Electronic supplementary information

Upgrading of Glycerol Acetals through Thermal Catalyst-free Transesterification of Dialkyl Carbonates under Continuous-Flow Conditions

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Contents

Synthesis of DBnC

Dibenzyl carbonate (DBnC) was prepared via a single step transesterification procedure recently reported by us.[1] Accordingly, a mixture of benzyl alcohol (502,86 mmol, 52 mL), dimethyl carbonate DMC (49.84 mmol, 4.2 mL), and CsF/α-Al_2O_3 as a catalyst (0.01 molar equiv. with respect to DMC) was set to react at 90 °C. DBnC was isolated as a white solid (77%) with a very high purity (>99% by GC/MS).

GC calibration curve

A GC calibration curve for GlyF was obtained using *n*-tetradecane (C_{14}) as external standard. Four different solutions of commercial GlyF [mixtures of isomers 5-hydroxy-1,3-dioxane (**1a**) and (1,3-dioxolan-4-yl)methanol (**1a'**) in a ~3:2 ratio] in ethyl acetate were prepared at 0.08, 0.06, 0.04 and 0.02 M concentration. In particular 406, 302, 207 and 101 mg of **1a+1a'** were used. To each solution, the same quantity of *n*-tetradecane was added. Figure S 1 shows the results of the calibration test.

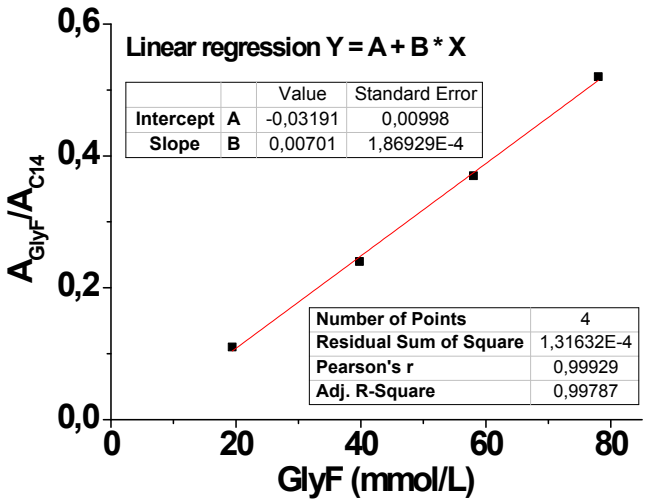

Figure S 1: Calibration curve for GlyF. *n*-tetradecane (C_{14}) was used as a standard. A_{GlyF}/A_{C14} was the ratio of GC area responses of GlyF and C_{14}.

^{1}H NMR of the mixture of isomers 1,3-dioxan-5-yl methyl carbonate (2a) and (1,3-dioxolan-4-yl)methyl methyl carbonate (2a').

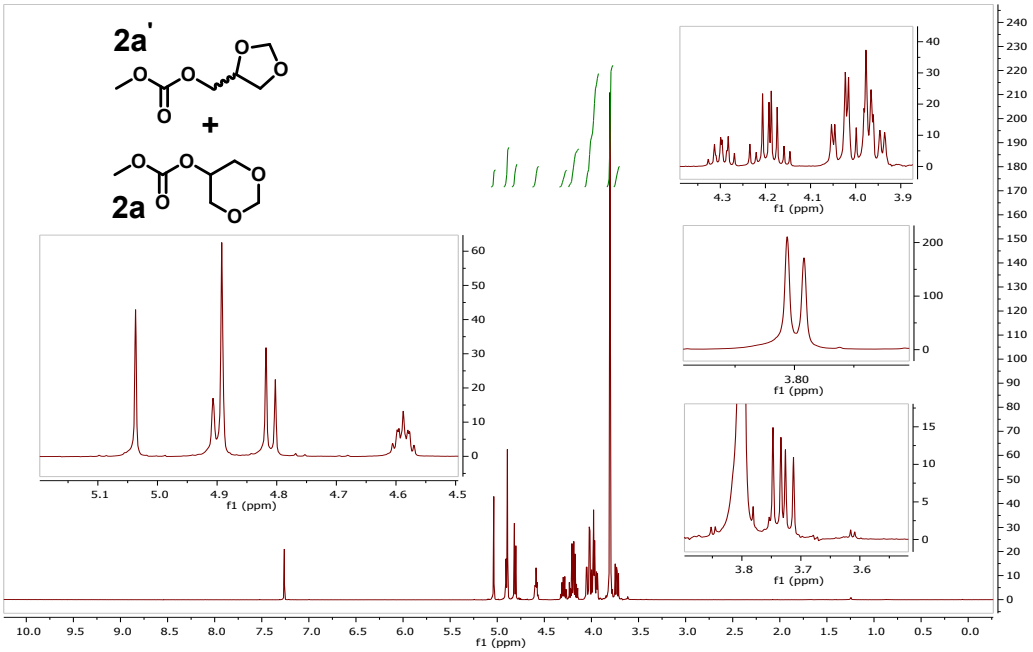

Figure S 2: ^{1}H NMR spectra of mixture product **2a+2a'**

^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm): 5.04 (s, 1H), 4.89 (m, 2H), 4.81 (d, *J* = 6.2 Hz, 1H), 4.59 (m, 1H), 4.30 (qnt, 1H), 4.25 – 4.13 (m, 2H), 4.07 – 3.92 (m, 5H), 3.80 (s, 3H), 3.79 (s, 3H), 3.73 (dd, *J* = 8.5, 5.4 Hz, 1H).

^{13}C NMR of the mixture of product 2a and 2a'

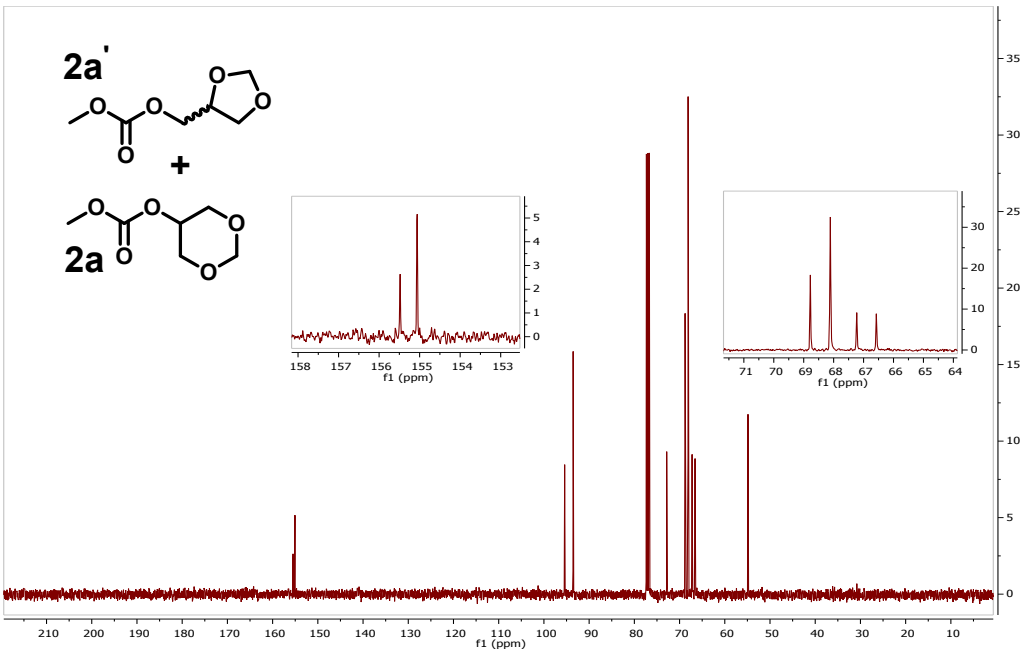

Figure S 3: ^{13}C NMR spectra of mixture product **2a+2a'**

^{13}C NMR ($CDCl_3$, 100MHz) δ (ppm): 155.5 , 155.1 , 95.4 , 93.5 , 72.8 , 68.8 , 68.1 , 67.2 , 66.6 , 54.9.

GC/MS spectrum of product 2a

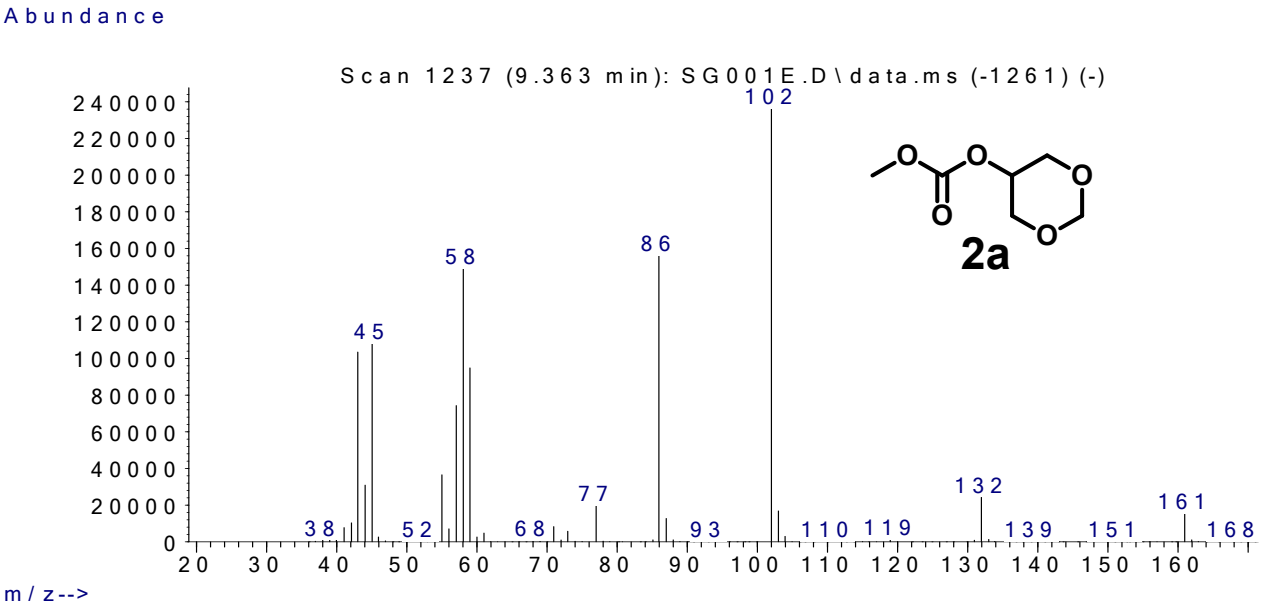

Figure S 4: MS spectra of product **2a**

GC/MS (relative intensity, 70eV) *m/z*: 162 (M^+, <1%), 161 ($[M-H]^+$, 6), 132 (10), 102 (100), 86 (63), 59 (38), 58 (60), 57 (30), 55 (15), 45 (44), 44 (12), 43 (42).

