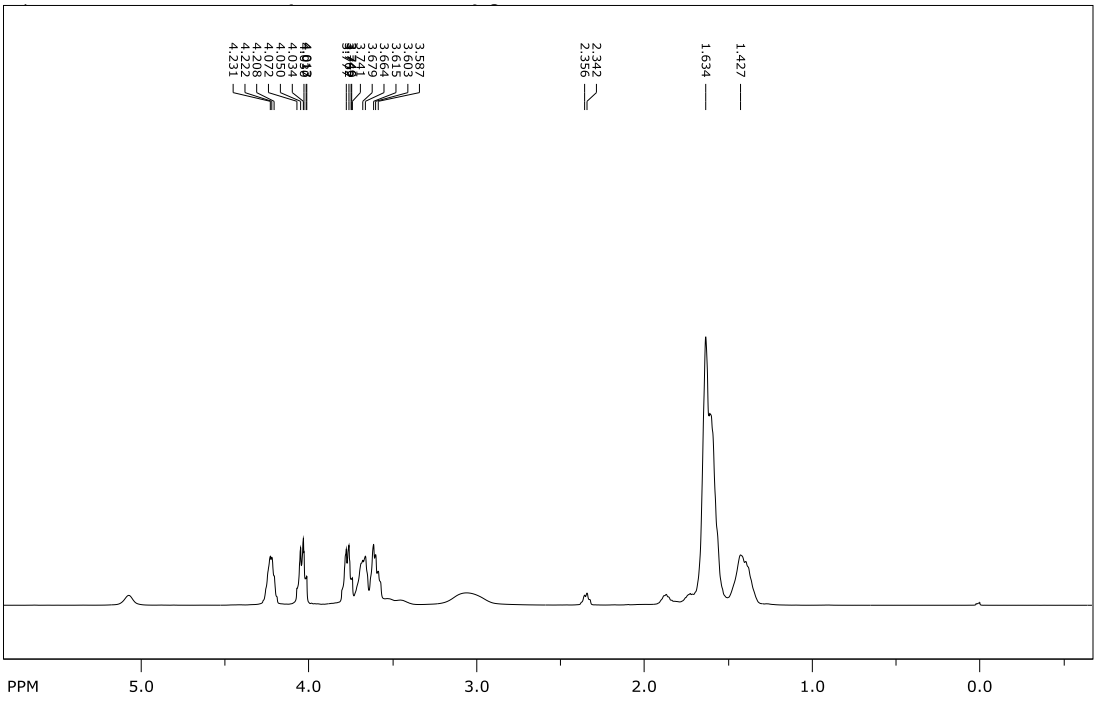


Figure S19. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 1,4-dioxaspiro[4.5]dec-2-yl methanol (**4**).

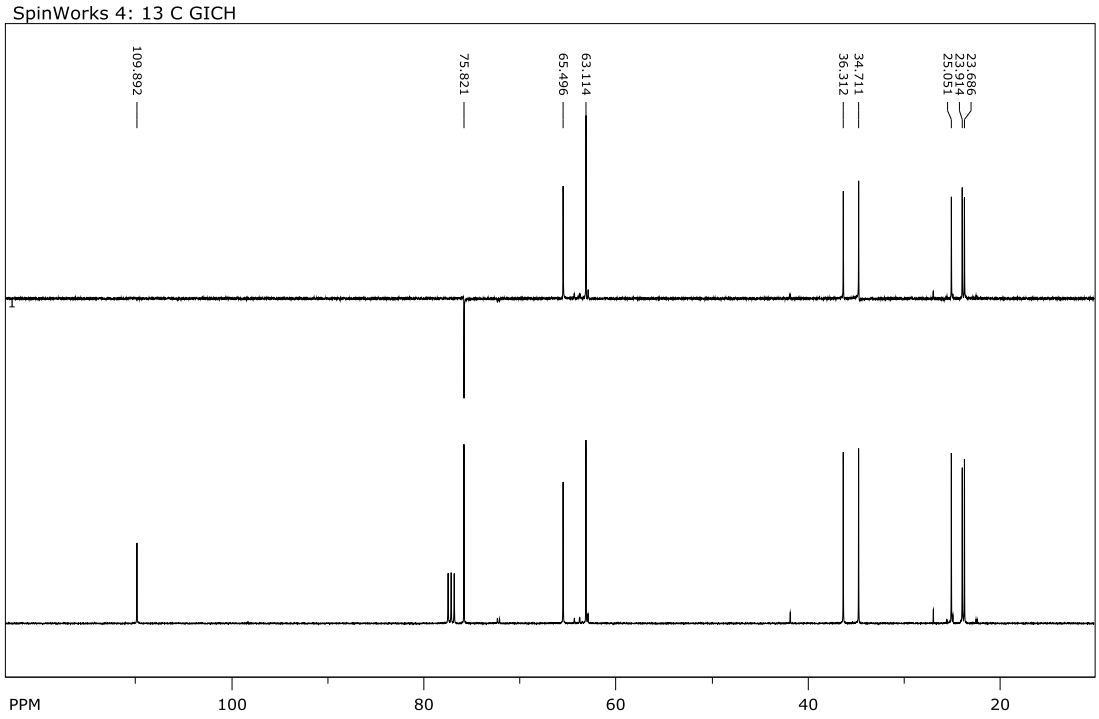


Figure S20. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of 1,4-dioxaspiro[4.5]dec-2-yl methanol (**4**).

2-Methyl-2-phenyl-1,3-dioxolane (**5**)

GC t_R = 17.32 min

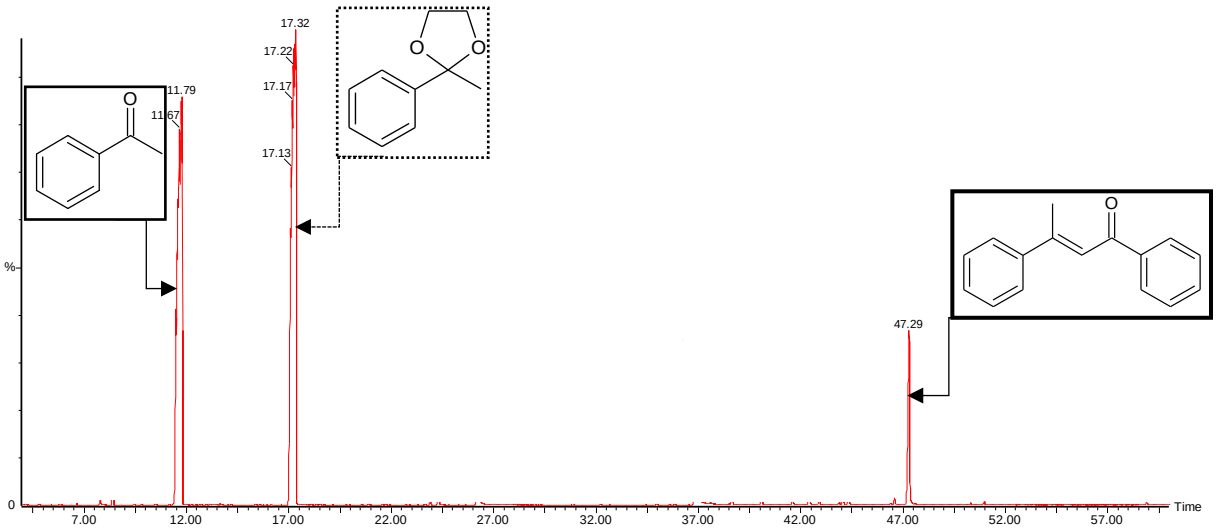


Figure S21. GC chromatogram of 2-methyl-2-phenyl-1,3-dioxolane (**5**).

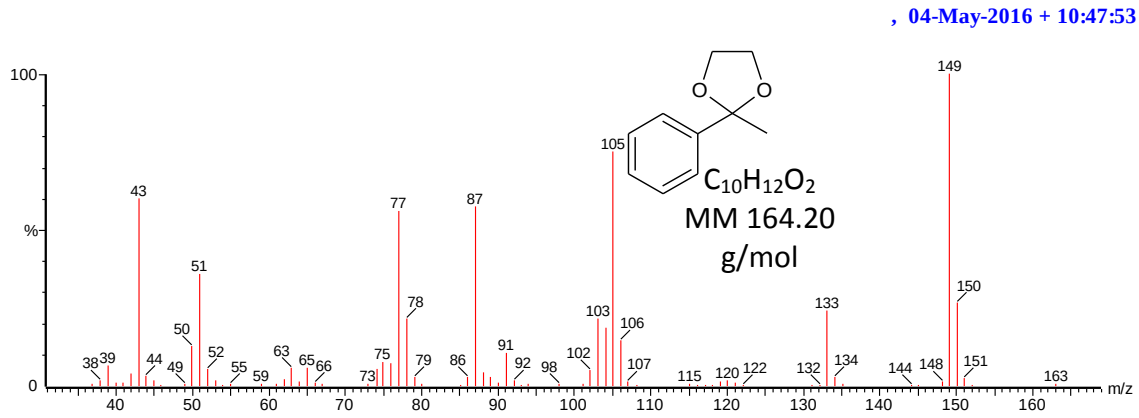


Figure S22. Mass spectrum of 2-methyl-2-phenyl-1,3-dioxolane (**5**).

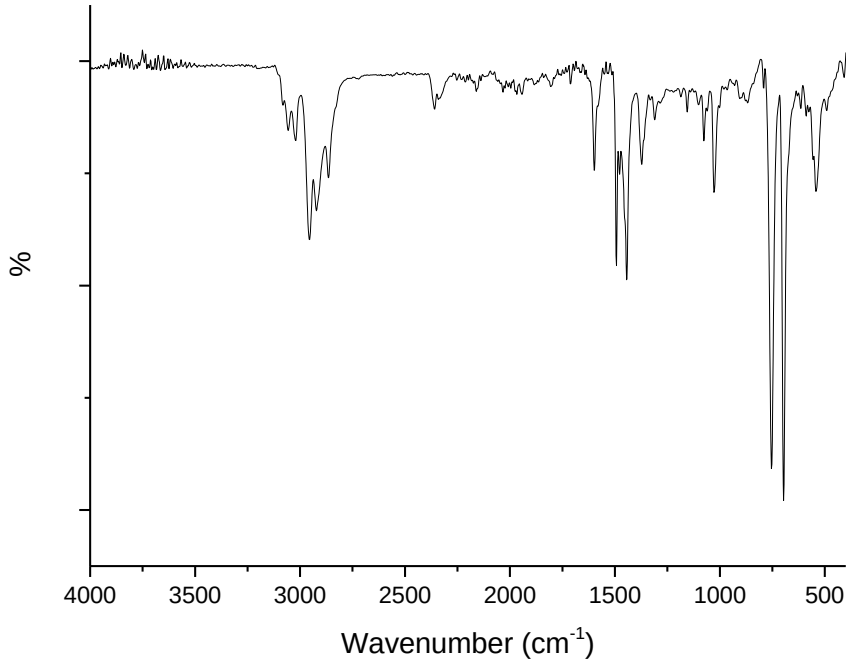


Figure S23. IR spectrum (KBr) of 2-methyl-2-phenyl-1,3-dioxolane (**5**).

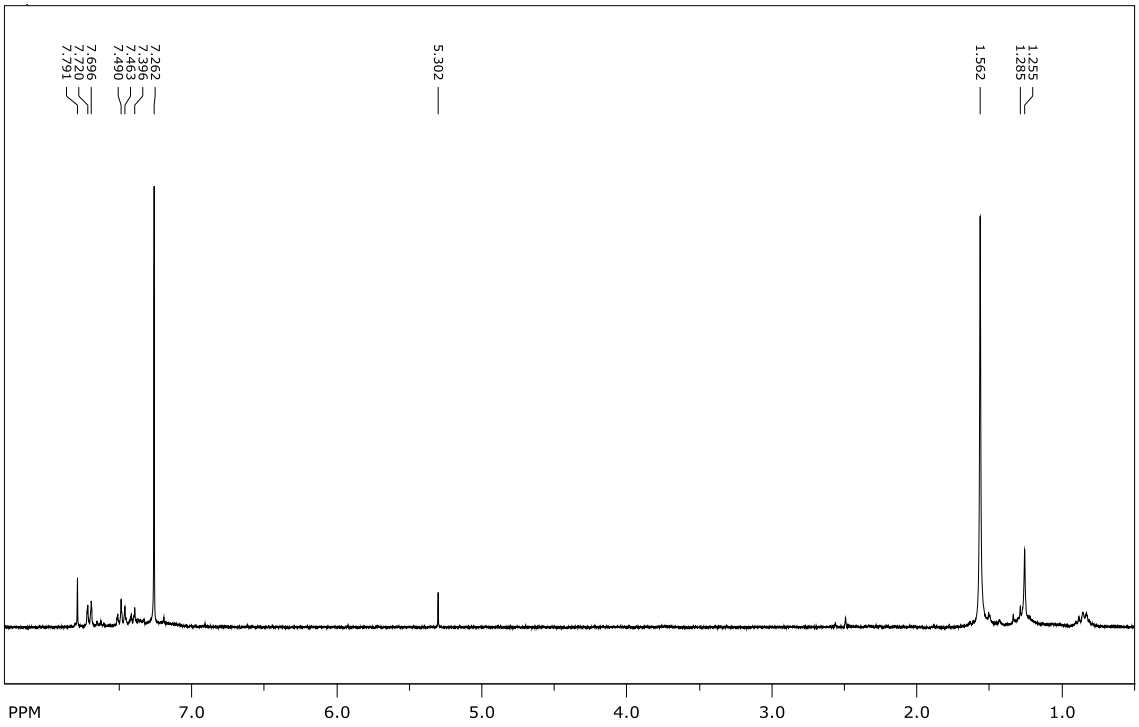


Figure S24. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-methyl-2-phenyl-1,3-dioxolane (**5**).

