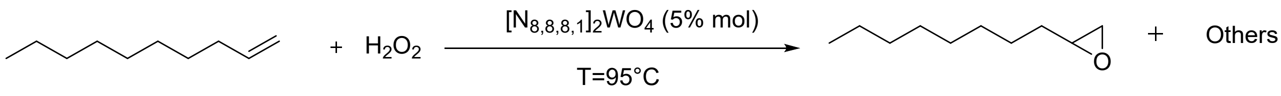
Electronic Supplementary Information

Direct oxidative carboxylation of terminal olefins to cyclic carbonates by tungstate assisted-tandem catalysis.

Roberto Calmanti, Maurizio Selva and Alvise Perosa*

Contents



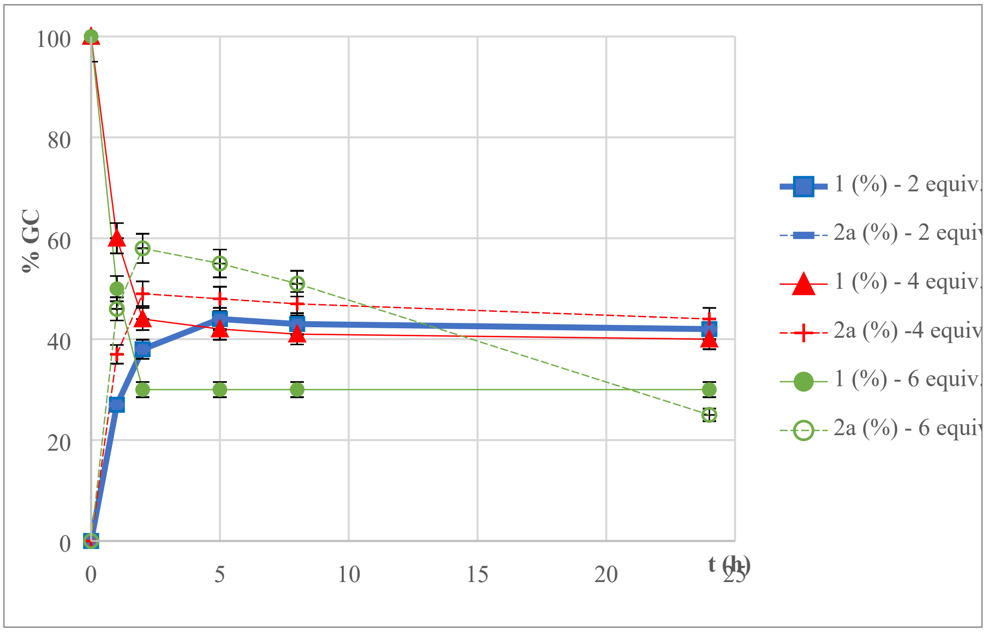


Figure S1. The epoxidation of 1-decene (**1**) with different amounts of H_2O_2 in the presence of $[N_{8,8,8,1}]_2[WO]_4$ as catalyst [Reaction conditions: **1** (4 mmol), H_2O_2 (30% w/w, 2-6 equivalents), $[N_{8,8,8,1}]_2[WO_4]$ (5% mol) T = 95 °C, t = 24 h].