GC/MS spectrum of product 2a'

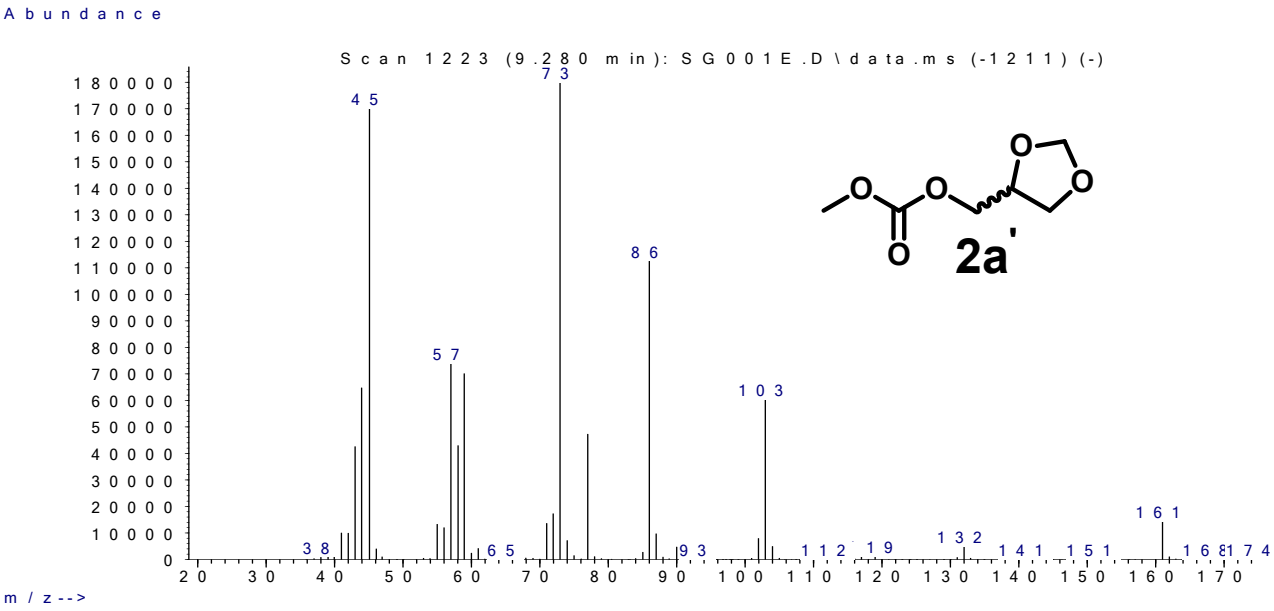

Figure S 5: MS spectra of product **2a'**

GC/MS (relative intensity, 70eV) *m/z*: 162 (M^+, <1%), 161 ($[M-H]^+$, 8), 103 (32), 86 (61), 77 (25), 73 (100), 59 (38), 58 (23), 57 (40), 45 (92), 44 (35), 43 (23).

^{1}H NMR of (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl methyl carbonate 2b

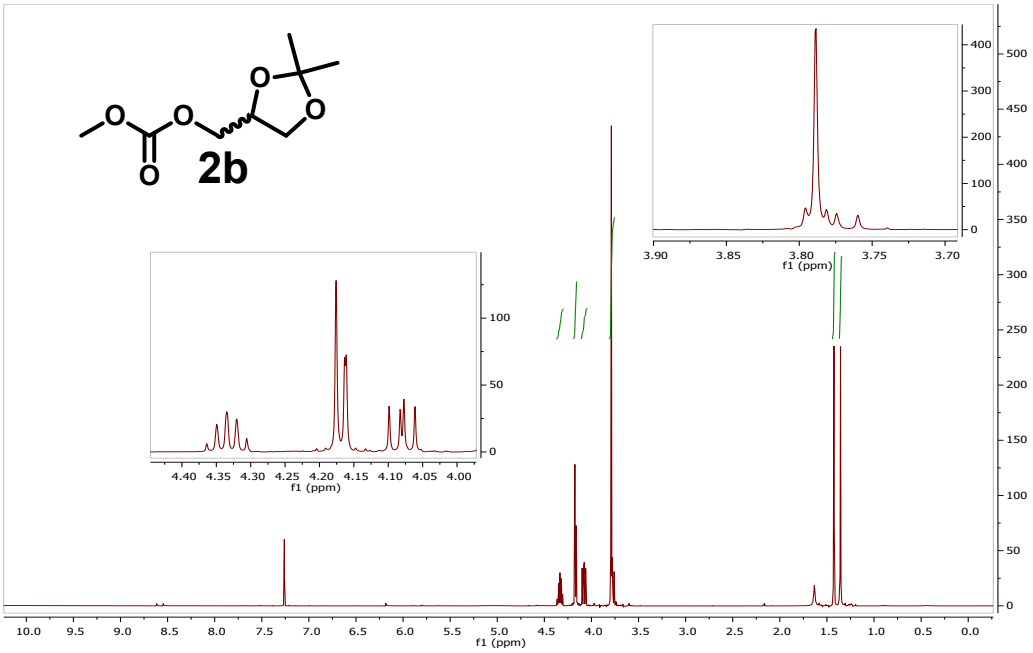

Figure S 6: ^{1}H NMR spectra of product **2b**

^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm): 4.38 – 4.29 (m, 1H), 4.19 – 4.15 (m, 2H), 4.08 (dd, *J* = 8.6, 6.4 Hz, 1H), 3.81 – 3.75 (m, 4H), 1.43 (s, 3H), 1.36 (s, 3H).

^{13}C NMR of product 2b

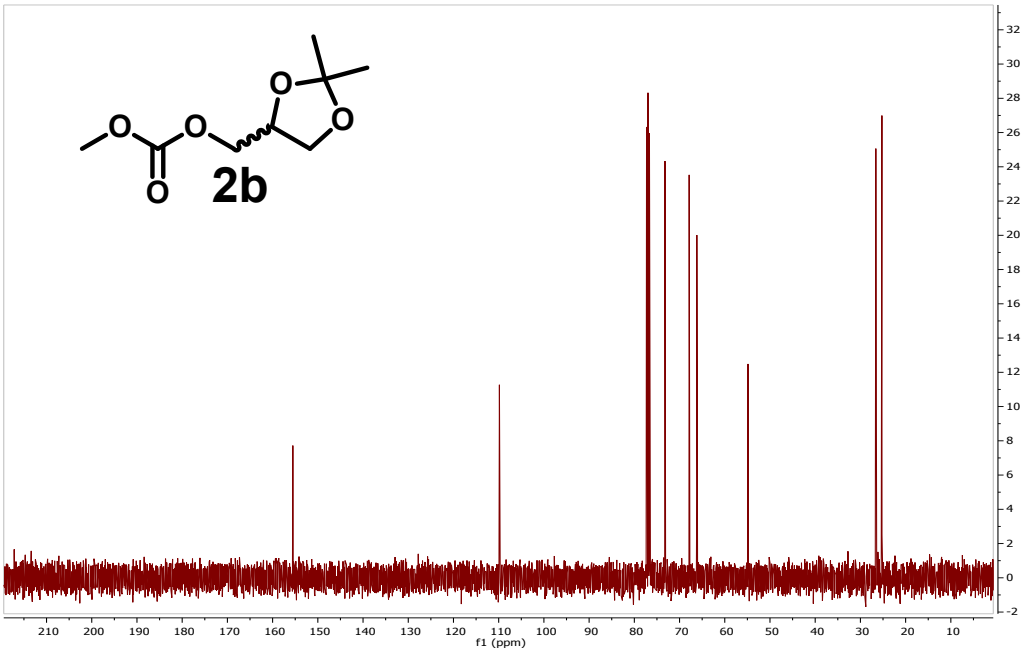

Figure S 7: ^{13}C NMR spectra of product **2b**

^{13}C NMR ($CDCl_3$, 100MHz) δ (ppm): 155.5 , 109.8 , 73.2 , 67.9 , 66.2 , 54.9 , 26.6 , 25.2.