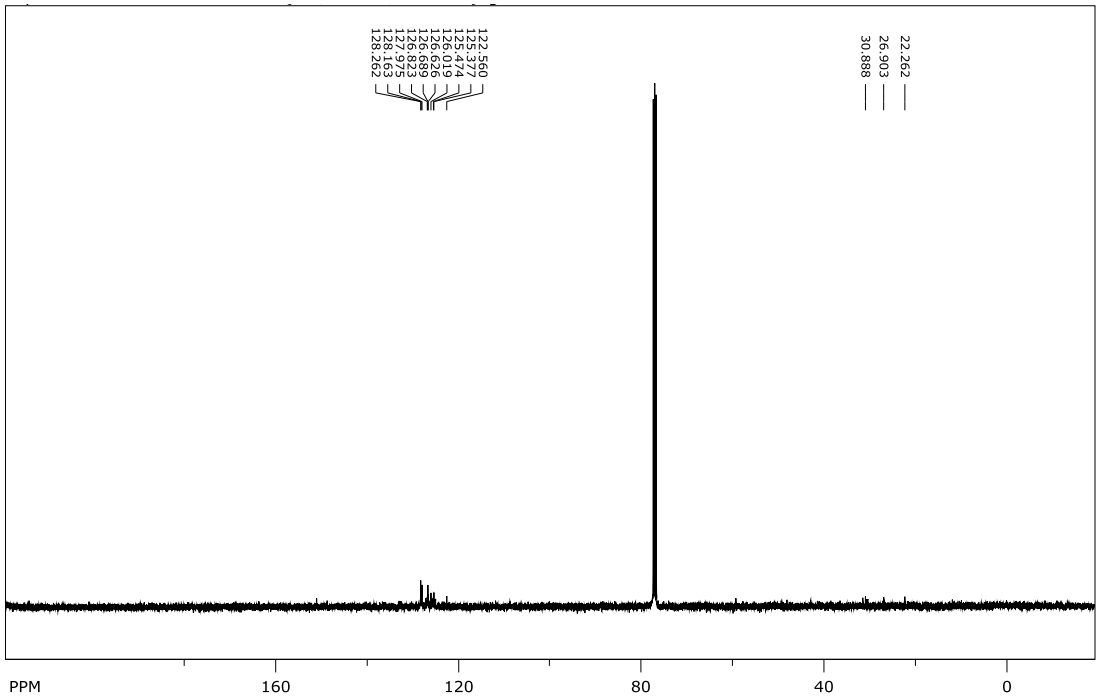


Figure S25. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2-methyl-2-phenyl-1,3-dioxolane (**5**).

2,5,5-Trimethyl-2-phenyl-1,3-dioxane (**6**)

GC t_R = 23.75 min

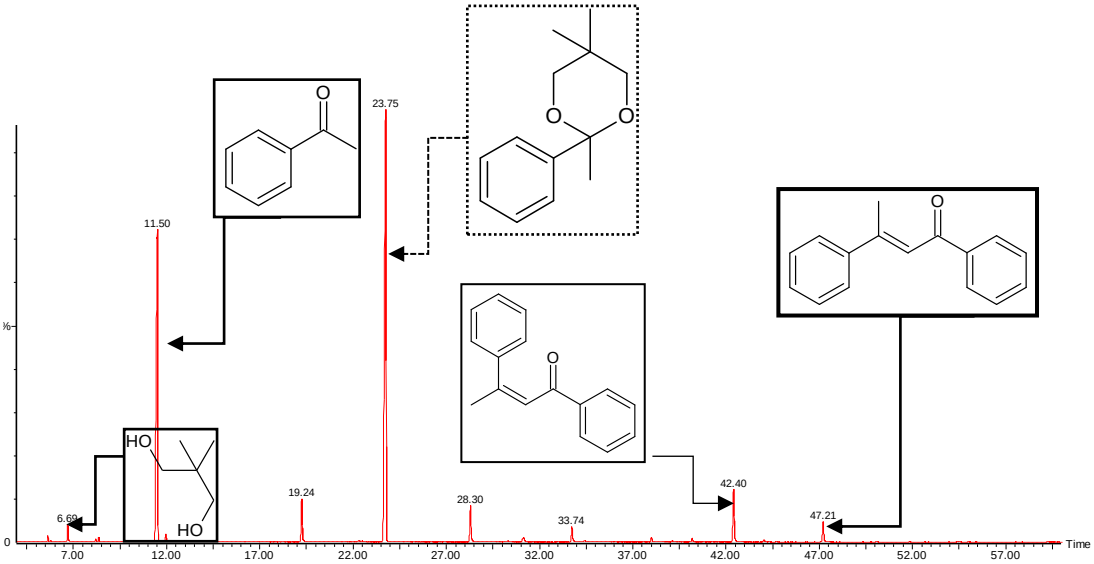


Figure S26. GC chromatogram of 2,5,5-trimethyl-2-phenyl-1,3-dioxane (**6**).

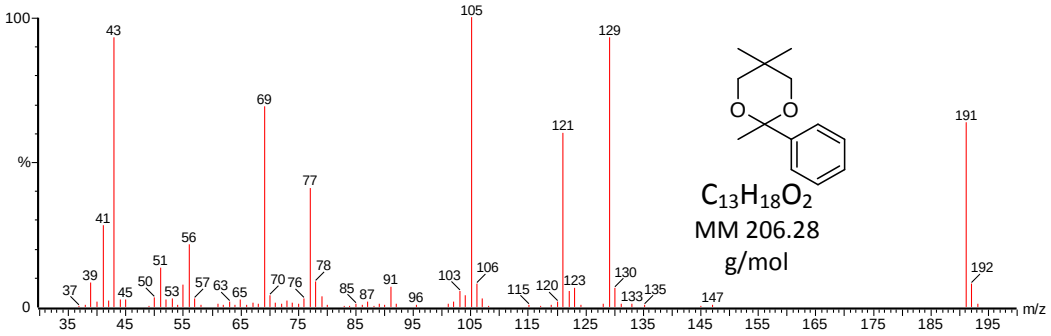


Figure S27. Mass spectrum of 2,5,5-trimethyl-2-phenyl-1,3-dioxane (**6**).

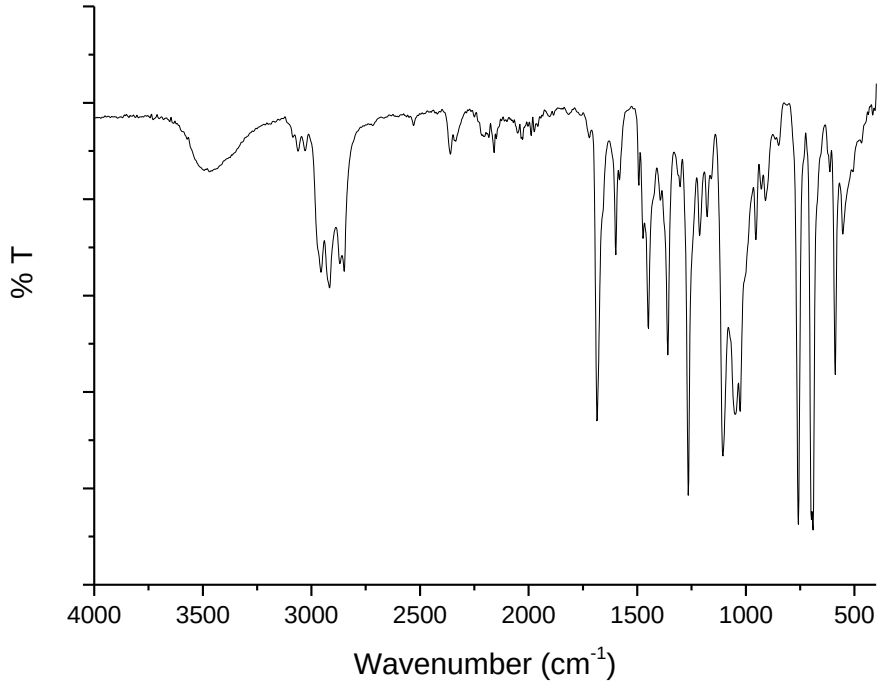


Figure S28. IR spectrum (KBr) of 2,5,5-trimethyl-2-phenyl-1,3-dioxane (**6**).

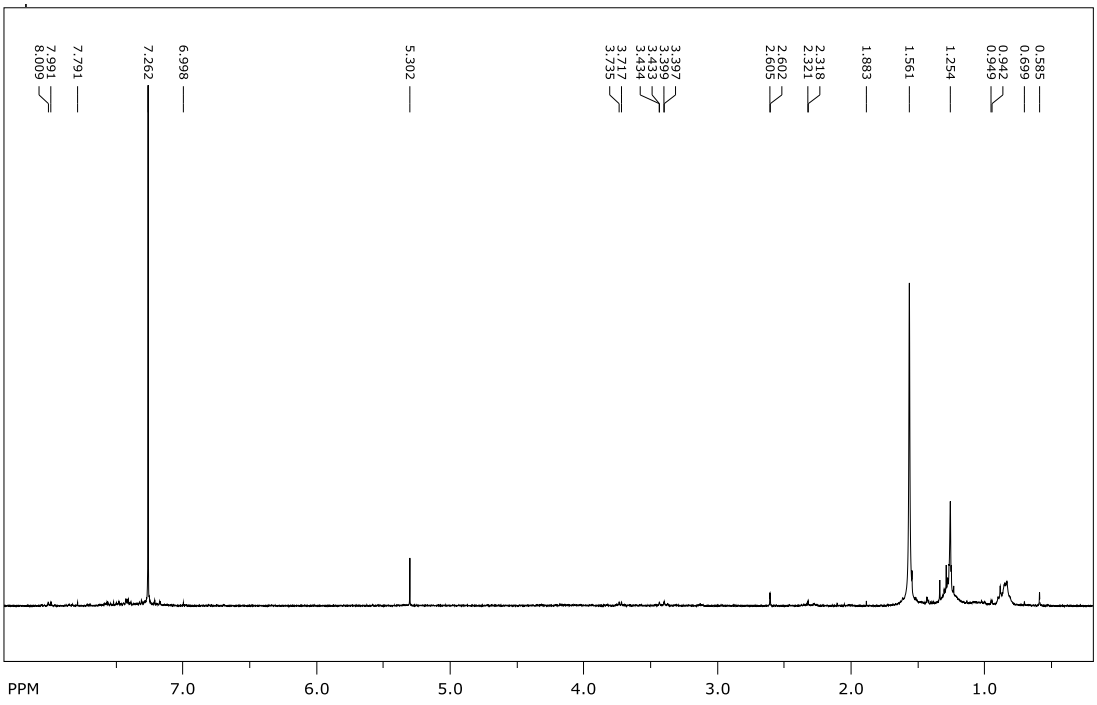


Figure S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2,5,5-trimethyl-2-phenyl-1,3-dioxane (**6**).

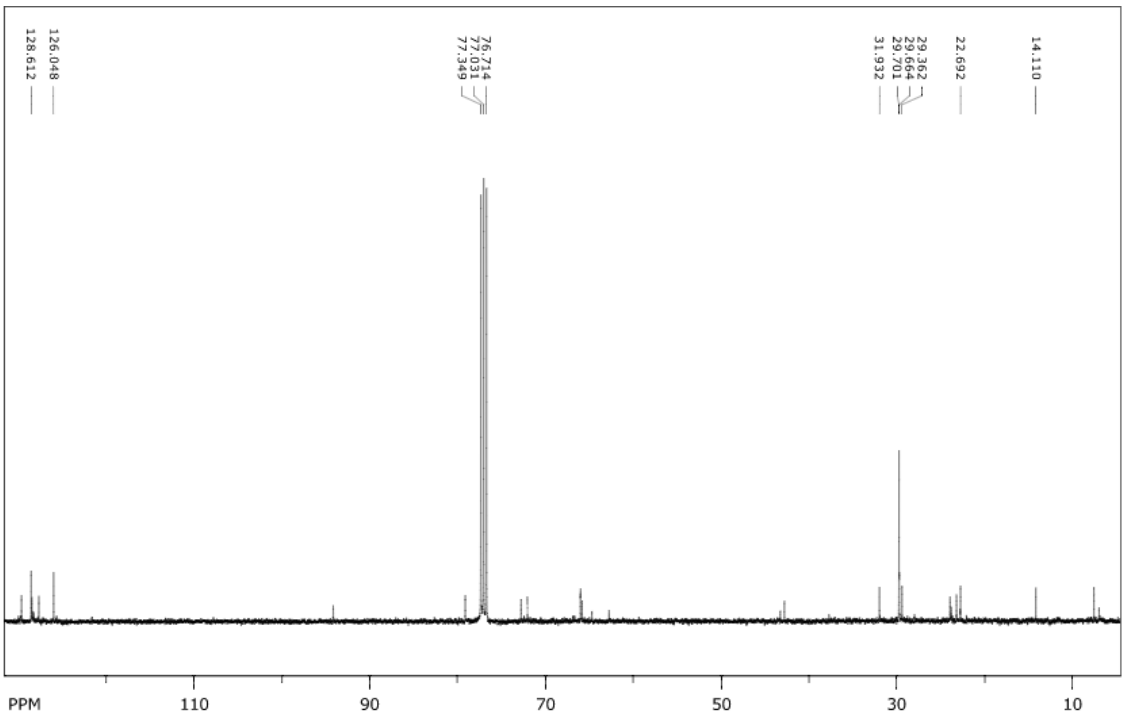


Figure S30. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2,5,5-trimethyl-2-phenyl-1,3-dioxane (**6**).

5-Ethyl-2-methyl-2-phenyl-1,3-dioxan-5-yl) methanol (**7**)

GC t_R = 38.27 min

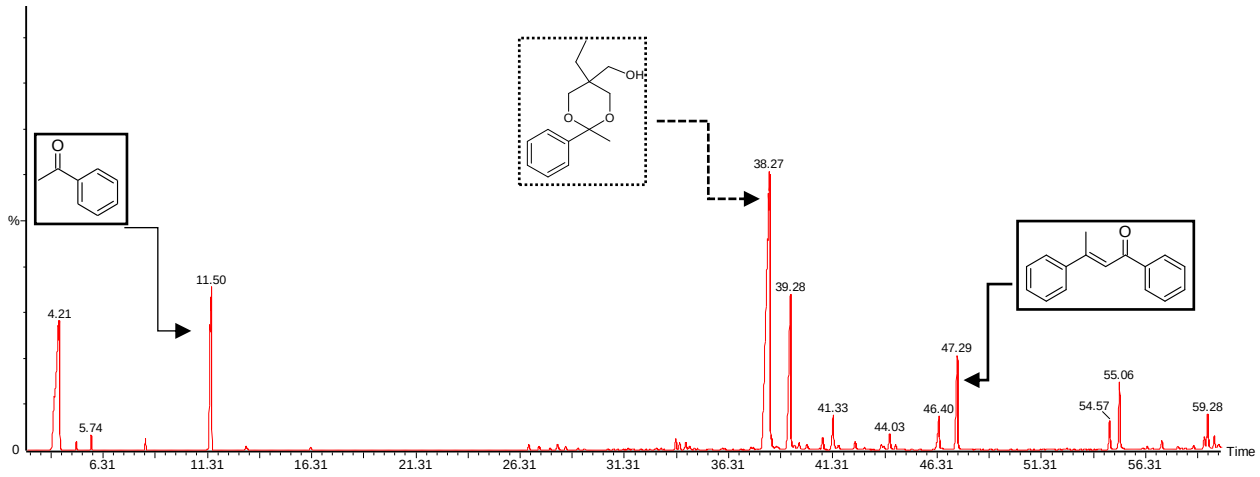
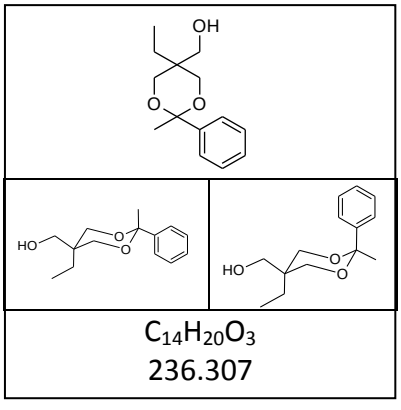


Figure S31. GC chromatogram of 5-ethyl-2-methyl-2-phenyl-1,3-dioxan-5-yl) methanol (**7**).