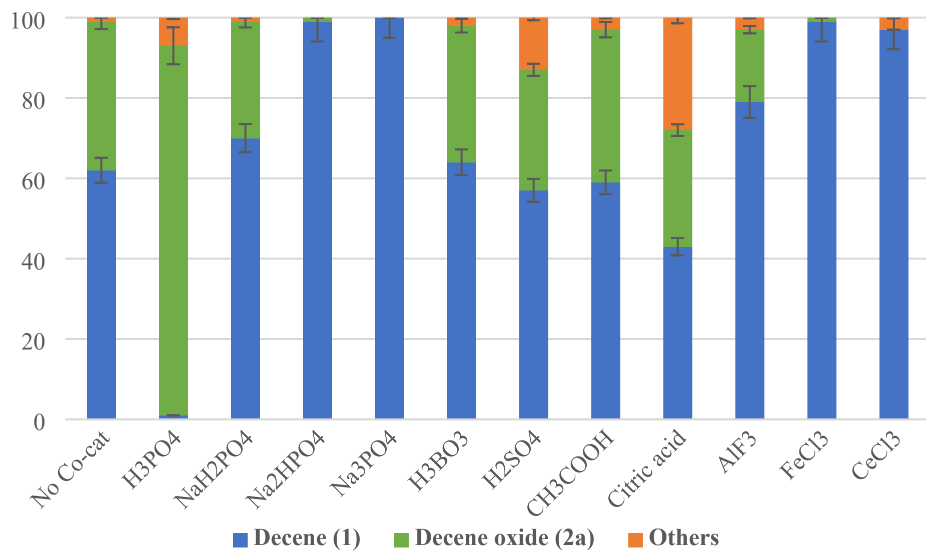


Figure S2. Product distribution as a function of different co-catalysts in the reaction of 1-decene (**1**) with H_2O_2 [Reaction conditions: **1** (4 mmol), H_2O_2 (2 equiv.), $[N_{8,8,8,1}]_2[WO_4]$ (2.5% mol), selected co-catalyst (1.25% mol) T = 85° C, 3h.

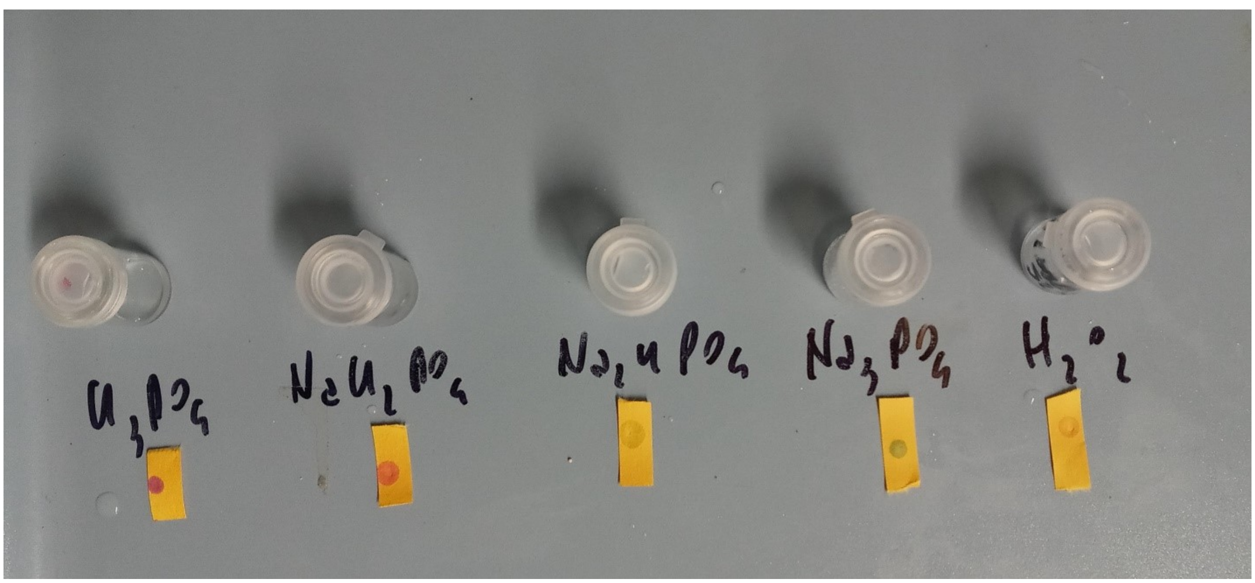


Figure S3. pH of the aqueous solution of H_2O_2 (30% wt, 0.73 ml) in the presence of the selected P-based co-catalyst (0.6% mol respect to H_2O_2). From left to right: H_3PO_4, NaH_2PO_4, Na_2HPO_4, Na_3PO_4, no co-catalyst. The litmus test gives a rough indication of the pH. We suggest that the acidity of the solution has governs the formation of different phosphoperoxotungstate species at different pH and with different P-based auxiliaries.