GC/MS spectrum of product 2b

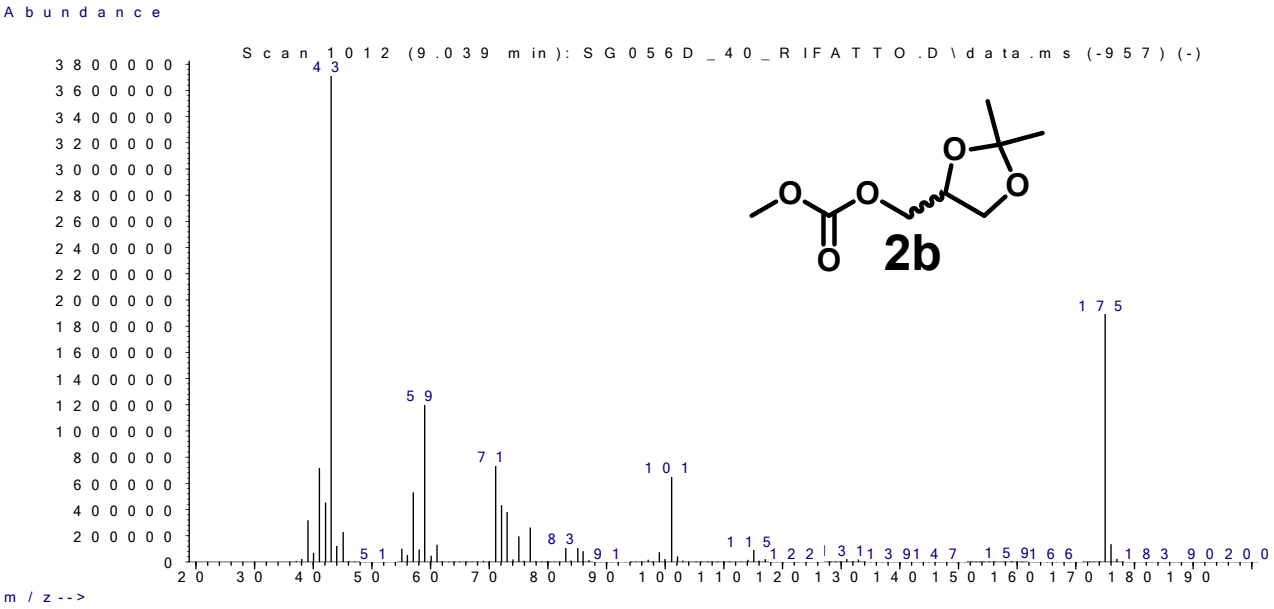

Figure S 8: MS spectra of product **2b**

GC/MS (relative intensity, 70eV) *m/z*: 190 (M^+, <1%), 175 (50), 101 (17), 73 (10), 72 (11), 71 (19), 59 (31), 57 (14), 43 (100), 42 (12), 41 (19).

^{1}H NMR of the mixture of isomers 1,3-Dioxan-5-yl ethyl carbonate (3a) and (1,3-dioxolan-4-yl)methyl ethyl carbonate (3a').

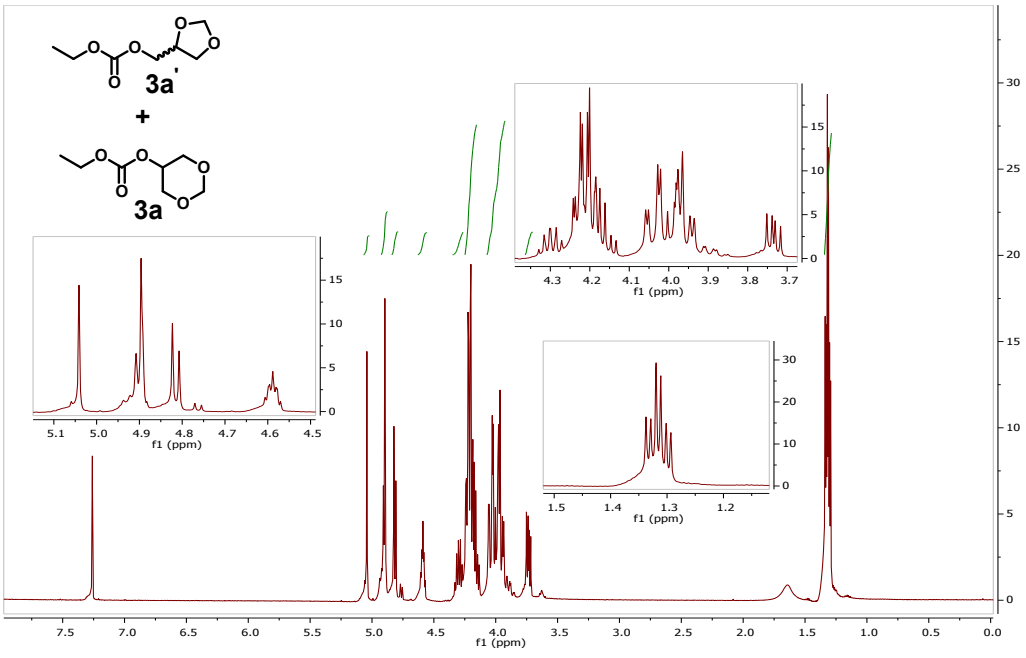

Figure S 9: ^{1}H NMR spectra of mixture product **3a+3a'**

^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm): 5.0 (s, 1H), 4.9 – 4.9 (m, 2H), 4.8 (d, *J* = 6.2 Hz, 1H), 4.6 (m, 1H), 4.3 (qnt, 1H), 4.3 – 4.1 (m, 6H), 4.1 – 3.9 (m, 5H), 3.7 (dd, *J* = 8.5, 5.4 Hz, 1H), 1.3 (dt, *J* = 7.1, 3.3 Hz, 6H).

^{13}C NMR of the mixture of isomers 3a and 3a'

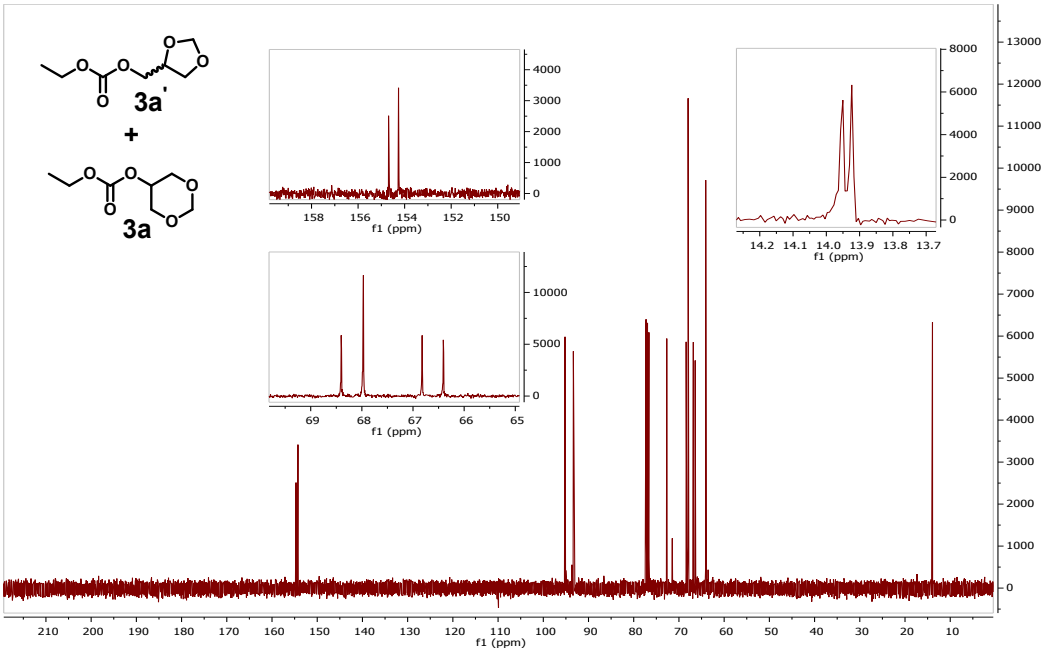

Figure S 10: ^{13}C NMR spectra of mixture product **3a+3a'**

^{13}C NMR ($CDCl_3$, 100MHz) δ (ppm): 154.7 , 154.3 , 95.2 , 93.3 , 72.7 , 68.4 , 68.0 , 66.8 , 66.4 , 64.1 , 14.0 , 13.9.

GC/MS spectrum of product 3a

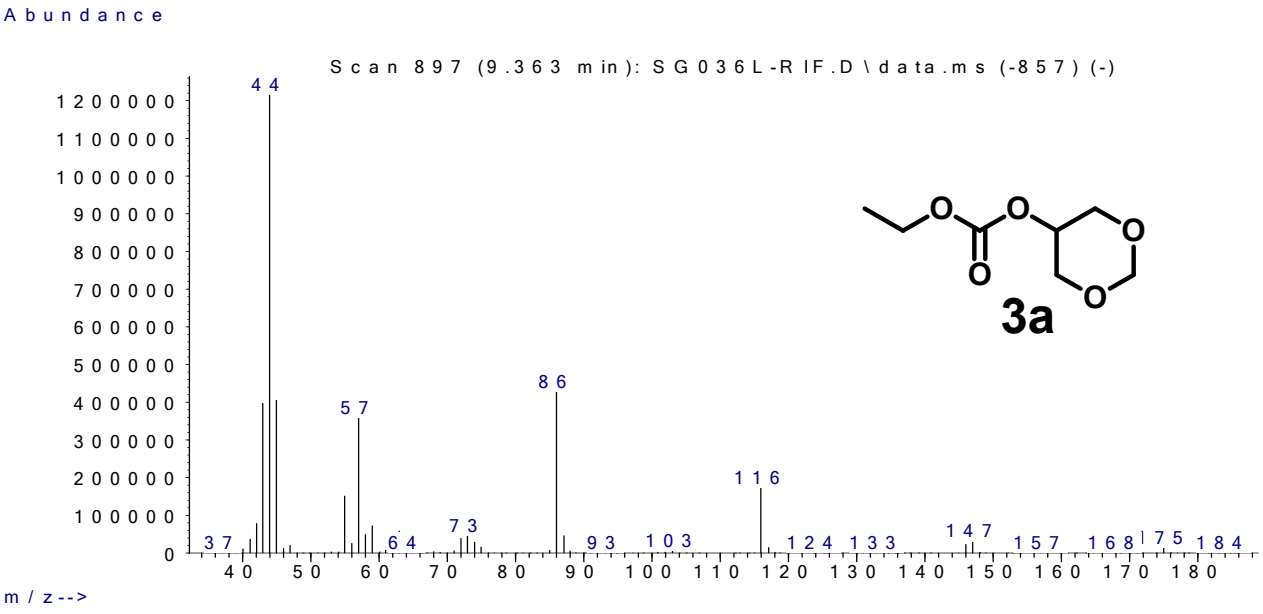

Figure S 11: MS spectra of product **3a**

GC/MS (relative intensity, 70eV) *m/z*: 176 (M^+,<1%), 175 ($[M-H]^+$, 1), 116 (14), 86 (34), 57 (28), 55 (12), 45 (32), 44 (100), 43 (31).