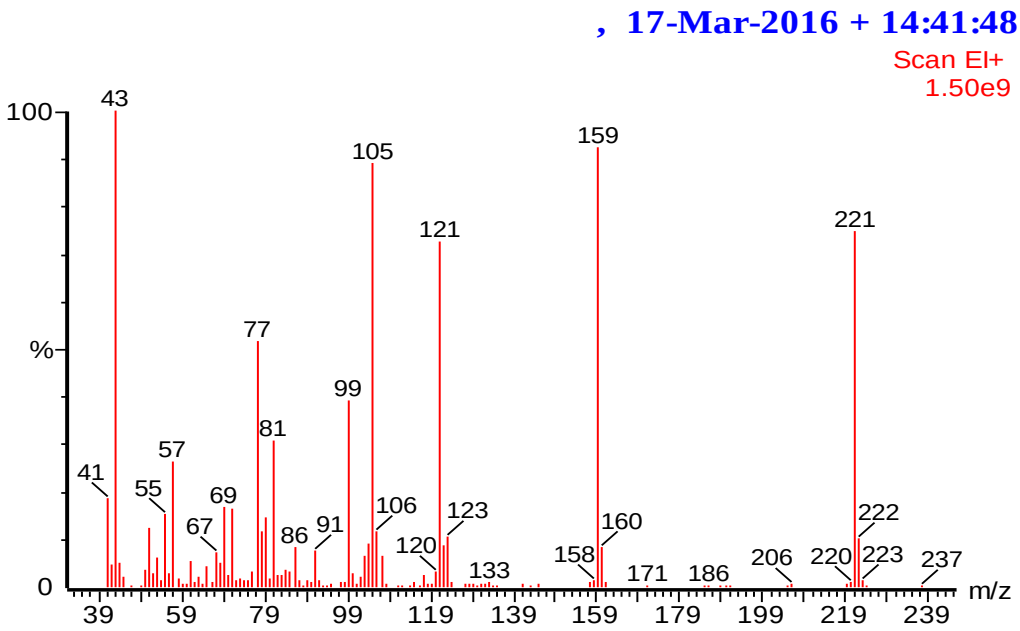


Figure S32. Mass spectrum of 5-ethyl-2-methyl-2-phenyl-1,3-dioxan-5-yl) methanol (**7**).

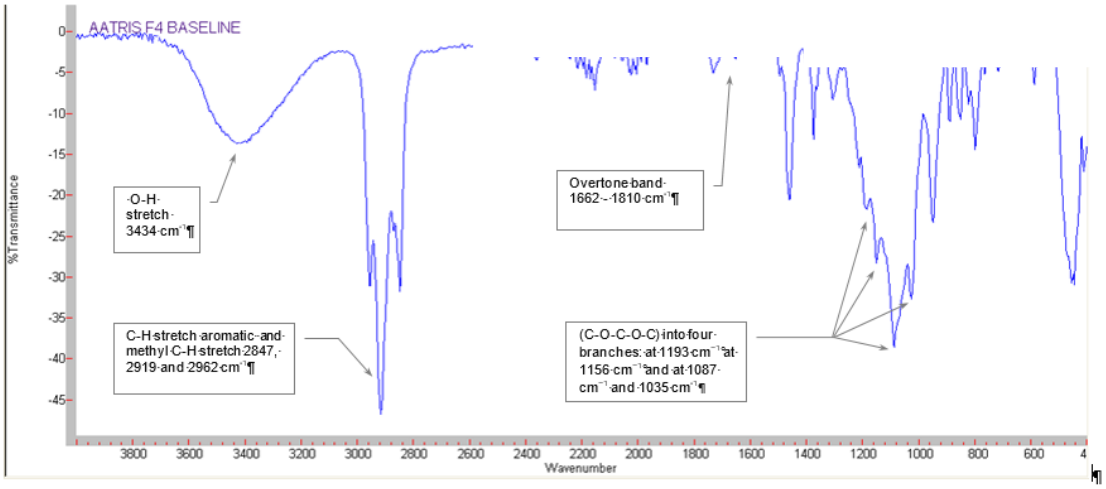


Figure S33. IR spectrum (KBr) of 5-ethyl-2-methyl-2-phenyl-1,3-dioxan-5-yl) methanol (**7**).

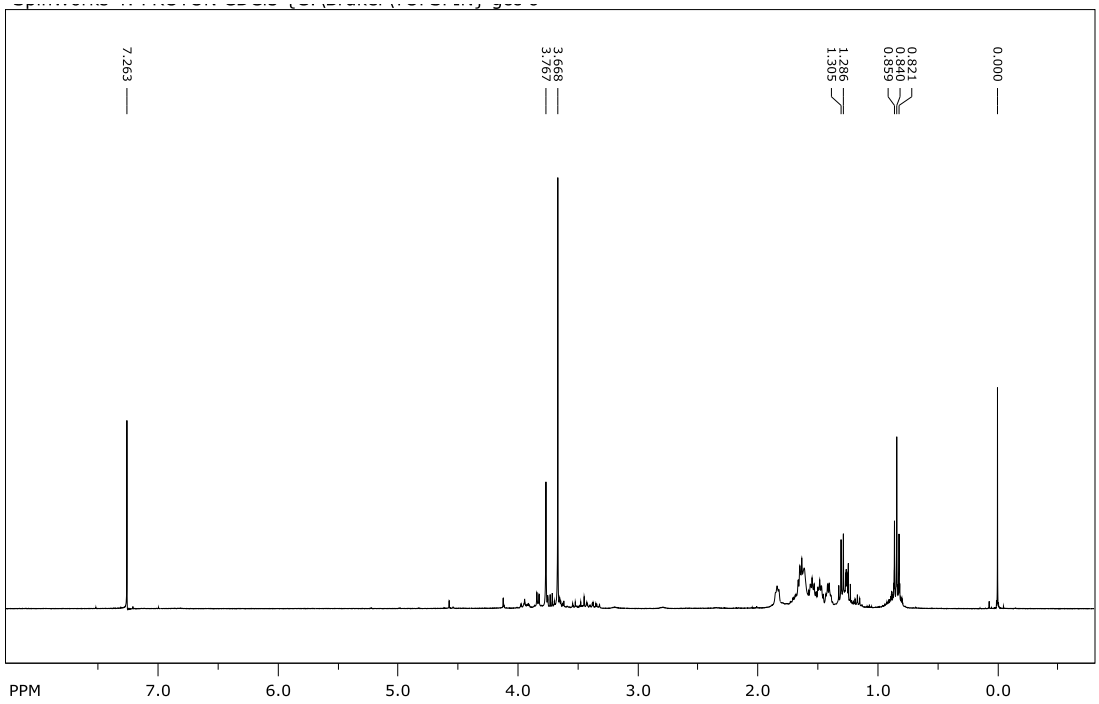


Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 5-ethyl-2-methyl-2-phenyl-1,3-dioxan-5-yl) methanol (**7**).

2-Methyl-2-phenyl-1,3-dioxolan-4-yl) metanol (**8**)

GC t_R = 36.35 min

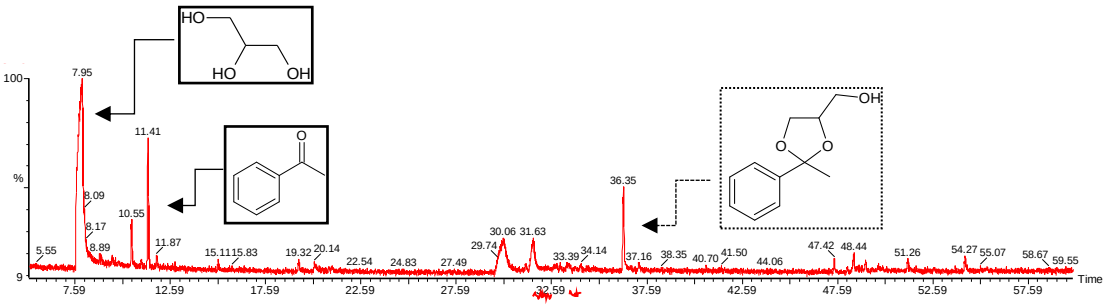


Figure S35. GC chromatogram of 2-methyl-2-phenyl-1,3-dioxolan-4-yl) metanol (**8**).

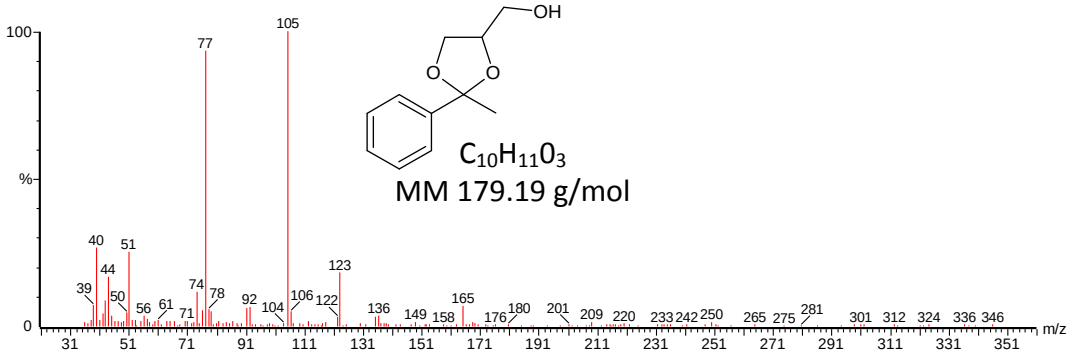


Figure S36. Mass spectrum of 2-methyl-2-phenyl-1,3-dioxolan-4-yl) metanol (**8**).

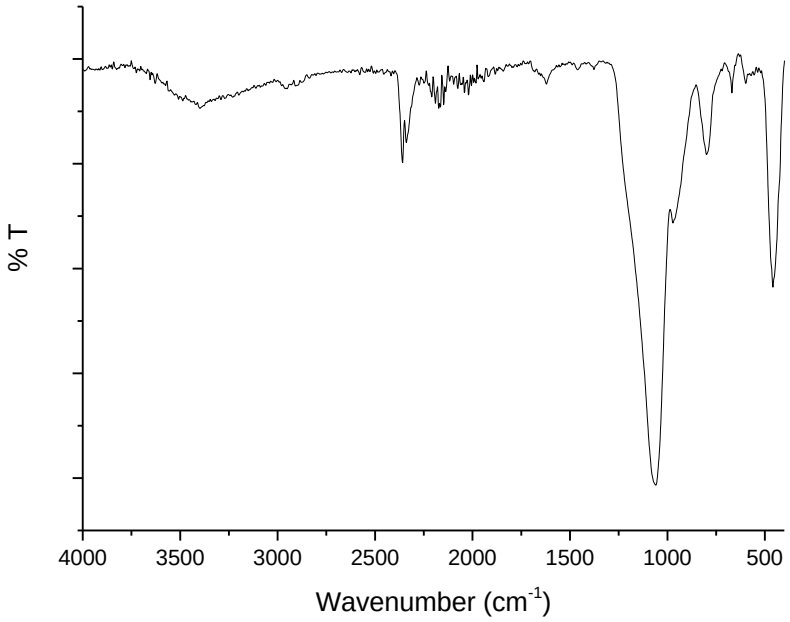


Figure S37. IR spectrum (KBr) of 2-methyl-2-phenyl-1,3-dioxolan-4-yl) metanol (**8**).

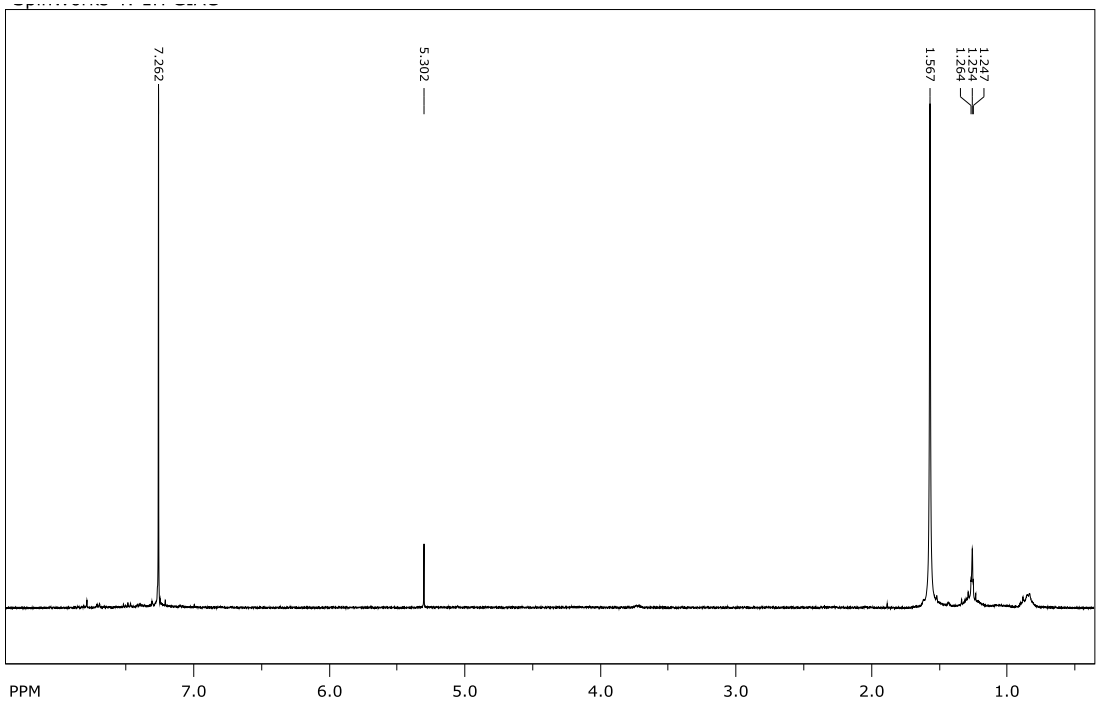


Figure S38. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 2-methyl-2-phenyl-1,3-dioxolan-4-yl) metanol (**8**).