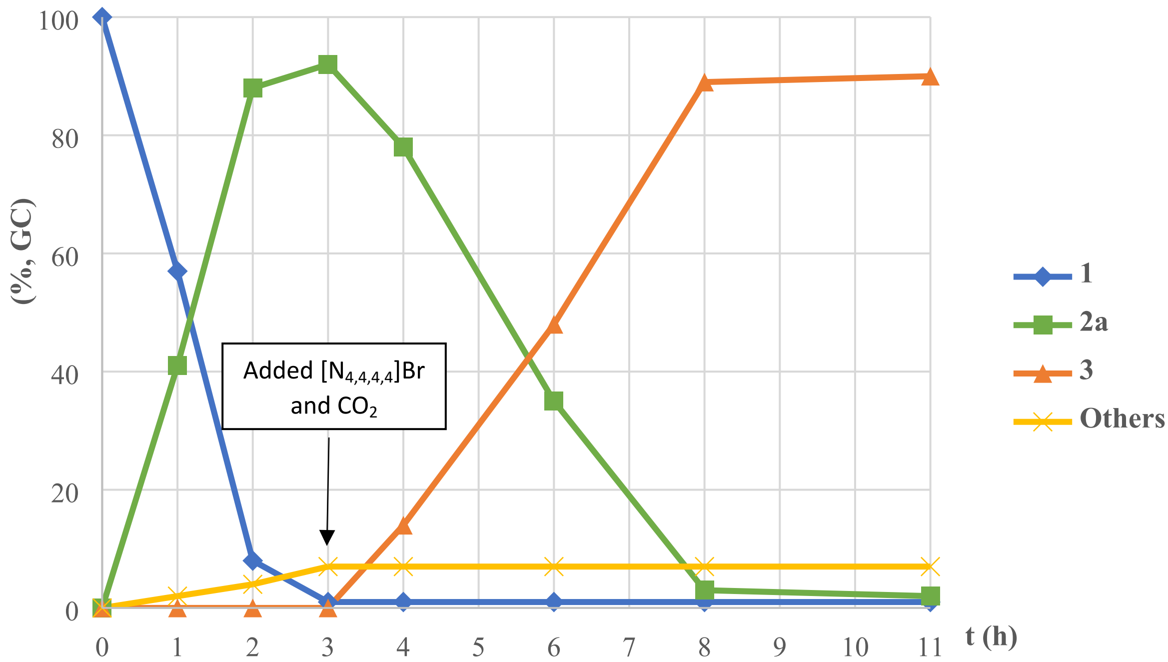


Figure S4. One-pot assisted tandem catalytic direct oxidative carboxylation of 1-decene (**1**) to 1-decene carbonate (**3**) [First step: 1-decene (4 mmol), H_2O_2 (30% w/w, 2 equivalents), $[N_{8,8,8,1}]_2[WO_4]$ (2.5% mol), H_3PO_4 (1.25% mol) T = 85 °C, t = 3 h. Second step: addition of $[N_{4,4,4,4}]Br$ (2.5% mol) and CO_2 (50 bar) without any intermediate work-up, T = 85 °C, t = 8 h. Product distribution determined by GC using mesytilene as internal standard].

^{31}P-NMR analysis of the phosphoperoxotungstate species

NMR experiments were performed in situ on a mixture of H_3PO_4, H_2O_2 and $[N_{8,8,8,1}]_2WO_4$. Procedure: a solution containing H_3PO_4 (4.4 mg, 0.045 mmol) in D_2O (0.3 ml) was analyzed by ^{31}P-NMR (red spectrum **a**). Next, H_2O_2 (30% w/w, 0.73 ml, 7.15 mmol) was added to the solution and the mixture was heated at 50°C for 30 minutes and then analyzed by ^{31}P-NMR (green spectrum, **b**). Finally $[N_{8,8,8,1}]_2WO_4$ (94.0 mg, 0.09 mmol) was added and the mixture heated at 50°C for 30 minutes and then analyzed by ^{31}P-NMR (blue spectrum **c**). Comparison of the spectra shows the shift of the ^{31}P-NMR resonance due to the formation of a phosphoperoxotungstate species ($[HPW_2O_{14}]^{2-}$) as reported elsewhere.[1]