GC/MS spectrum of product 3a'

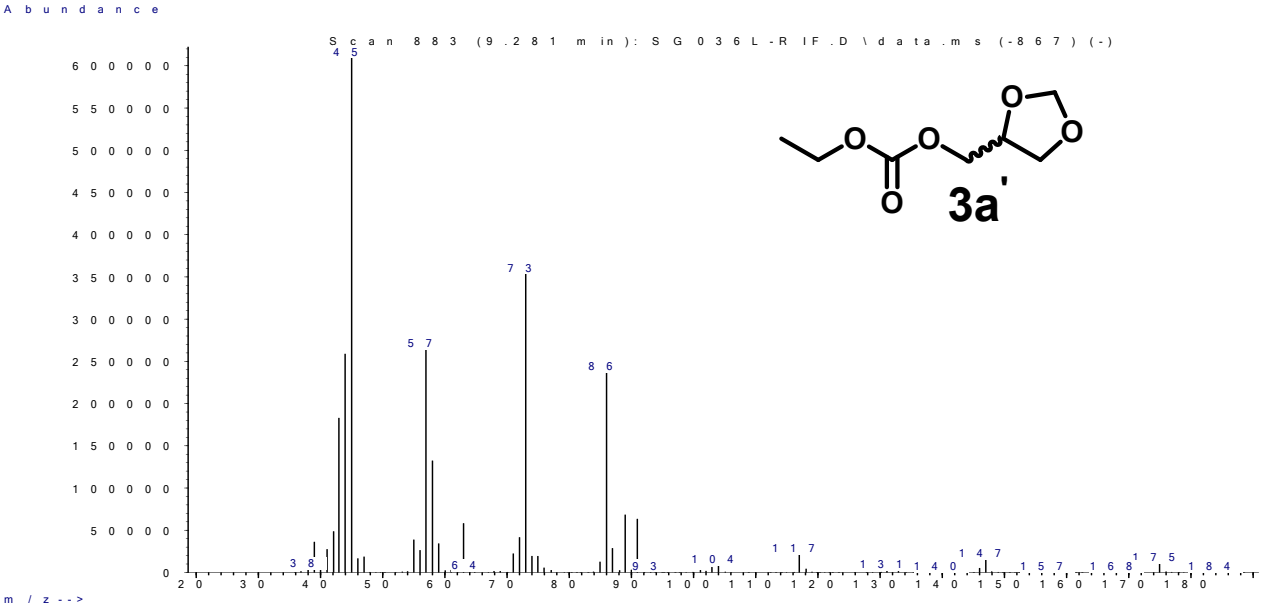

Figure S 12: MS spectra of product **3a'**

GC/MS (relative intensity, 70eV) *m/z*: 176 (M^+, <1%), 175 ($[M-H]^+$, 2), 91 (10), 89 (11), 86 (38), 73 (57), 58 (21), 57 (42), 45 (100), 44 (42), 43 (29).

^{1}H NMR of (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl ethyl carbonate 3b

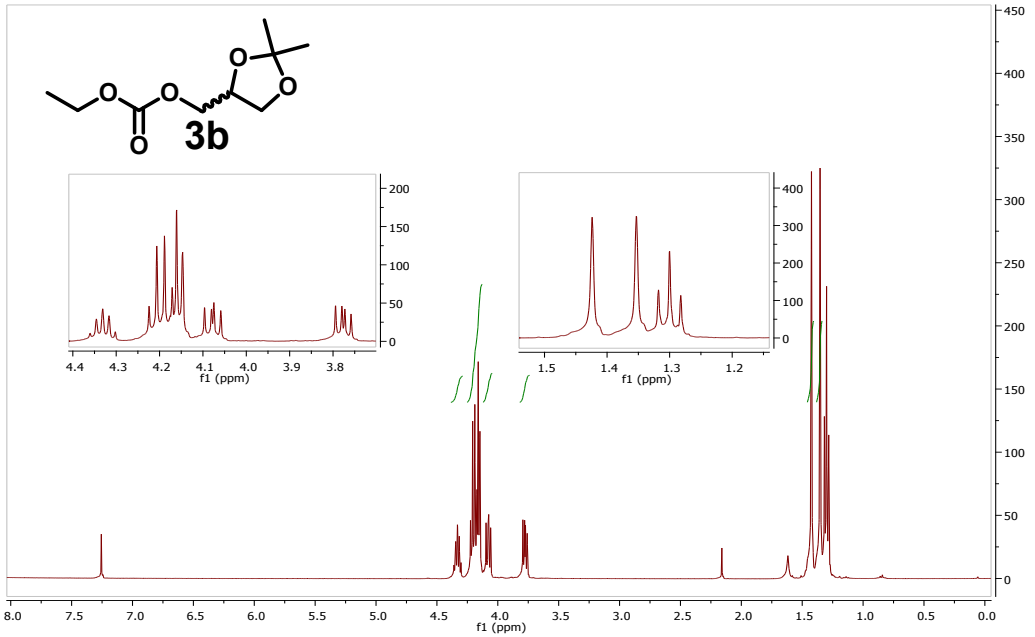

Figure S 13: ^{1}H NMR spectra of product **3b**

^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm): 4.33 (m, 1H), 4.24 – 4.13 (m, 4H), 4.08 (dd, *J* = 8.5, 6.4 Hz, 1H), 3.78 (dd, *J* = 8.5, 5.8 Hz, 1H), 1.42 (s, 3H), 1.35 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR of product 3b

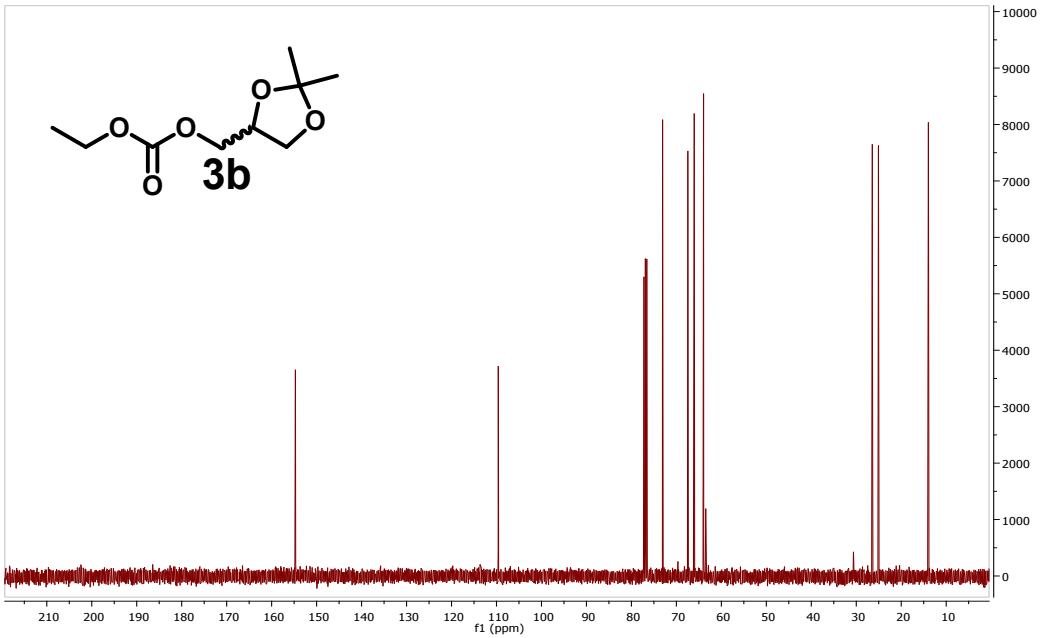

Figure S 14: ^{13}C NMR spectra of product **3b**

^{13}C NMR ($CDCl_3$, 100MHz) δ (ppm): 154.7 , 109.6 , 73.1 , 67.5, 66.0 , 64.0 , 26.4 , 25.1 , 14.0.