2,2-Diphenyl-1,3-dioxolane (**13**)

GC t_R = 39.98 min

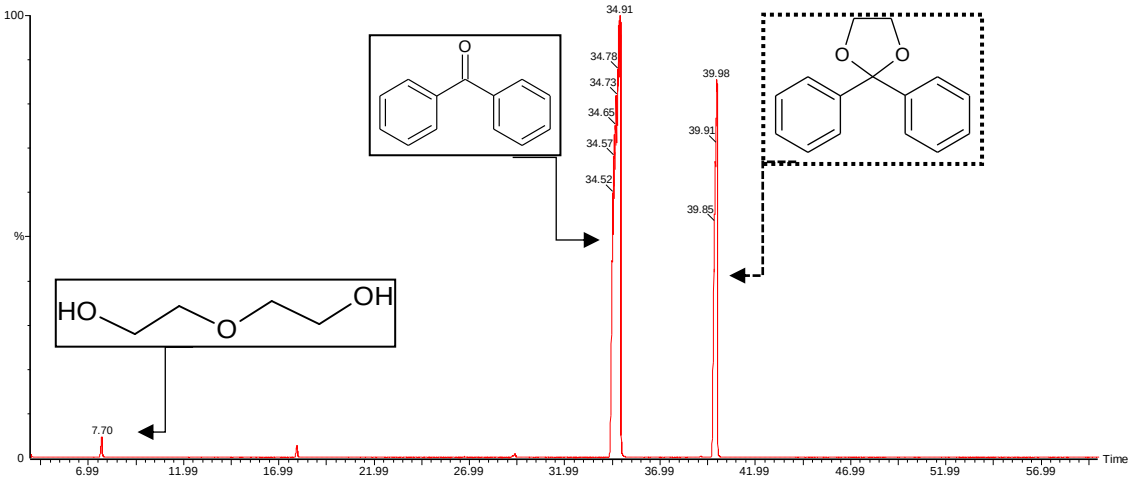


Figure S39. GC chromatogram of 2,2-diphenyl-1,3-dioxolane (**13**).

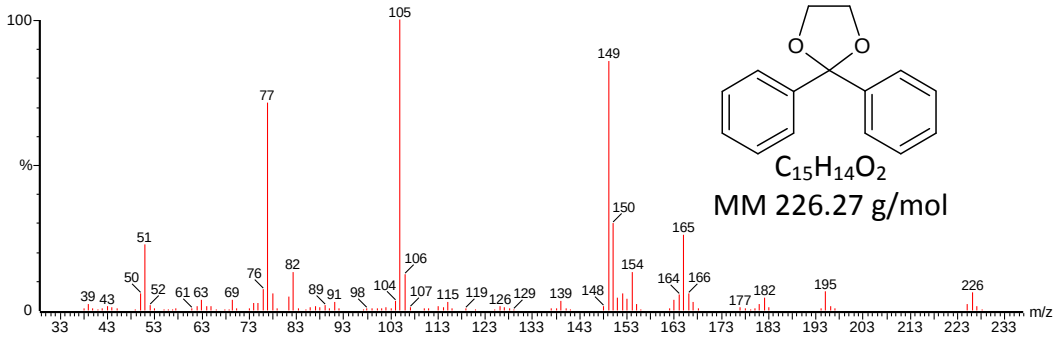


Figure S40. Mass spectrum of 2,2-diphenyl-1,3-dioxolane (**13**).

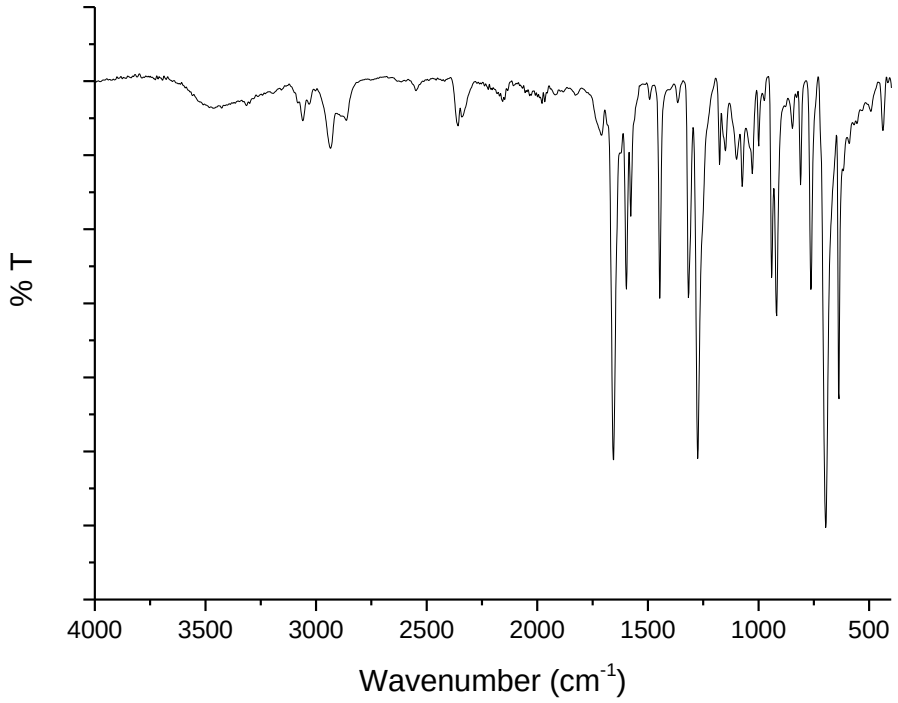


Figure S41. IR spectrum (KBr) of 2,2-diphenyl-1,3-dioxolane (**13**).

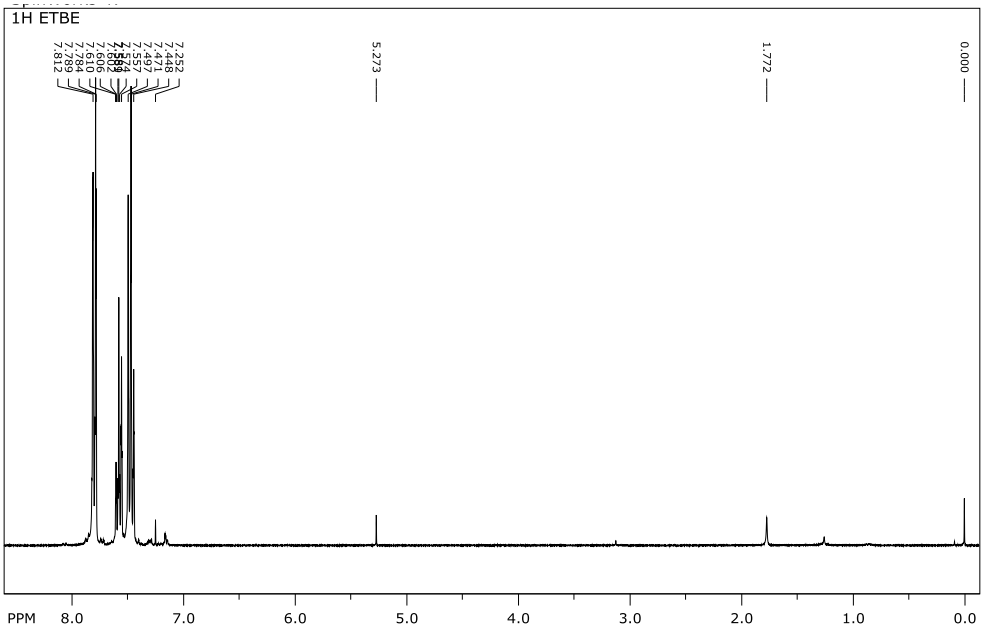


Figure S42. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2,2-diphenyl-1,3-dioxolane (**13**).

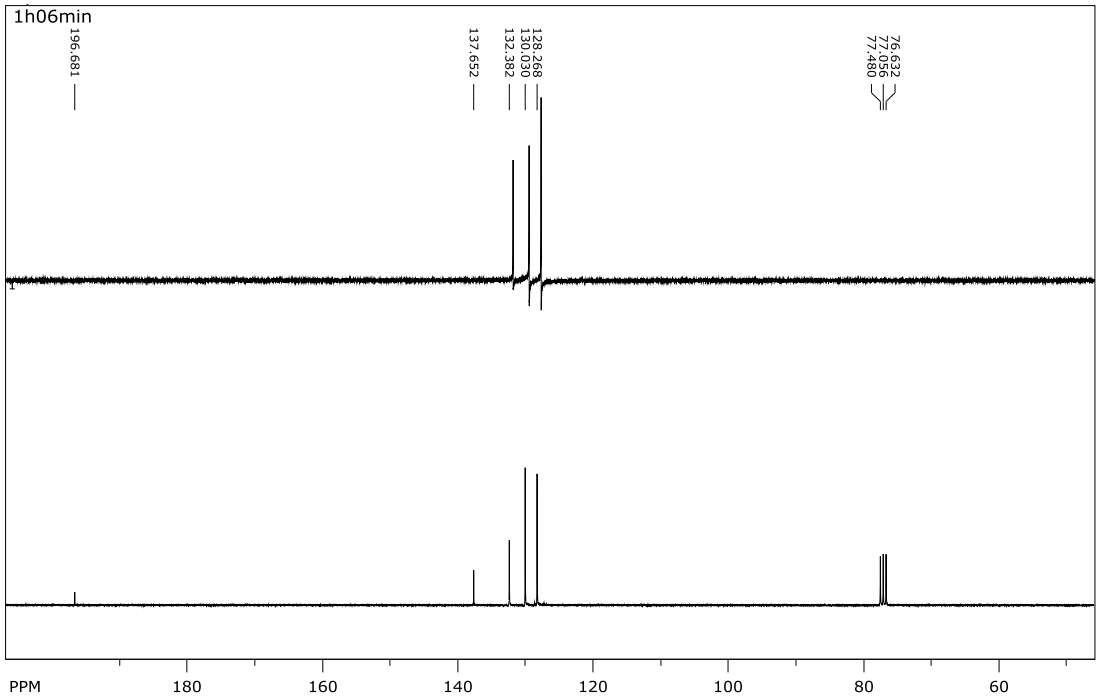


Figure S43. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2,2-diphenyl-1,3-dioxolane (**13**).

15,5-Dimethyl-2,2-diphenyl-1,3-dioxane (**14**)

GC t_R = 45.02 min

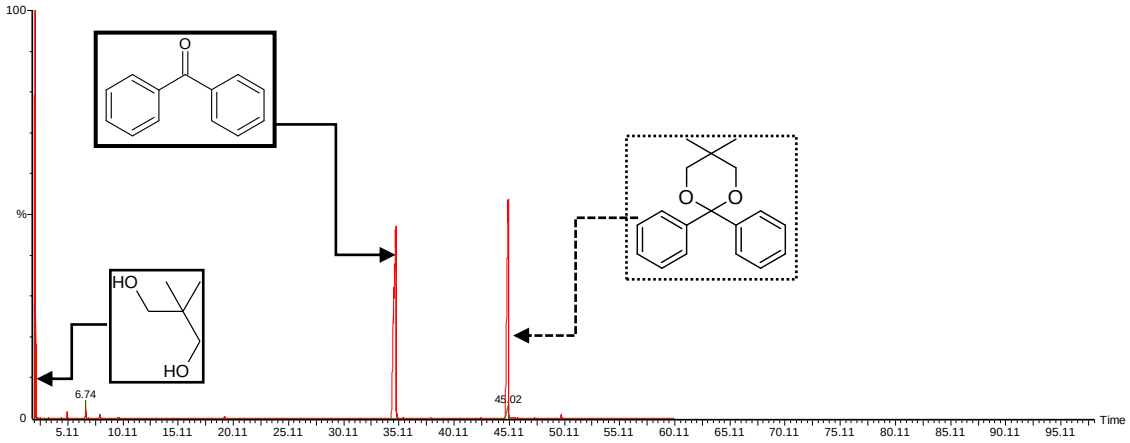


Figure S44. GC chromatogram of 5,5-dimethyl-2,2-diphenyl-1,3-dioxane (**14**).

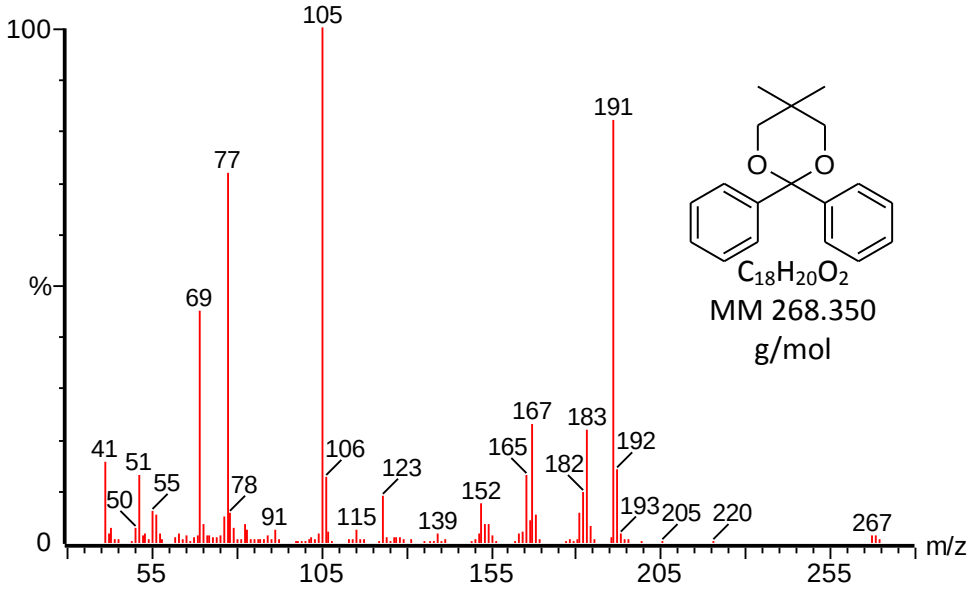


Figure S45. Mass spectrum of 5,5-dimethyl-2,2-diphenyl-1,3-dioxane **(14)**.

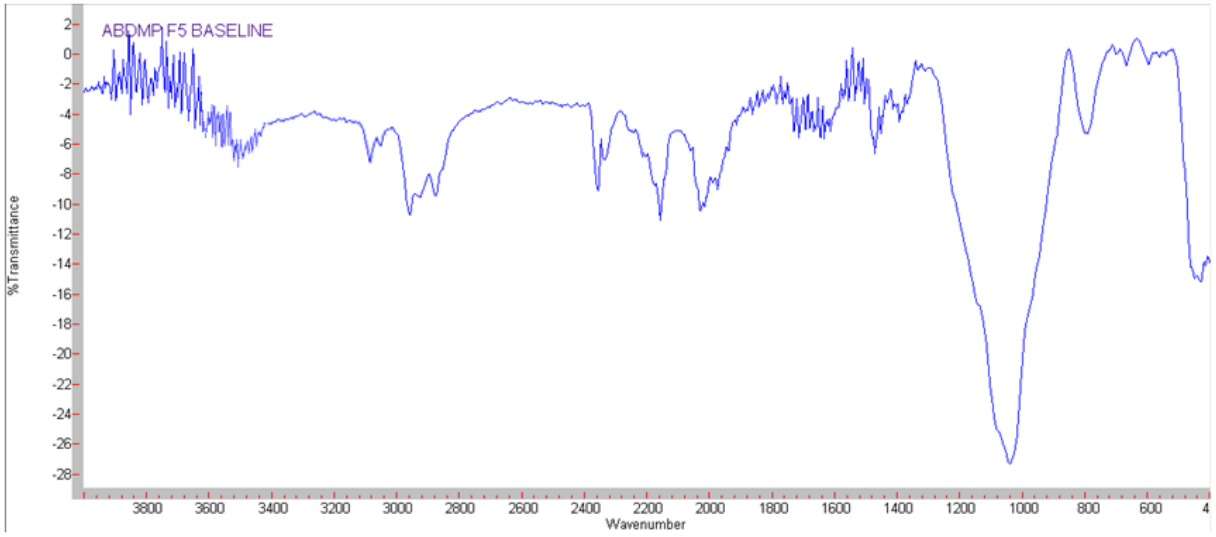


Figure S46. IR spectrum (KBr) of 5,5-dimethyl-2,2-diphenyl-1,3-dioxane (**14**).