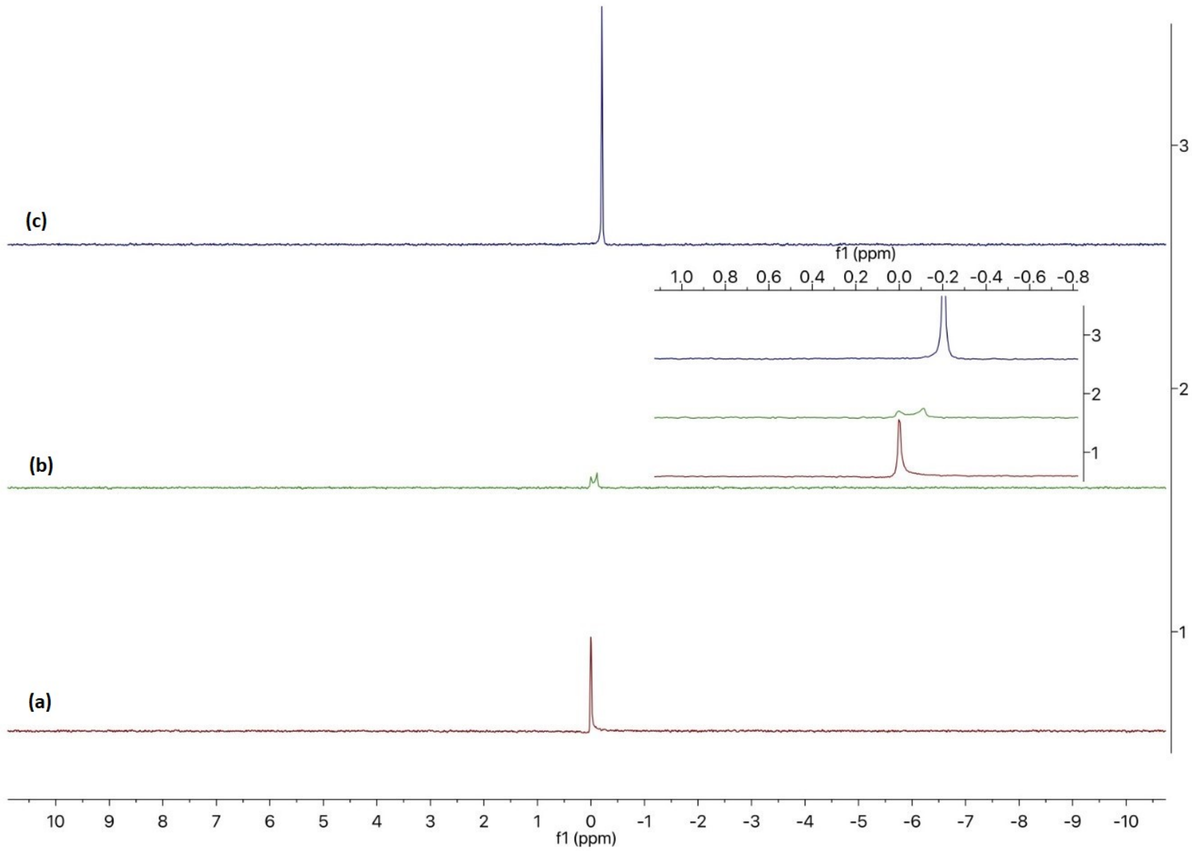


Figure S5. ^{31}P-NMR spectra (a) H_3PO_4 in D_2O (red spectrum); (b) H_3PO_4 + H_2O_2 in D_2O (green spectrum); (c) H_3PO_4 + H_2O_2 + $[N_{8,8,8,1}]_2WO_4$ in D_2O (blue spectrum).

^{183}W-NMR NMR spectra

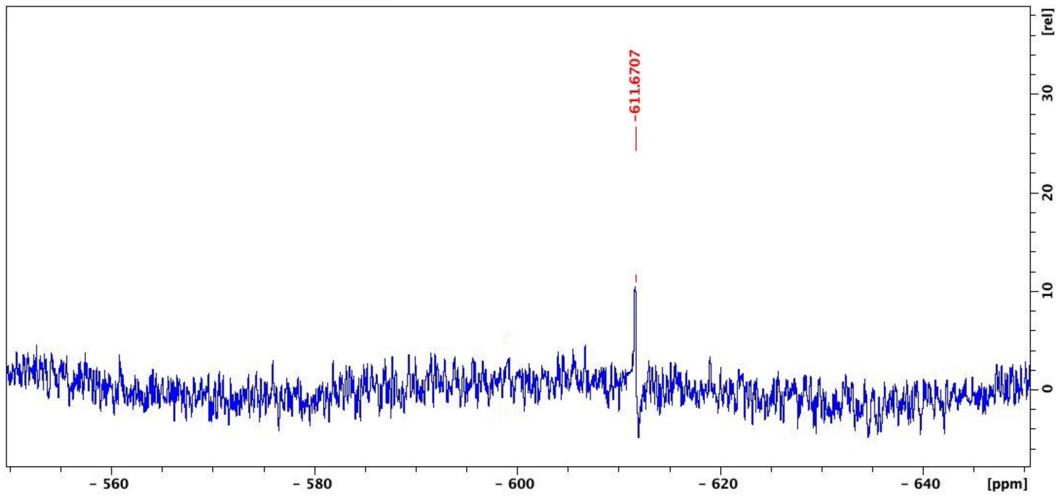


Figure S6. ^{183}W-NMR spectrum of the peroxotungstate species formed by reaction of $[N_{8,8,8,1}]_2WO_4$ with hydrogen peroxide in D_2O as solvent.