GC/MS spectrum of product 3b

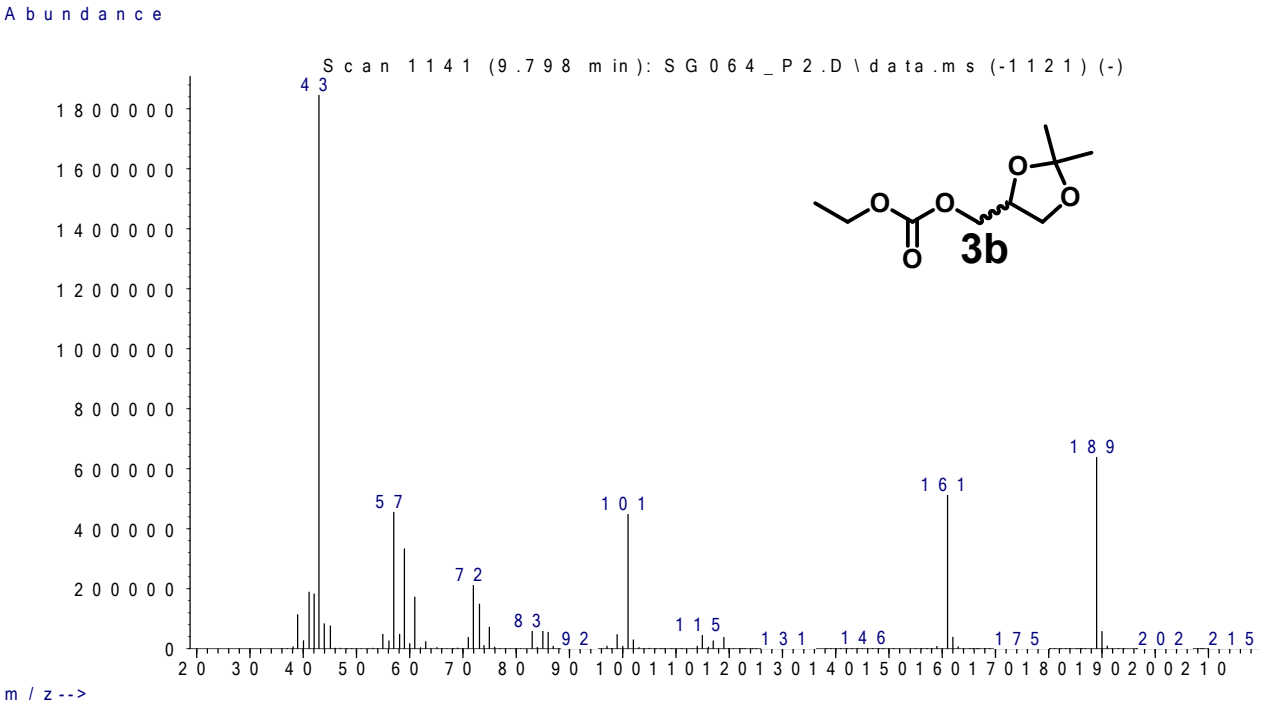

Figure S 15: MS spectra of product **3b**

GC/MS (relative intensity, 70eV) *m/z*: 204 (M^+,<1%), 189 (39), 161 (31), 101 (27), 72 (12), 61 (10), 59 (18), 57 (25), 43 (100), 42 (10).

^{1}H NMR of Benzyl 1,3-dioxan-5-yl carbonate 6a

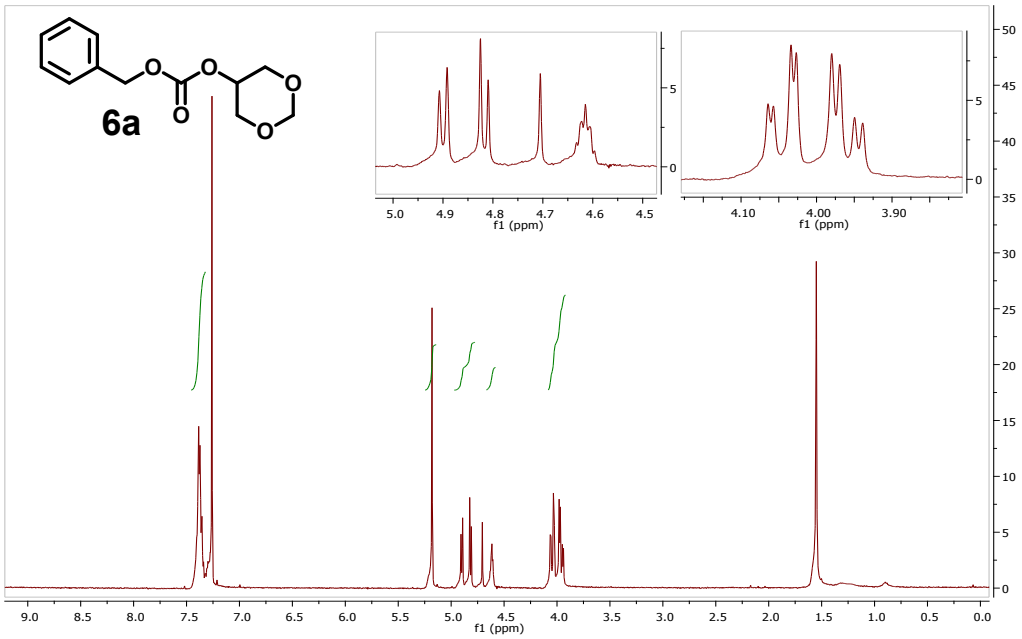

Figure S 16: ^{1}H NMR spectra of product **6a**

^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm): 7.5 – 7.3 (m, 5H), 5.2 (s, 1H), 4.9 (d, *J* = 6.2 Hz, 1H), 4.8 (d, *J* = 6.3 Hz, 1H), 4.7 – 4.6 (m, 1H), 4.0 (dd, *J* = 12.1, 2.8 Hz, 1H), 4.0 (dd, *J* = 12.1, 4.3 Hz, 1H).

^{13}C NMR of product 6a

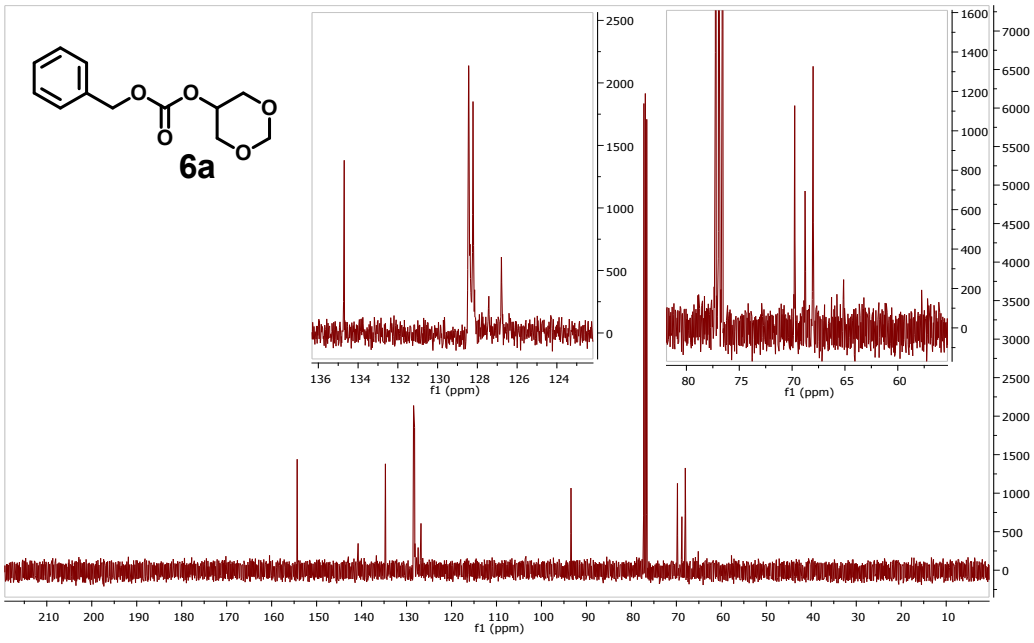

Figure S 17: ^{13}C NMR spectra of product **6a**

^{13}C NMR ($CDCl_3$, 100MHz) δ (ppm): 154.3, 140.8, 134.7, 128.4, 128.2, 93.4, 69.8, 68.8, 68.0.

GC/MS spectrum of product 6a

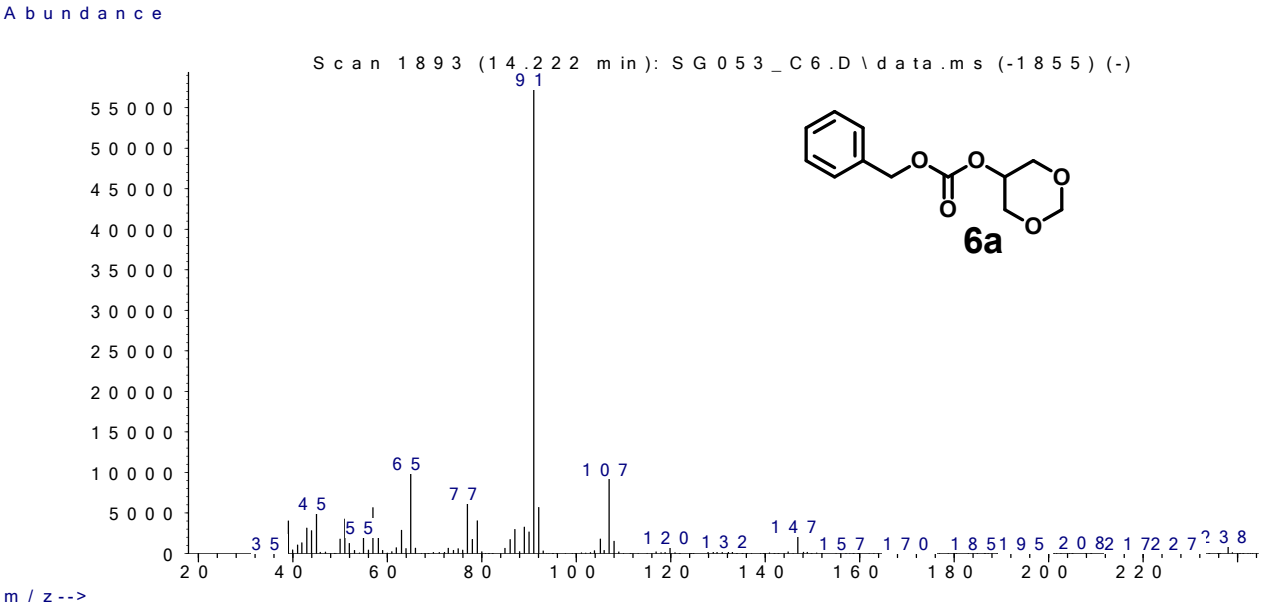

Figure S 18: MS spectra of product **6a**

GC/MS (relative intensity, 70eV) *m/z*: 238 (M^+, 1%), 107 (15), 92 (10), 91(100), 77 (10), 65 (17), 57(10).