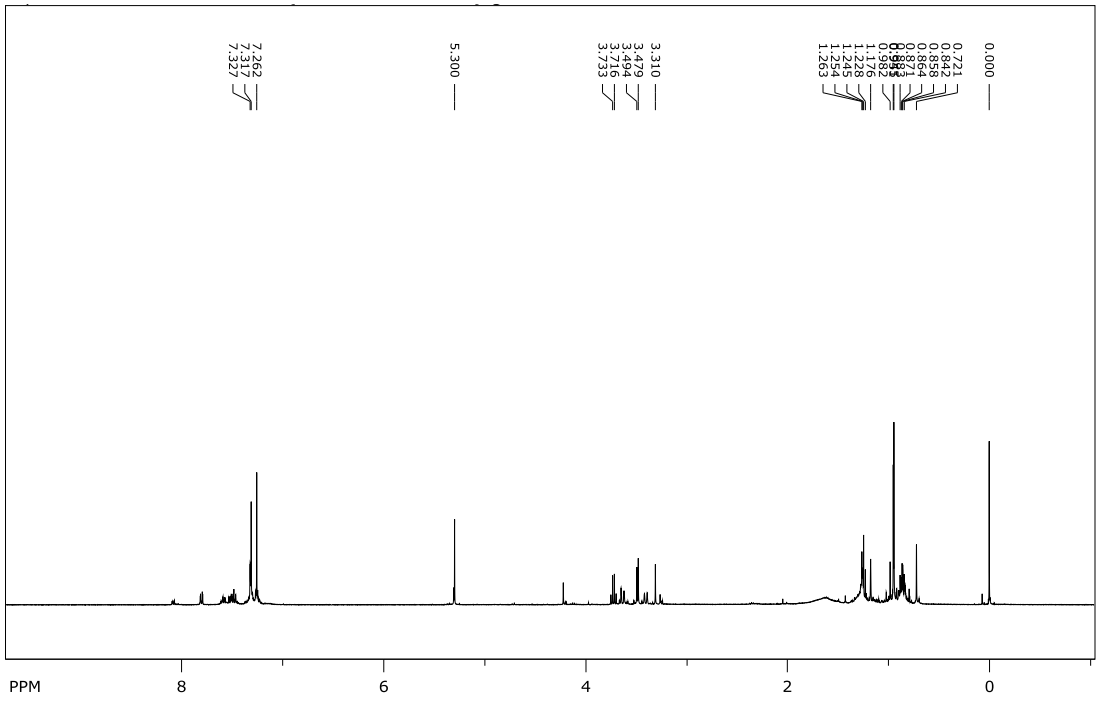


Figure S47. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 5,5-dimethyl-2,2-diphenyl-1,3-dioxane (**14**).

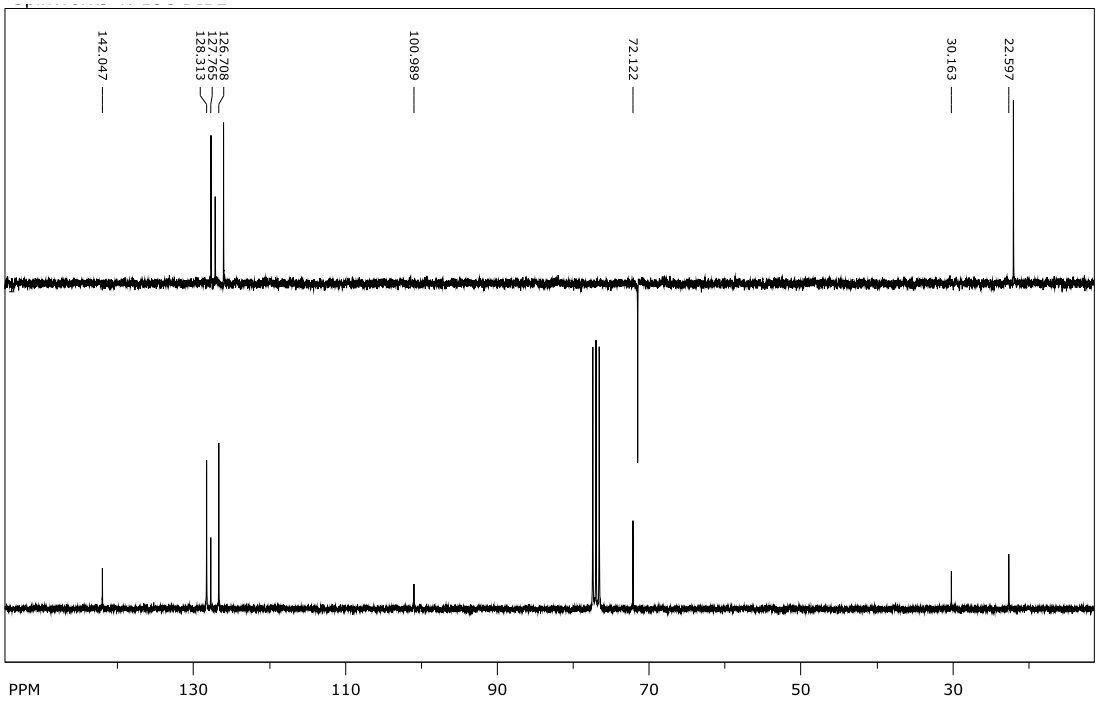


Figure S48. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 5,5-dimethyl-2,2-diphenyl-1,3-dioxane (**14**).

(5-Ethyl-2,2-diphenyl-1,3-dioxan-5-yl) metanol (**15**)

GC – t_R = 56.27 min.

GC

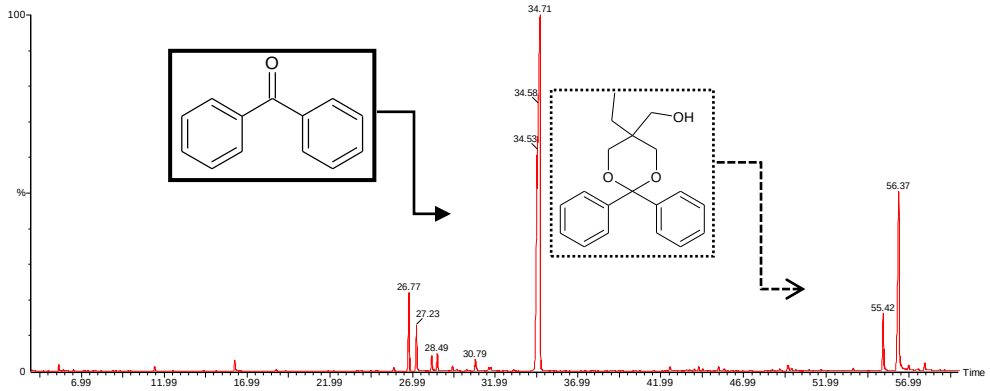


Figure S49. GC chromatogram of (5-ethyl-2,2-diphenyl-1,3-dioxan-5-yl) metanol (**15**).

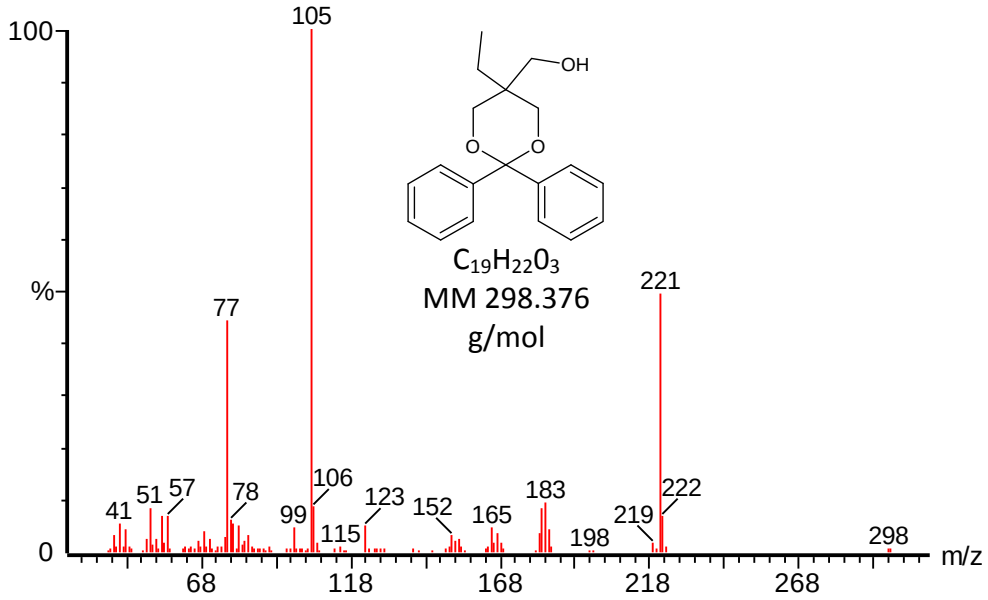


Figure S50. Mass spectrum of (5-ethyl-2,2-diphenyl-1,3-dioxan-5-yl) metanol (**15**).

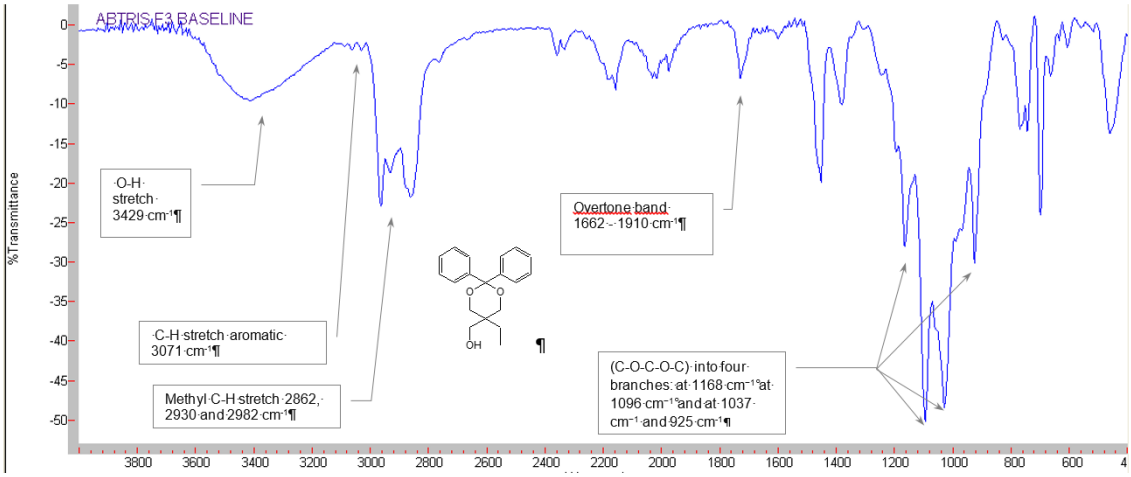


Figure S51. IR spectrum (KBr) of (5-ethyl-2,2-diphenyl-1,3-dioxan-5-yl) methanol (**15**).

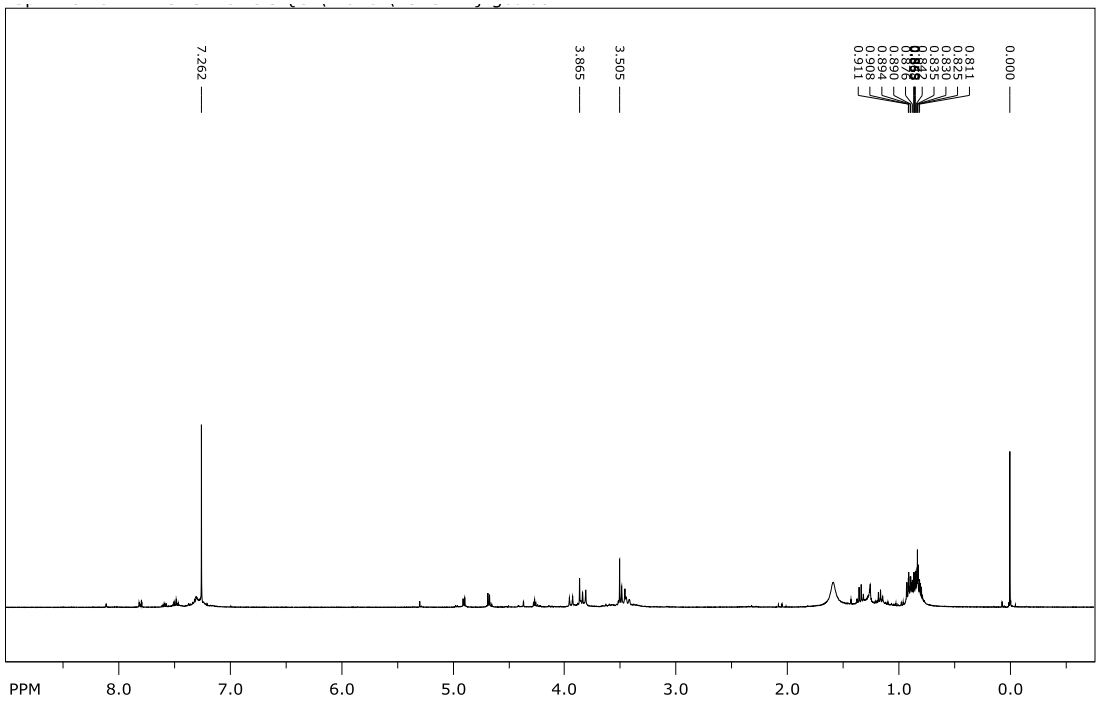


Figure S52. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (5-ethyl-2,2-diphenyl-1,3-dioxan-5-yl) metanol (**15**).