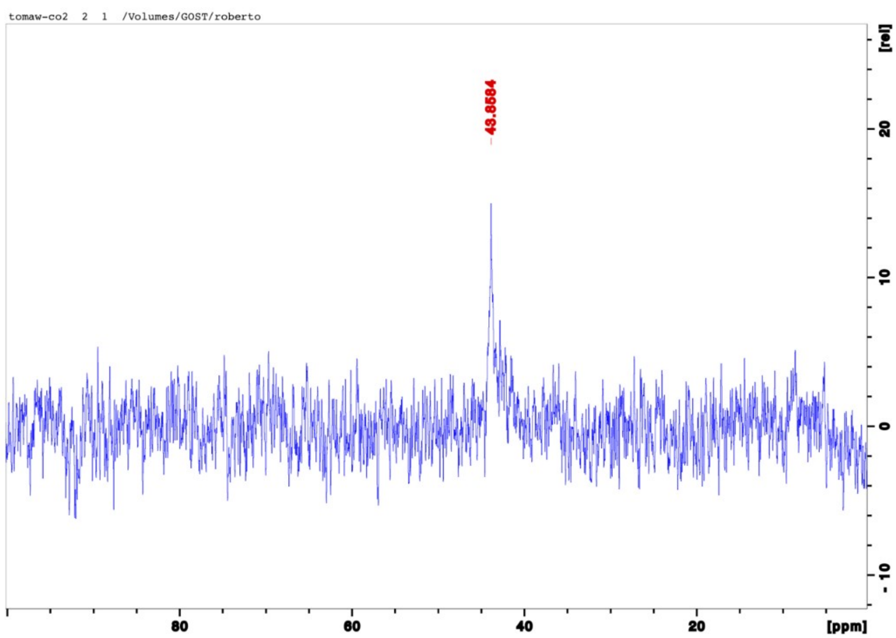


Figure S7. ^{183}W-NMR spectrum of the adduct $WO_4{\cdot}CO_2$. An NMR tube was charged with $[N_{8,8,8,1}]_2WO_4$ (0.2 g), D_2O (0.4 ml) and placed in an autoclave that was sealed, degassed via two vacuum-CO_2 cycles and pressurized with 10 bar of CO_2. The mixture was held at 85°C for 5 hours, then the autoclave was slowly vented and the NMR spectrum was recorded.

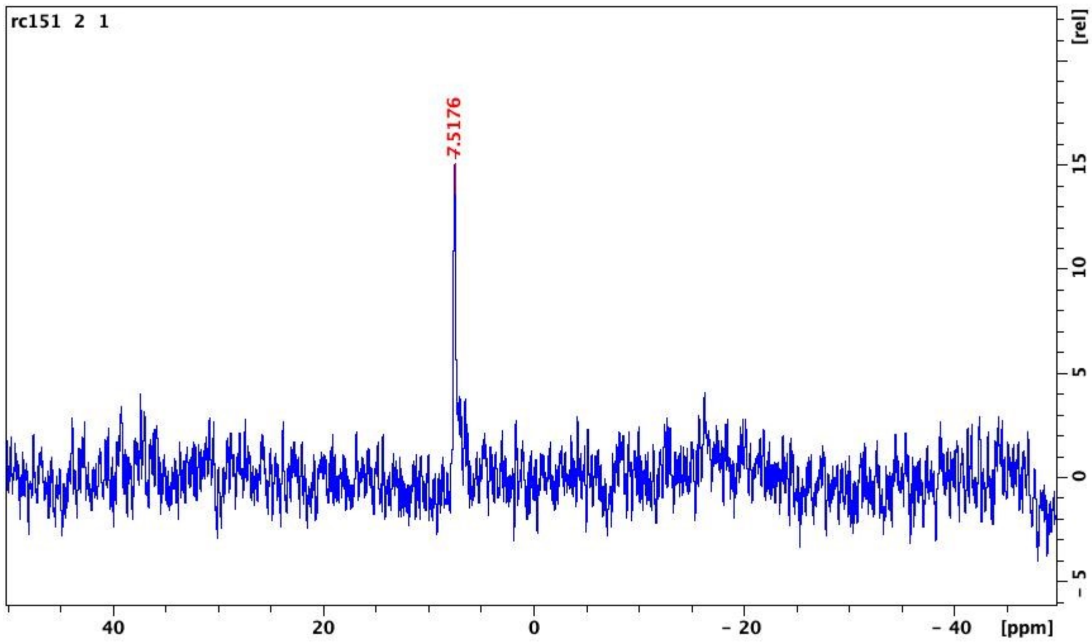


Figure S8. ^{183}W-NMR spectrum of $[N_{8,8,8,1}]_2WO_4$ in D_2O

Product characterization

1,2-Decylene oxide (**2a**)