^{1}H NMR of (1,3-dioxolan-4-yl)methyl benzyl carbonate 6a'

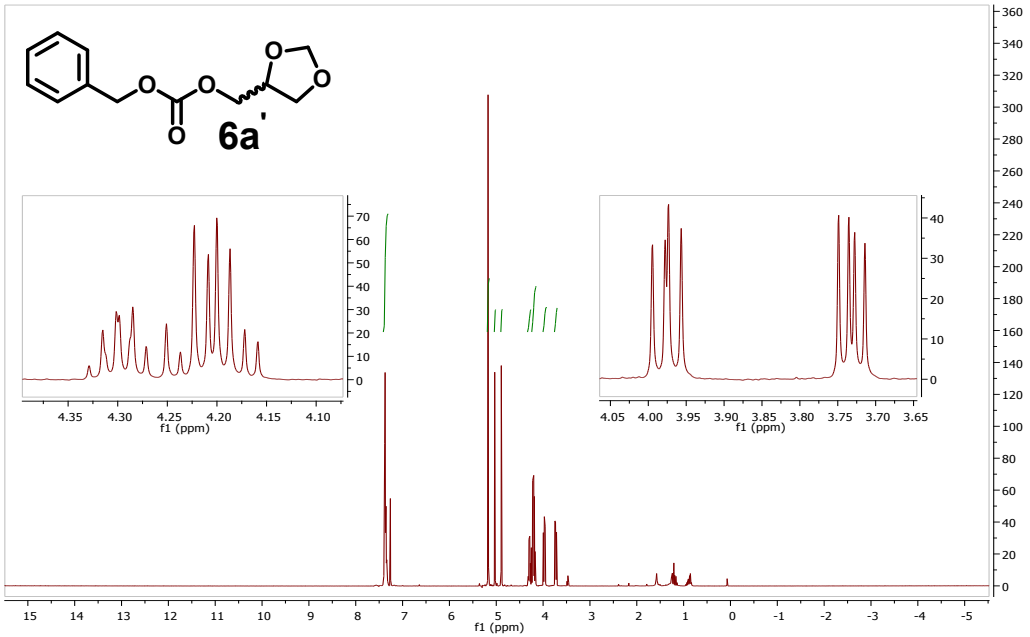

Figure S 19: ^{1}H NMR spectra of product **6a'**

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.5 – 7.3 (m, 5H), 5.2 (s, 2H), 5.0 (s, 1H), 4.9 (s, 1H), 4.3 (m, 1H), 4.3 – 4.2 (m, 2H), 4.0 (dd, *J* = 8.5, 6.7 Hz, 1H), 3.7 (dd, *J* = 8.5, 5.4 Hz, 1H).

^{13}C NMR of product 6a'

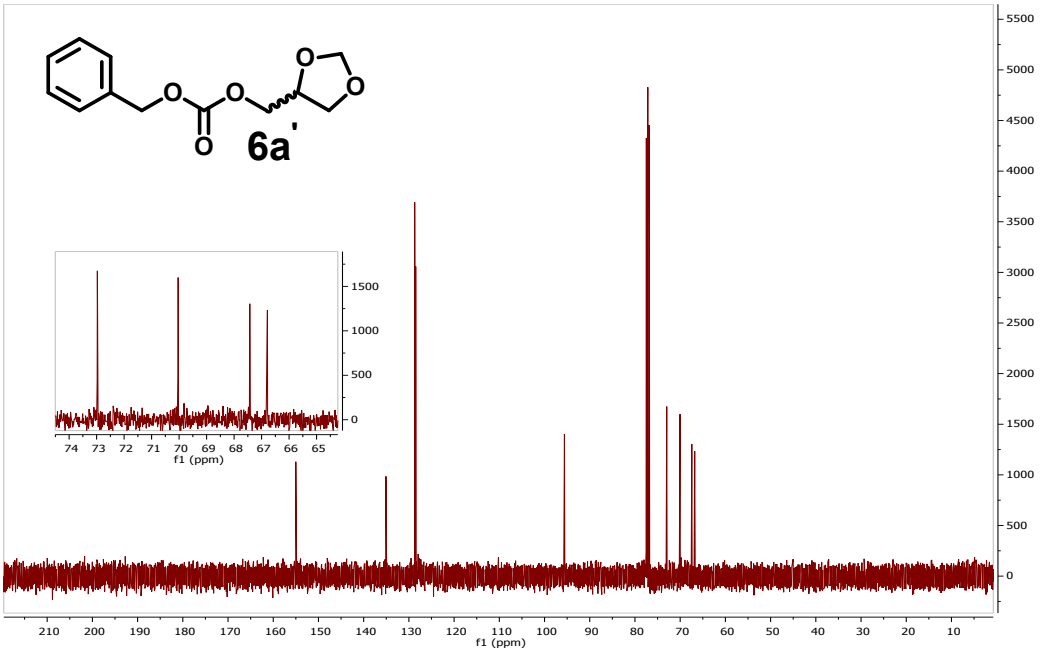

Figure S 20: ^{13}C NMR spectra of product **6a'**

^{13}C NMR ($CDCl_3$, 100MHz) δ (ppm): 155.0 , 135.1 , 128.7 ,128.7, 128.5, 95.6 , 73.0 , 70.0 , 67.4 , 66.8.

^{1}H-^{1}H DQFCOSY of product 6a'

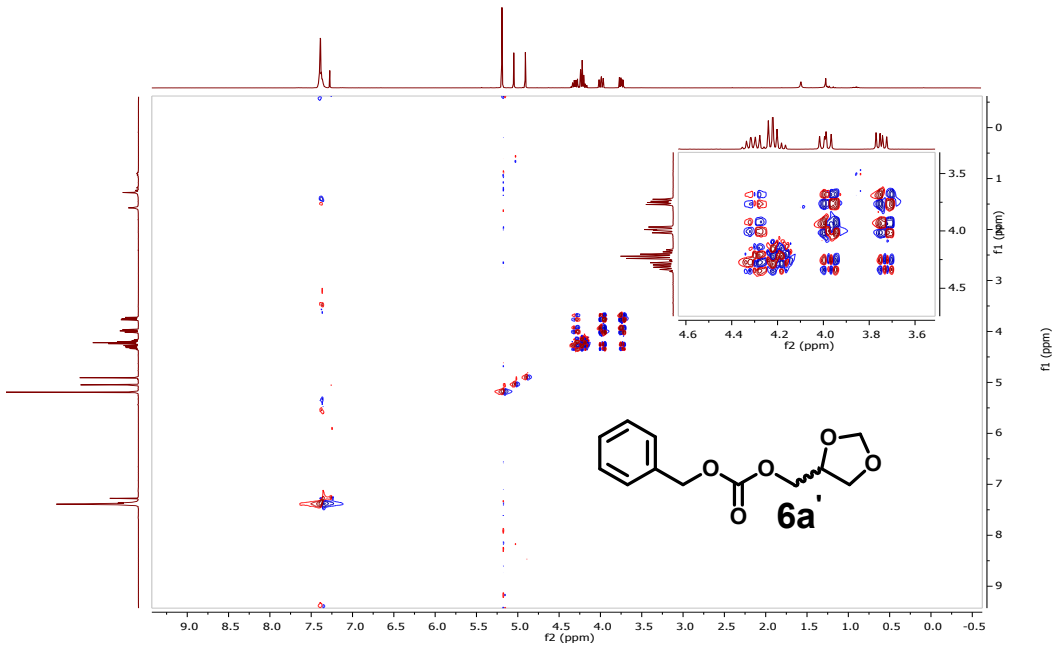

Figure S 21: ^{1}H-^{1}H DQFCOSY spectra of product **6a'**

^{1}H-^{13}C HMQC of product 6a'

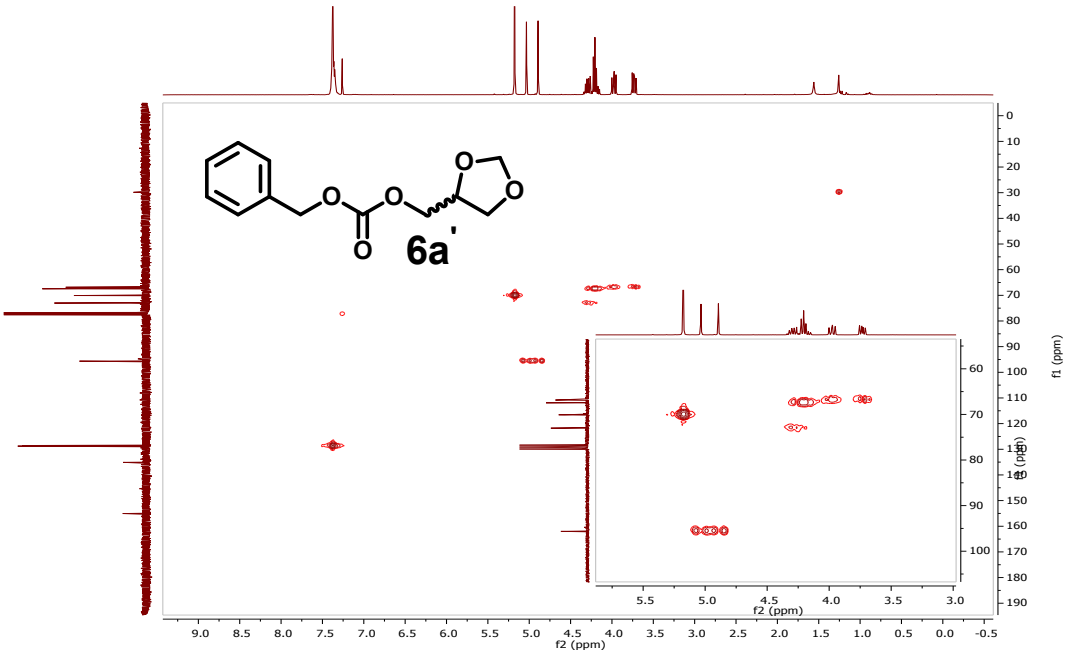

Figure S 22: ^{1}H-^{13}C HMQC spectra of product **6a'**

^{1}H-^{13}C HMBC of product 6a'