(*E*)-1,3-Diphenylbut-2-en-1-one (**18**)

GC t_R = 47.32 min

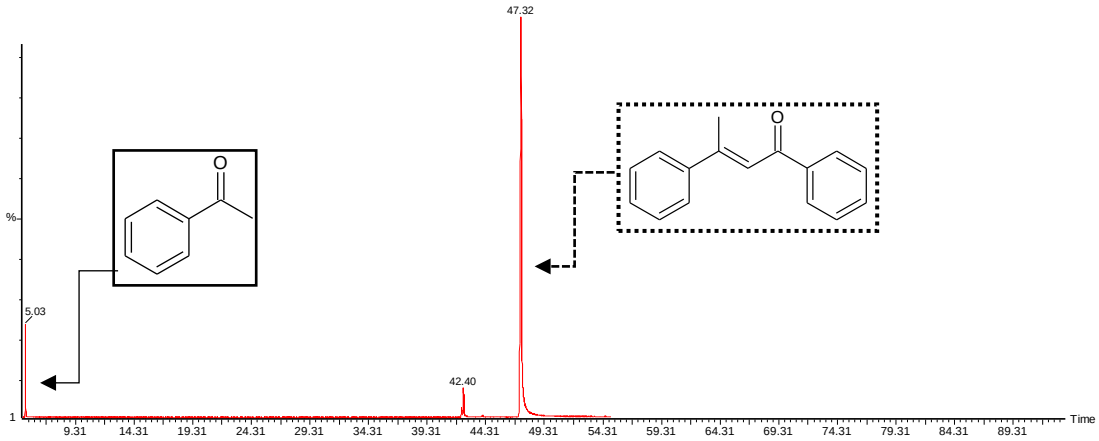


Figure S53. GC chromatogram of (*E*)-1,3-diphenylbut-2-en-1-one (**18**).

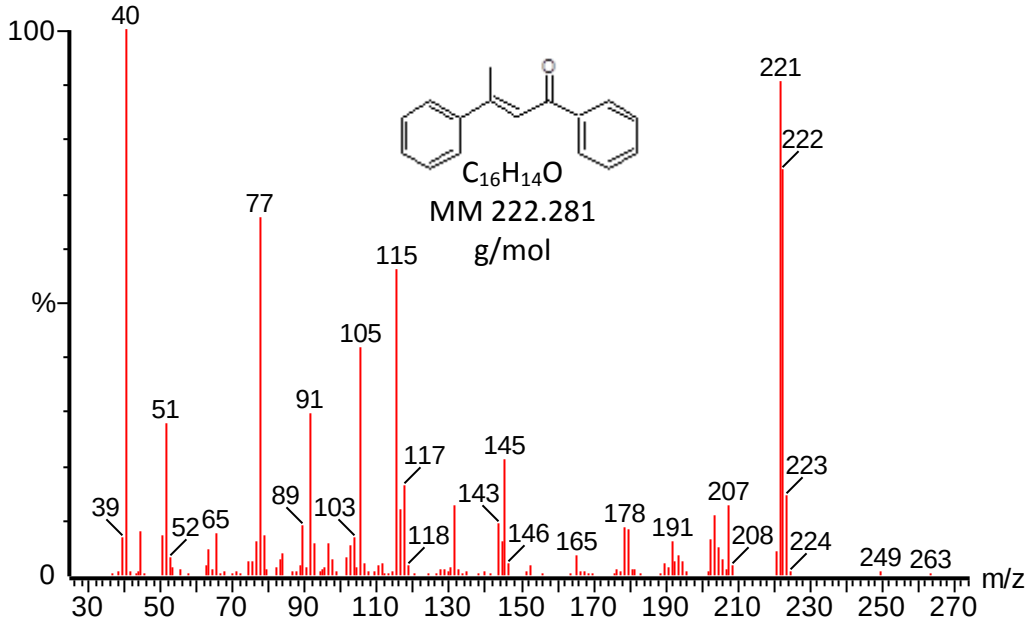


Figure S54. Mass spectrum of (*E*)-1,3-diphenylbut-2-en-1-one (**18**).

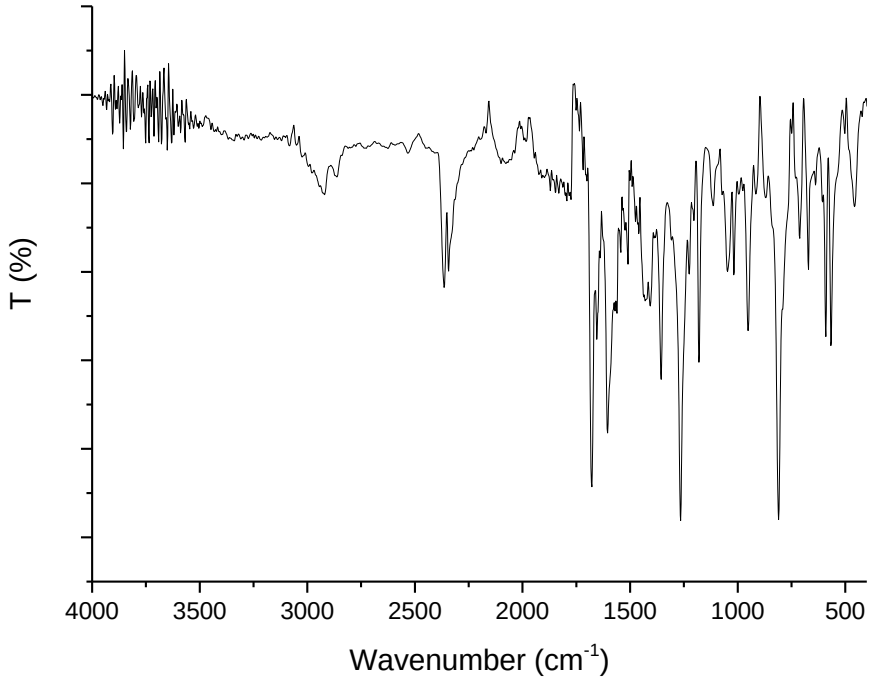


Figure S55. IR spectrum (KBr) of (*E*)-1,3-diphenylbut-2-en-1-one (**18**).

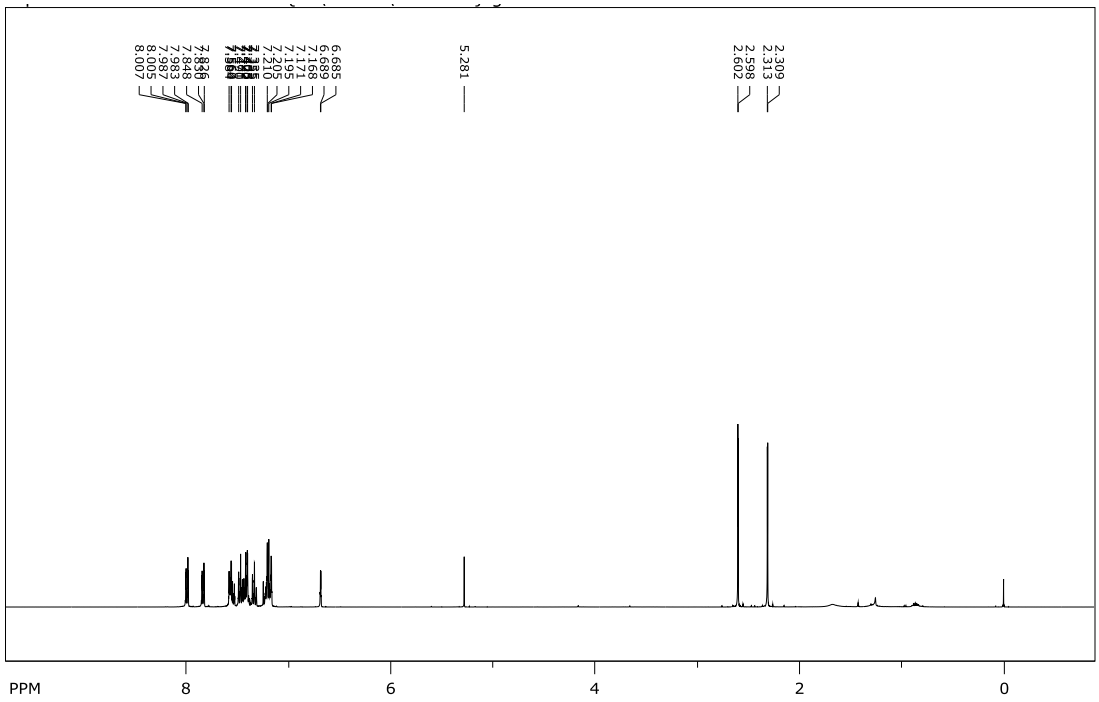


Figure S56. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*E*)-1,3-diphenylbut-2-en-1-one (**18**).

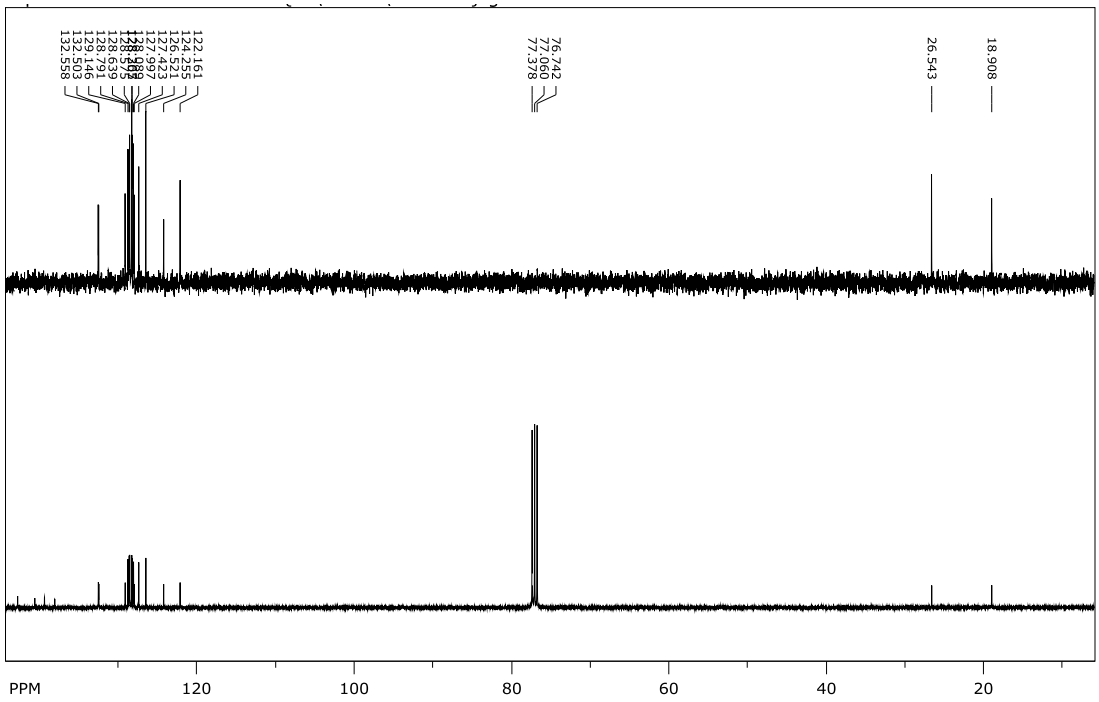


Figure S57. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*E*)-1,3-diphenylbut-2-en-1-one (**18**).

[1,1'-Bi(cyclohexylidene)]-2-one (**19**)

GC t_R = 30.50 min

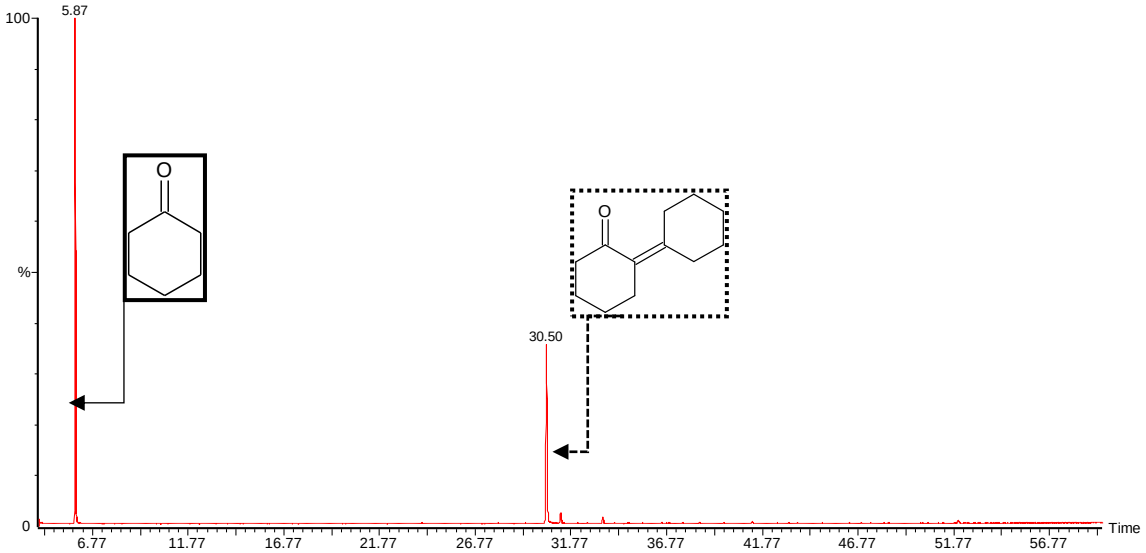


Figure S58. GC chromatogram of [1,1'-bi(cyclohexylidene)]-2-one (**19**).

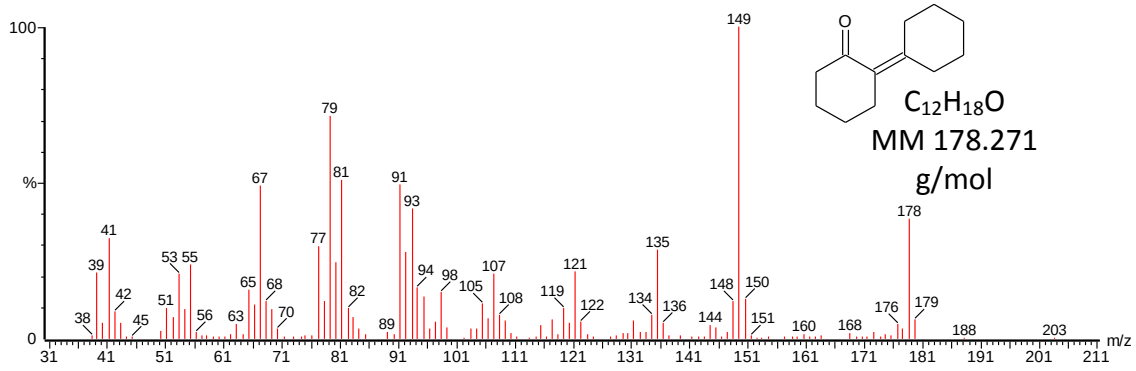


Figure S59. Mass spectrum of [1,1'-bi(cyclohexylidene)]-2-one (**19**).

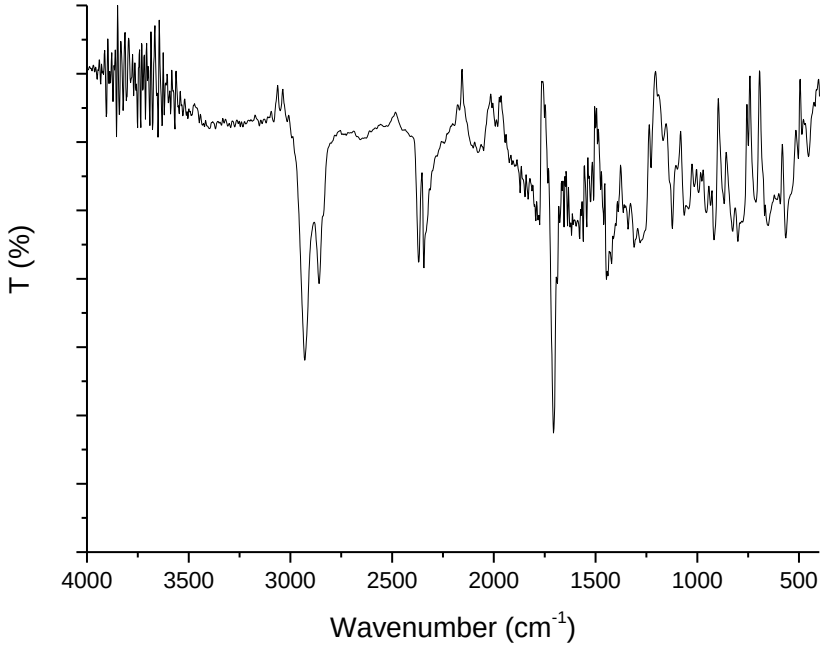


Figure S60. IR spectrum (KBr) of [1,1'-bi(cyclohexylidene)]-2-one (**19**).

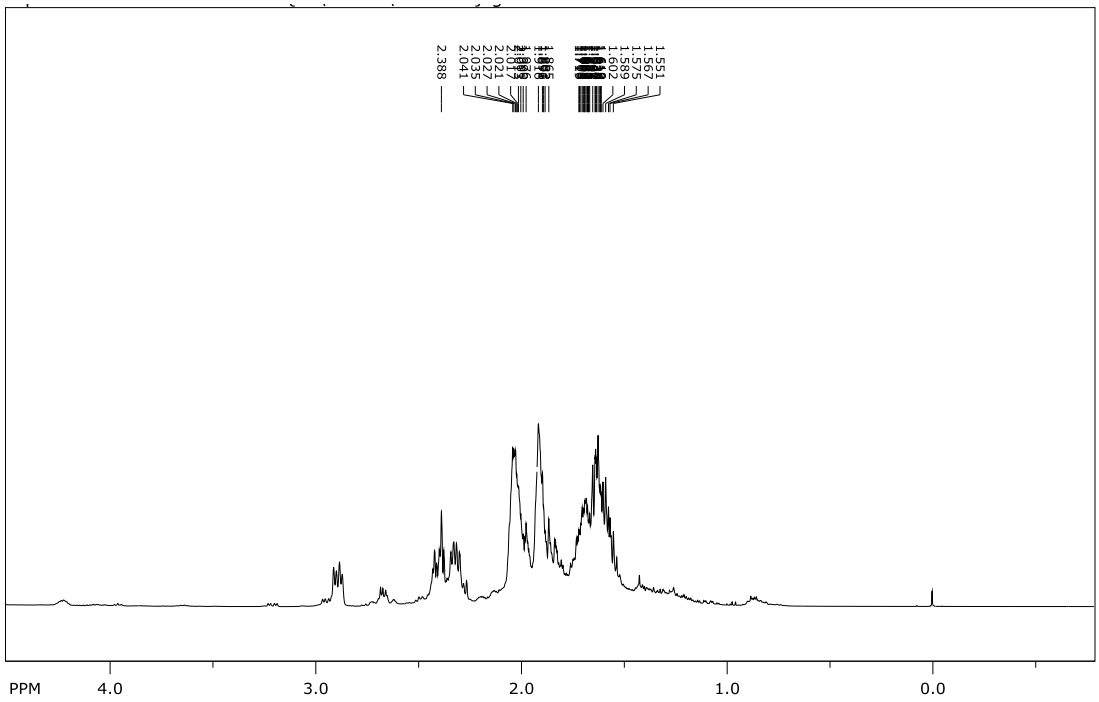


Figure S61. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of [1,1'-bi(cyclohexylidene)]-2-one (**19**).

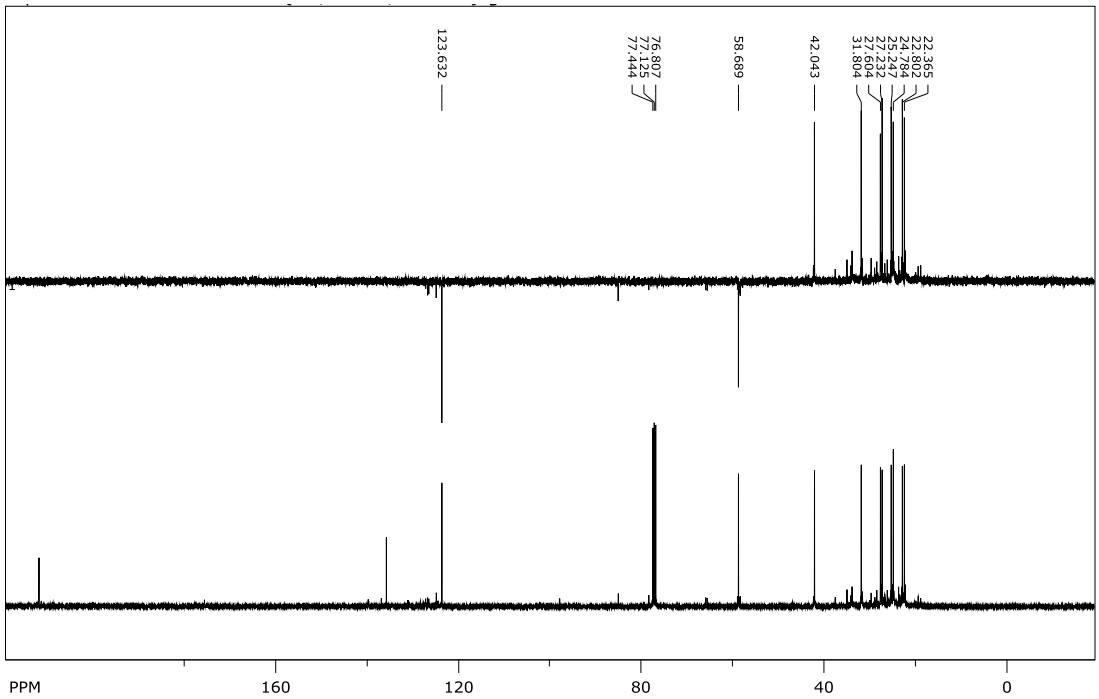


Figure S62. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of [1,1'-bi(cyclohexylidene)]-2-one (**19**).

(2*E*)-1,3-bis(4-Methylphenyl)but-2-en-1-one (**20**)

GC t_R = 54.80 min

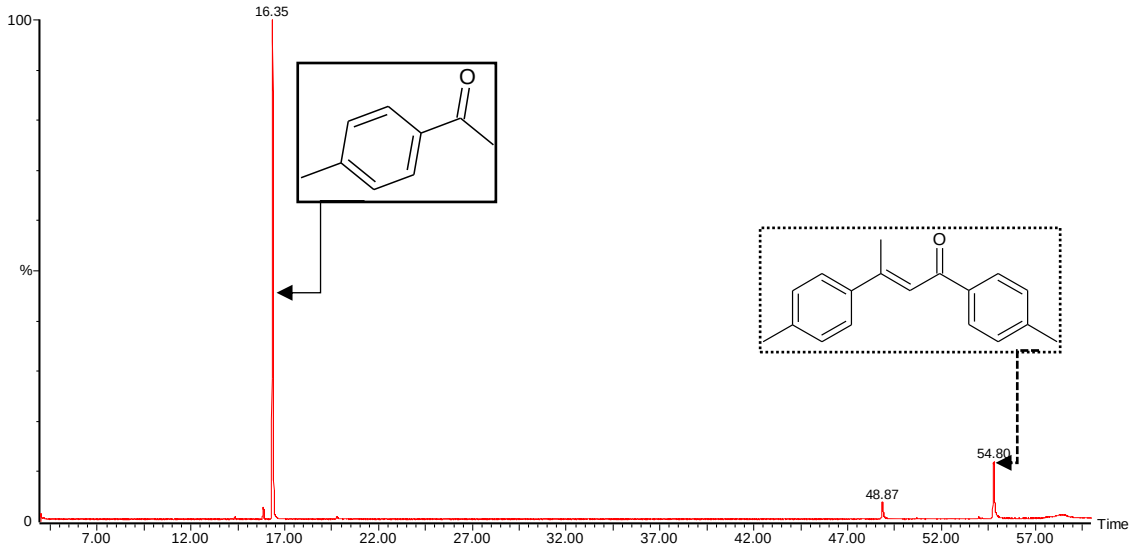


Figure S63. GC chromatogram of (2*E*)-1,3-bis(4-methylphenyl)but-2-en-1-one (**20**).

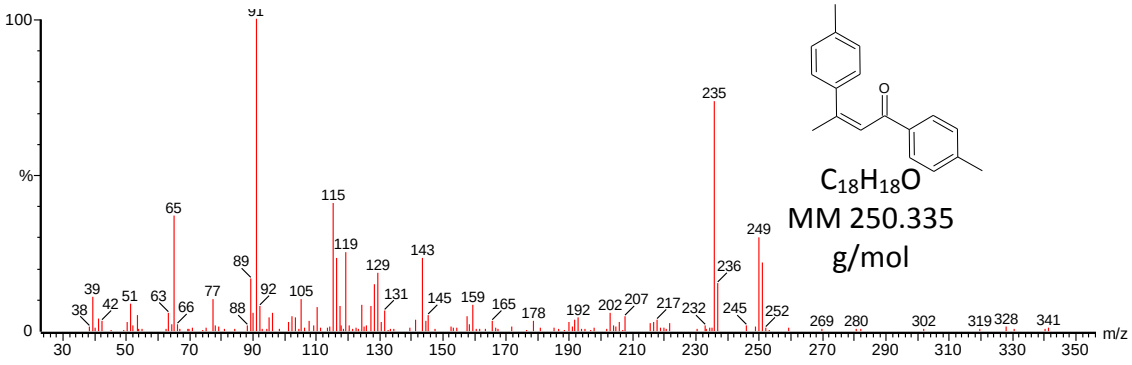


Figure S64. Mass spectrum of (2*Z*)-1,3-bis(4-methylphenyl)but-2-en-1-one (**20**).

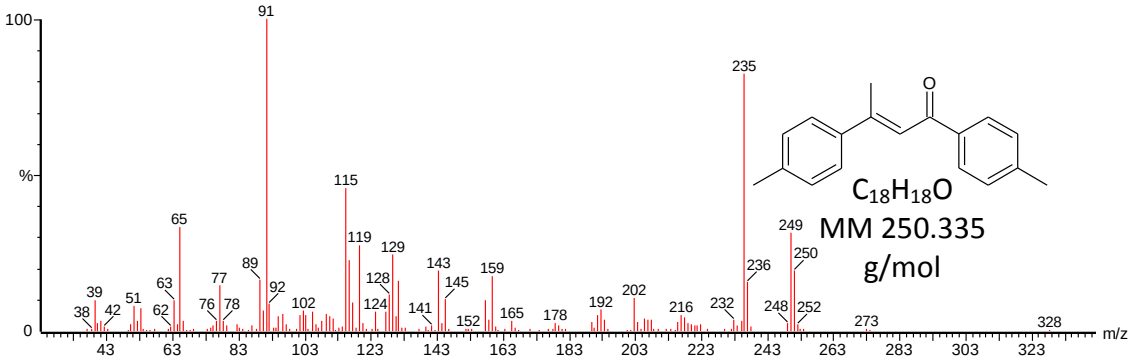


Figure S65. Mass spectrum of (2*E*)-1,3-bis(4-methylphenyl)but-2-en-1-one (**20**).

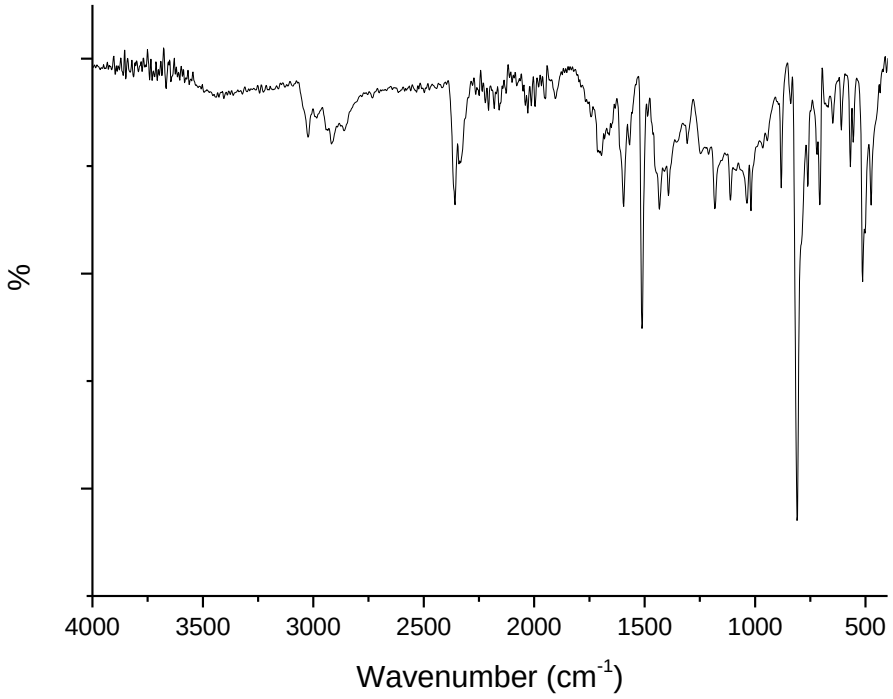


Figure S66. IR spectrum (KBr) of (2*E*)-1,3-bis(4-methylphenyl)but-2-en-1-one (**20**).