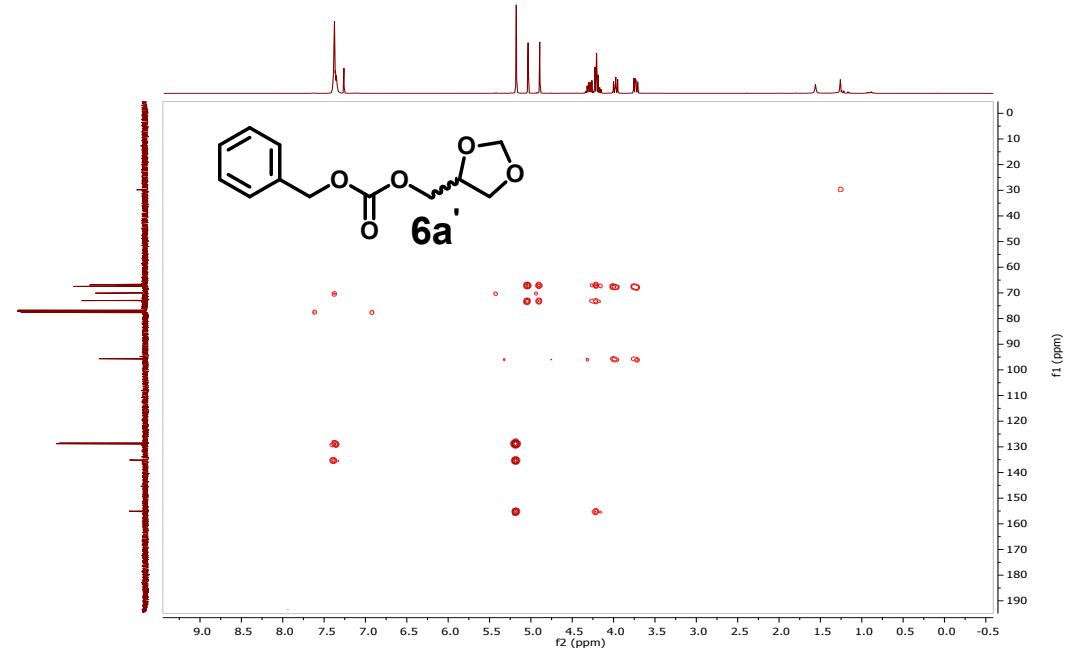

Figure S 23: ^{1}H-^{13}C HMBC spectra of product **6a'**

^{1}H-^{1}H NOESY of product 6a'

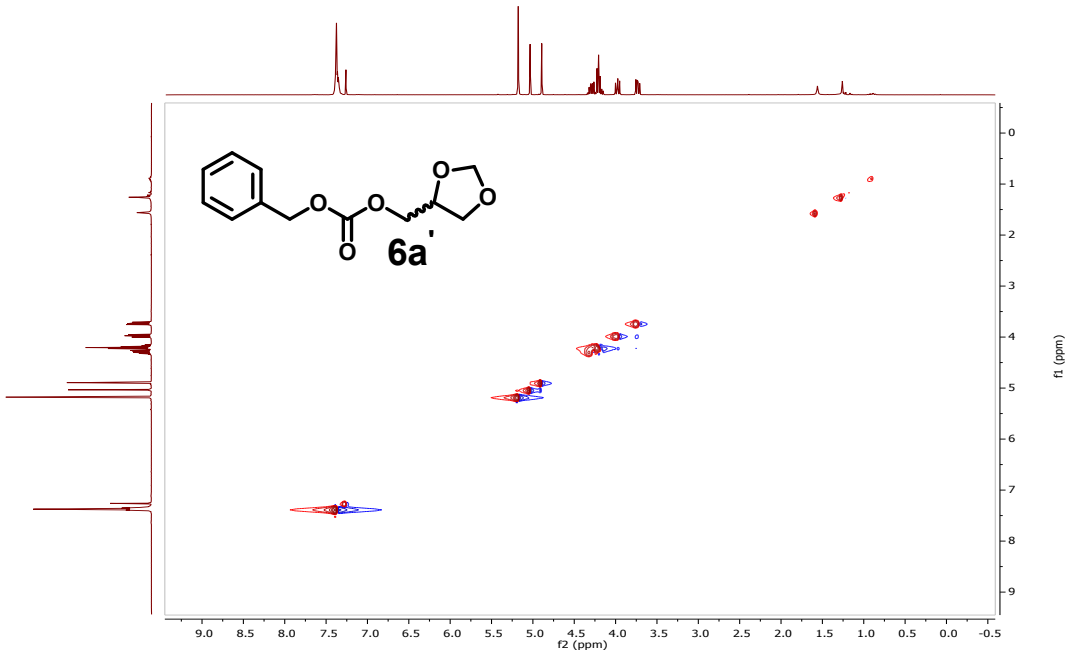

Figure S 24: ^{1}H-^{1}H NOESY spectra of product **6a'**

GC/MS of product 6a'

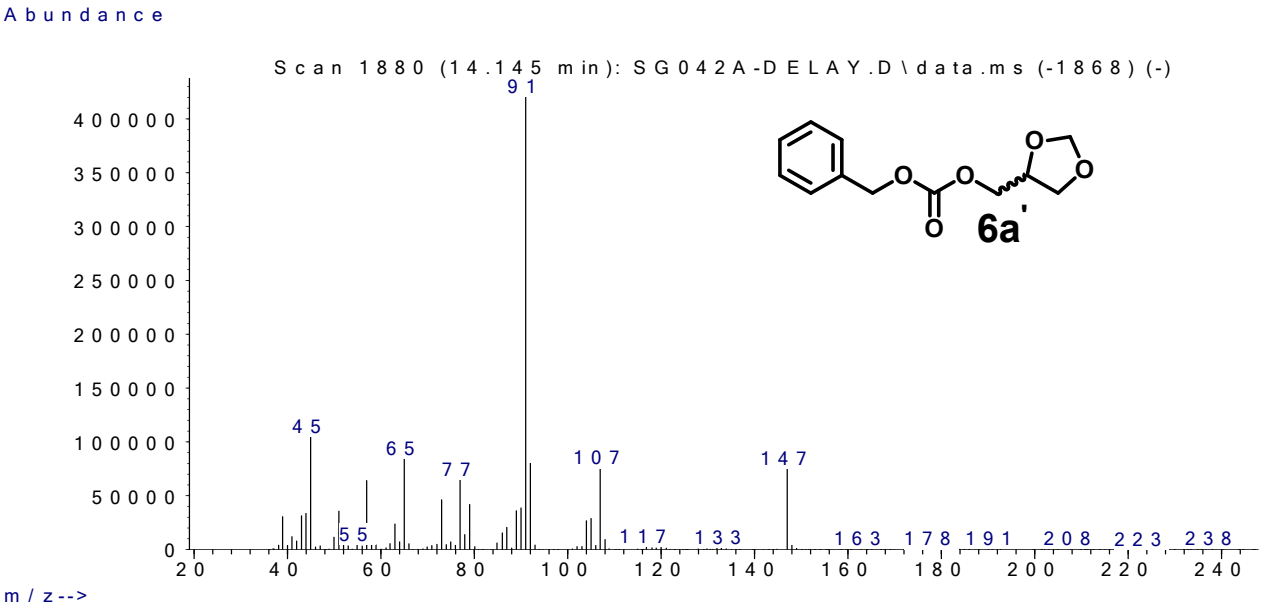

Figure S 25: MS spectra of product **6a'**

GC/MS (relative intensity, 70eV) *m/z*: 238 (M^{+}, <1%), 147(17), 107(17), 92 (18), 91(100), 79 (10), 77 (15), 73 (11), 65 (19), 57 (15), 45 (24).

GC/MS spectrum of product 4a

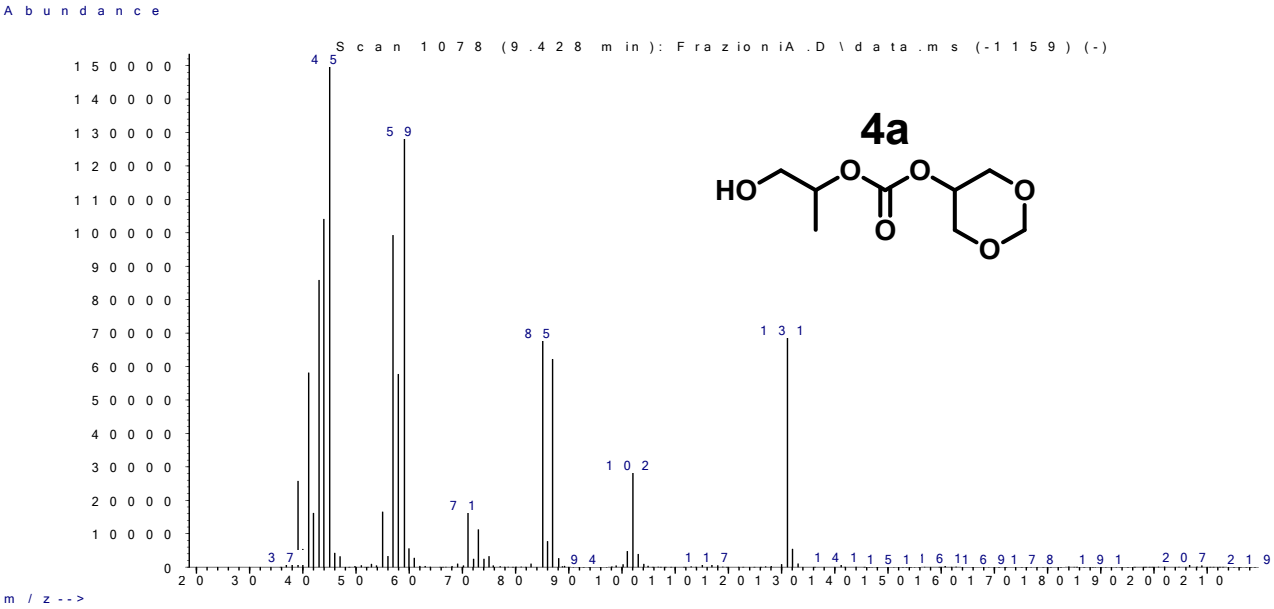

Figure S 26: MS spectra of product **4a**

GC/MS (relative intensity, 70eV) *m/z*: 206 (M^+, <1%), 131 (45), 102 (18), 87 (41), 85 (44), 71 (11), 59 (84), 58 (38), 57 (65), 55 (11), 45 (100), 44 (68), 43 (56), 42 (11), 41 (38), 39 (17).