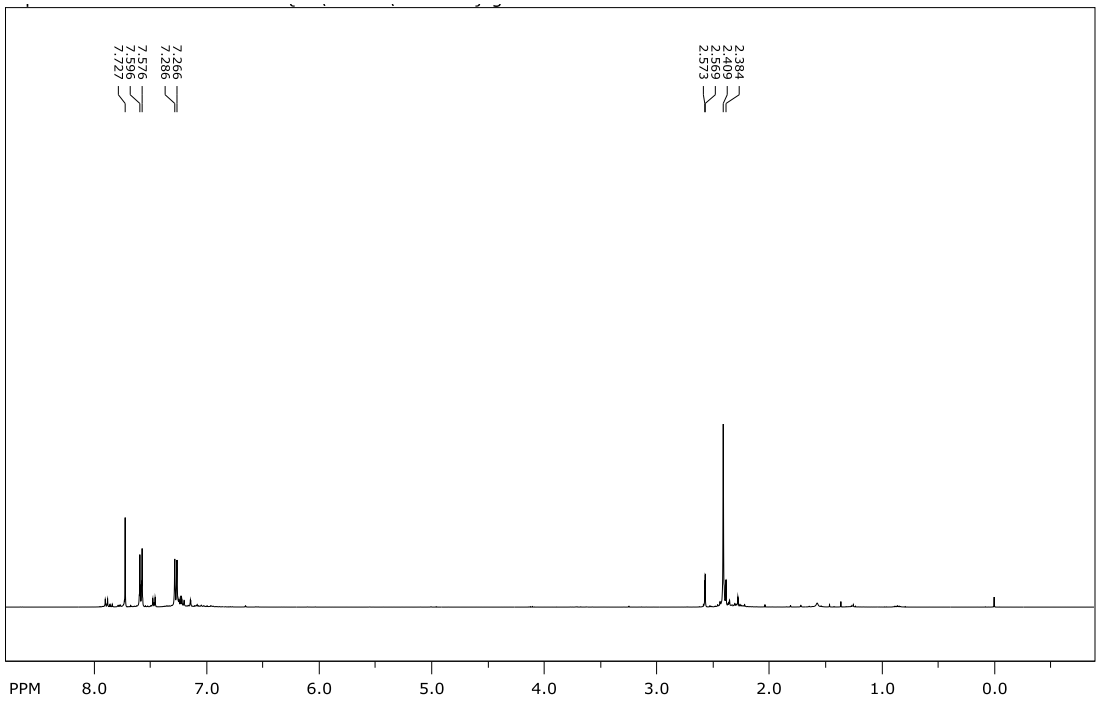


Figure S67. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (2*E*)-1,3-bis(4-methylphenyl)but-2-en-1-one (**20**).

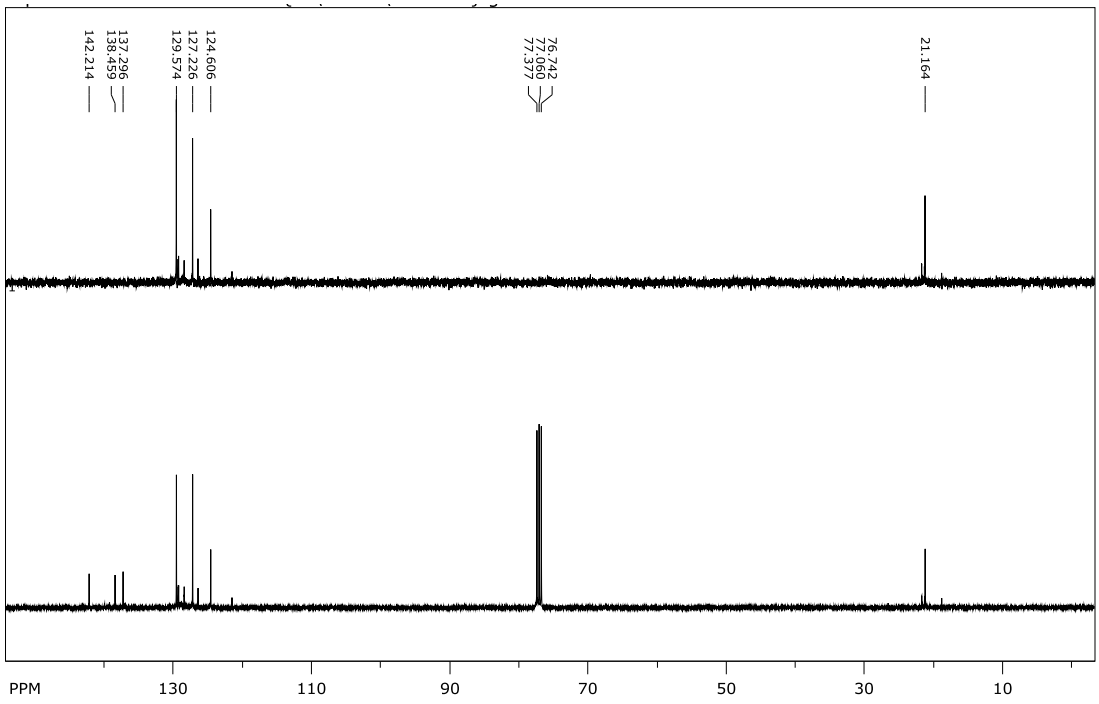


Figure S68. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of (2*E*)-1,3-bis(4-methylphenyl)but-2-en-1-one (**20**).

Hidrolys of ketals

2,5,5-Trimethyl-2-phenyl-1,3-dioxane

GC t_R = 23.62 min

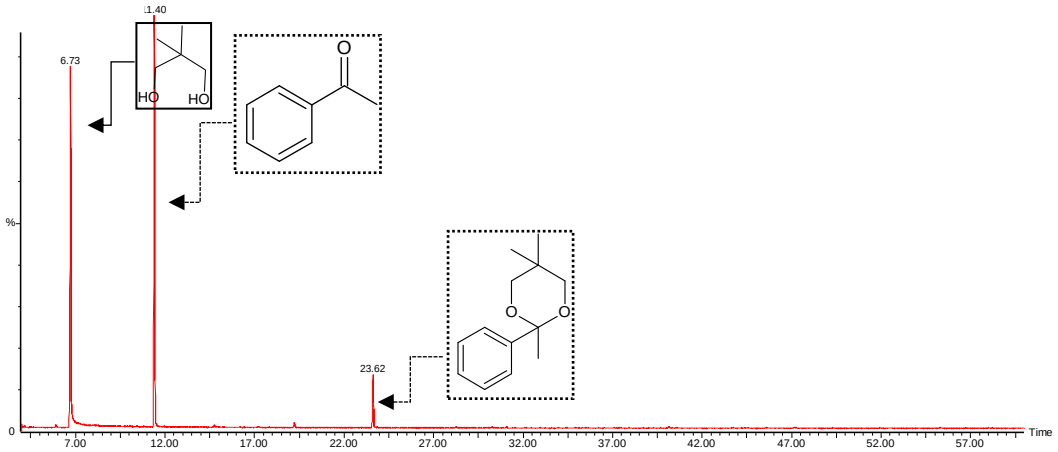


Figure S69. GC chromatogram of 2,5,5-trimethyl-2-phenyl-1,3-dioxane.

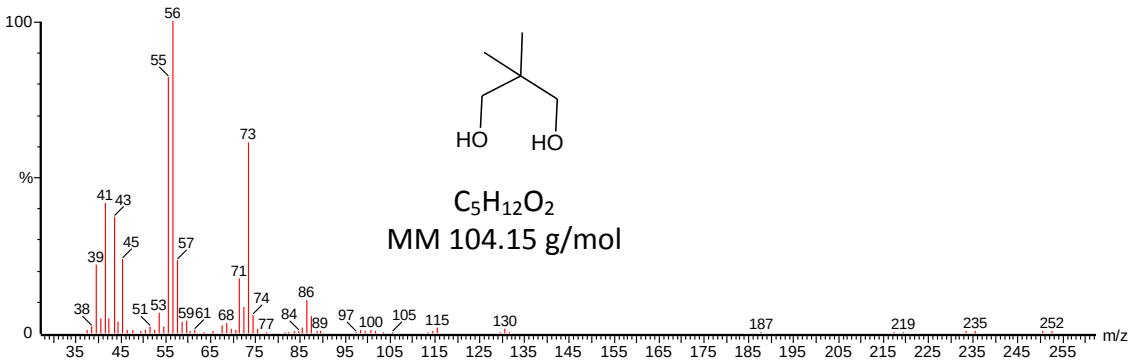


Figure S70. Mass spectrum of 2,2-dimethylpropane-1,3-diol.

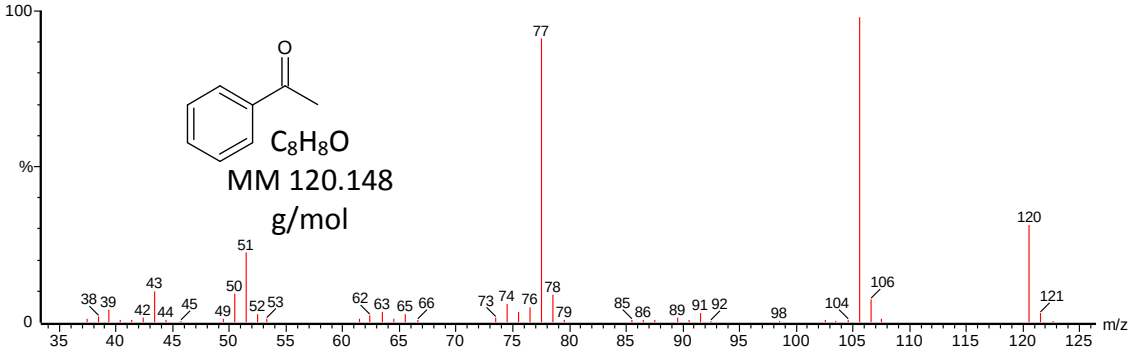


Figure S71. Mass spectrum of acetophenone.

Reusable catalyst

1st Reusable catalyst: 2,5,5-trimethyl-2-phenyl-1,3-dioxane

GC t_R = 23.76 min

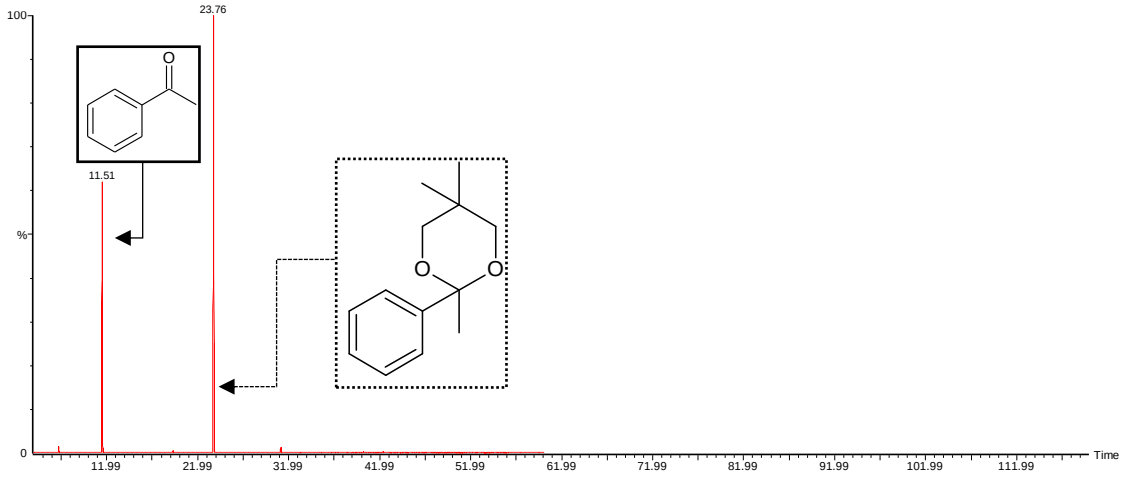


Figure S72. GC chromatogram of 2,5,5-trimethyl-2-phenyl-1,3-dioxane.

2nd Reusable catalyst: 2,5,5-trimethyl-2-phenyl-1,3-dioxane

GC t_R = 23.79 min

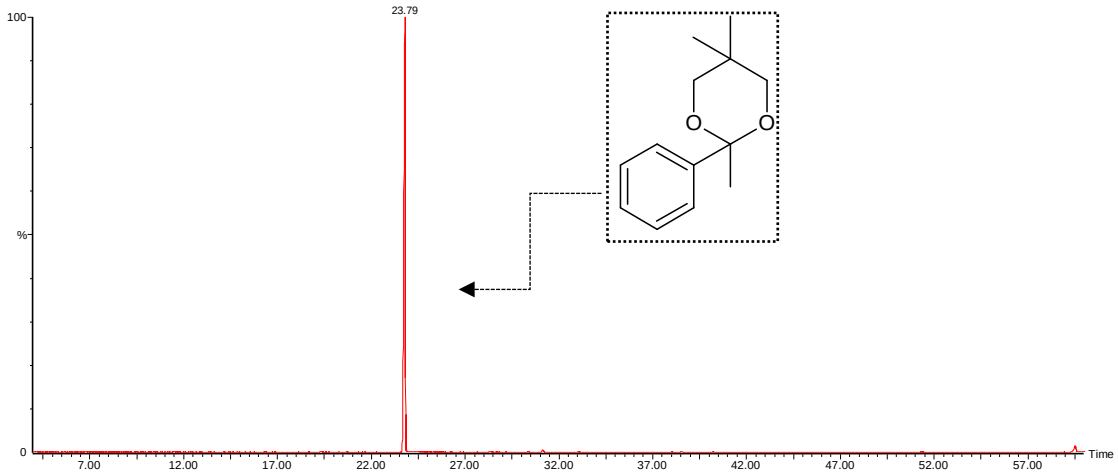


Figure S73. GC chromatogram of 2,5,5-trimethyl-2-phenyl-1,3-dioxane.

3rd Reusable catalyst: 2,5,5-trimethyl-2-phenyl-1,3-dioxane

GC t_R = 23.73 min

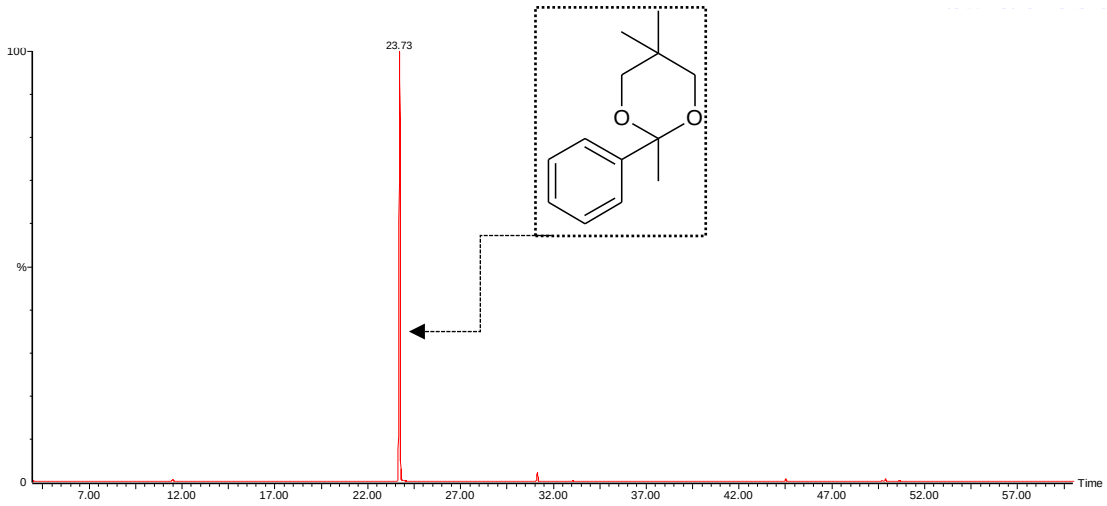


Figure S74. GC chromatogram of 2,5,5-trimethyl-2-phenyl-1,3-dioxane.