GC/MS spectrum of product 4a'

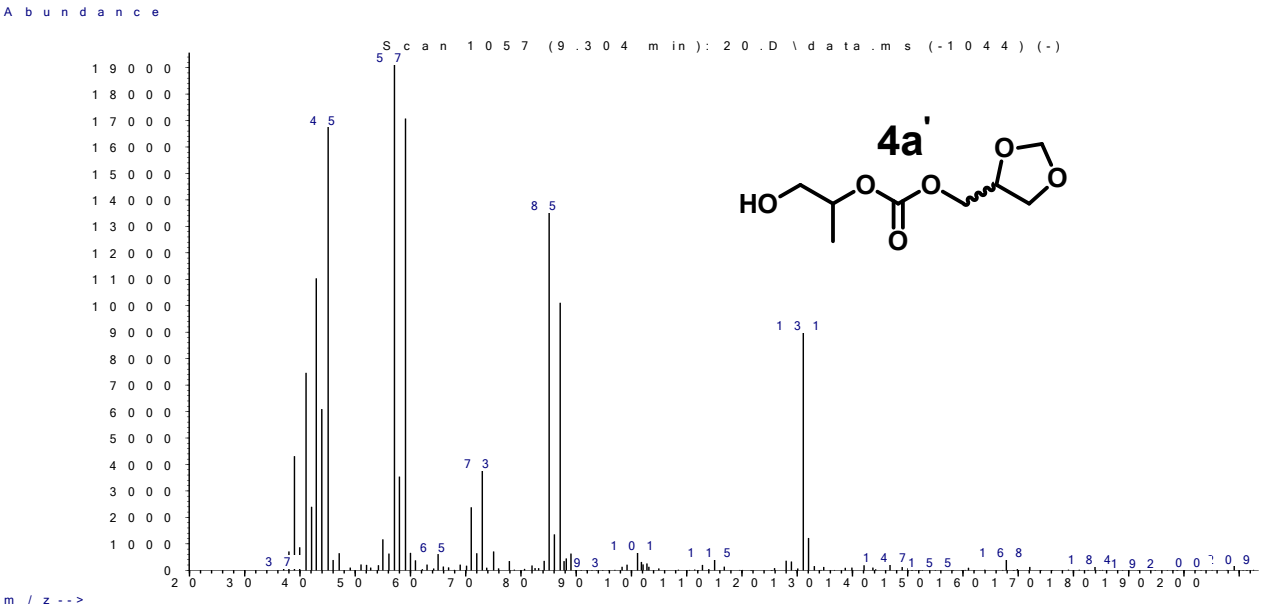

Figure S 27: MS spectra of product **4a'**

GC/MS (relative intensity, 70eV) *m/z*: 206 (M^+, <1%), 131 (46), 87 (52), 85 (69), 73 (19), 71 (12), 59 (87), 58 (18), 57 (100), 45 (86), 44 (31), 43 (56), 42 (12), 41 (38), 39 (22).

GC/MS spectrum of product 5a

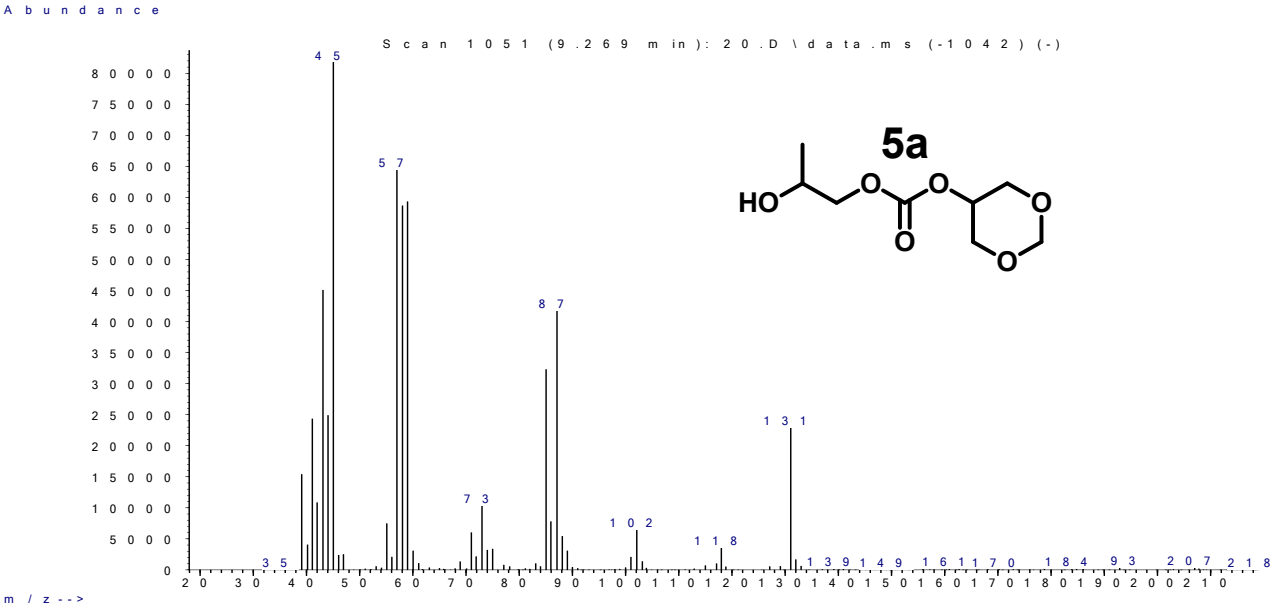

Figure S 28: MS spectra of product **5a**

GC/MS (relative intensity, 70eV) *m/z*: 206 (M^+, <1%), 131 (27), 87 (50), 85 (39), 73 (12), 59 (71), 58 (70), 57 (77), 45 (100), 44 (30), 43 (54), 42 (13), 41 (29), 39 (18).

GC/MS spectrum of product 5a'

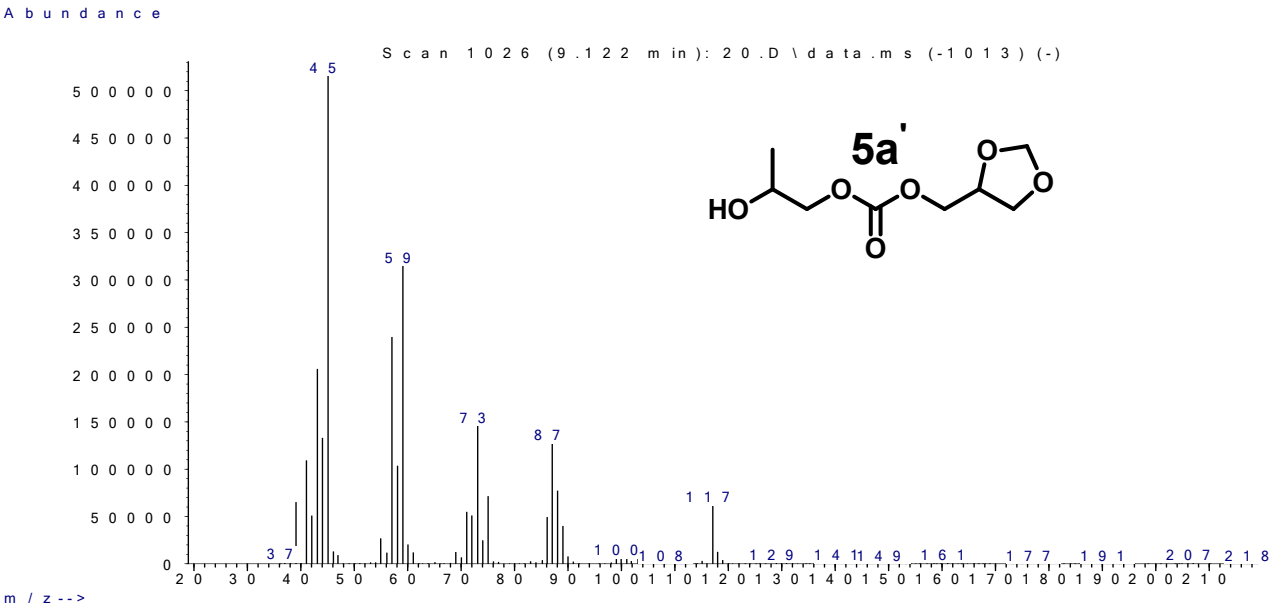

Figure S 29: MS spectra of product **5a'**

GC/MS (relative intensity, 70eV) *m/z*: 206 (M^+, <1%), 117 (12), 88 (15), 87 (24), 75 (13), 73 (27), 72 (10), 71 (10), 59 (59), 58 (19), 57 (45), 45 (100), 44 (25), 43 39), 42 (10), 41 (21), 39 (12).

References

1. G. Fiorani, M. Selva, *RSC Advances*, 2014, **4**, 1929-1937.
2. M. Selva, C. A. Marques and P. Tundo, *J. Chem. Soc., Perkin Trans. 1*, 1995, 1889-1893.