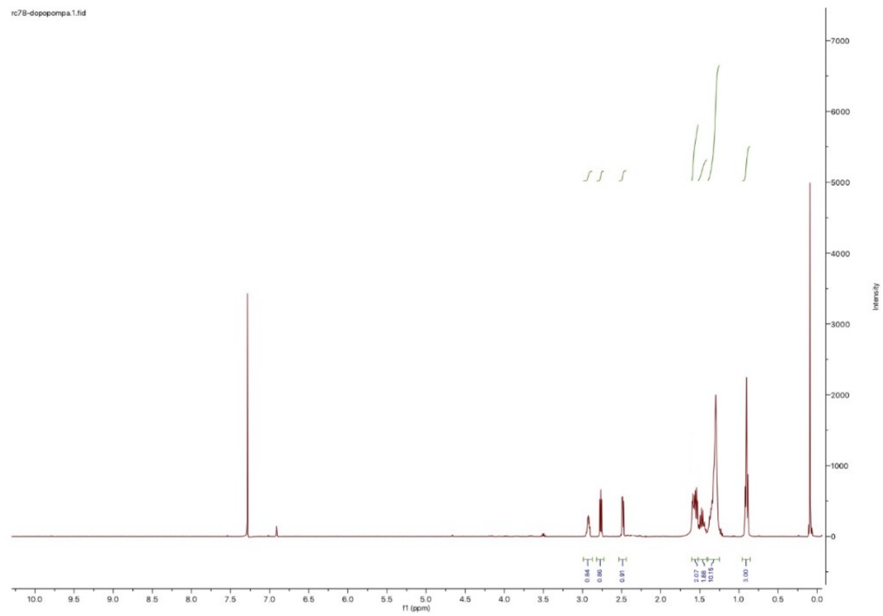


Figure S9. ^{1}H-NMR of **2a** (400 MHz, 298 K, $CDCl_3$). δ (ppm): 2.98-2,87 (m, 1H), 2.85-2.74 (dd, 1H), 2.59-2.42 (dd, 1H), 1.59-1.51 (m, 2H), 1.51-1.16 (m, 12H), 1.02-0.74 (m, 3H).

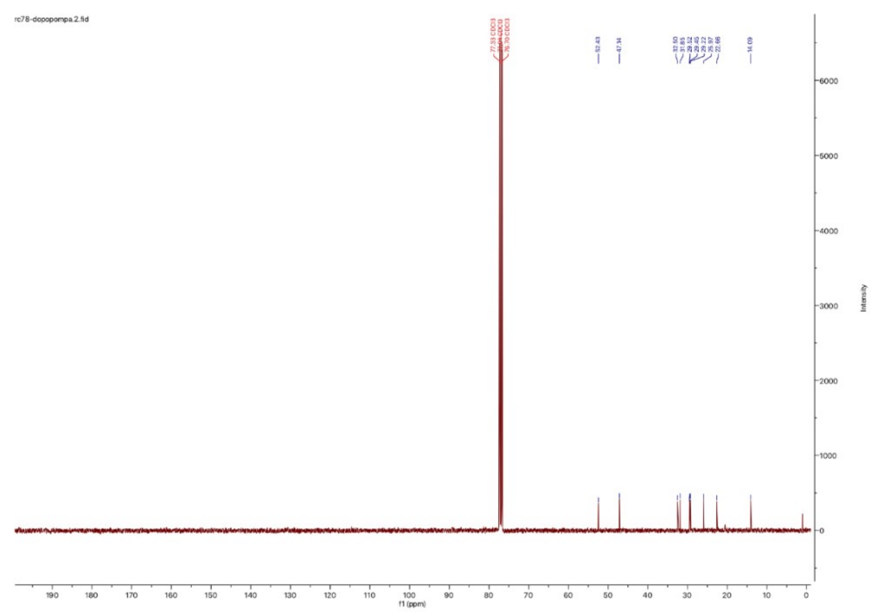


Figure S10. ^{13}C-NMR of **2a** (100 MHz, 298 K, $CDCl_3$). δ (ppm): 52.43, 47.14, 32.50, 31.85, 29.52, 29.45, 29.22, 25.97, 22.66, 14.09

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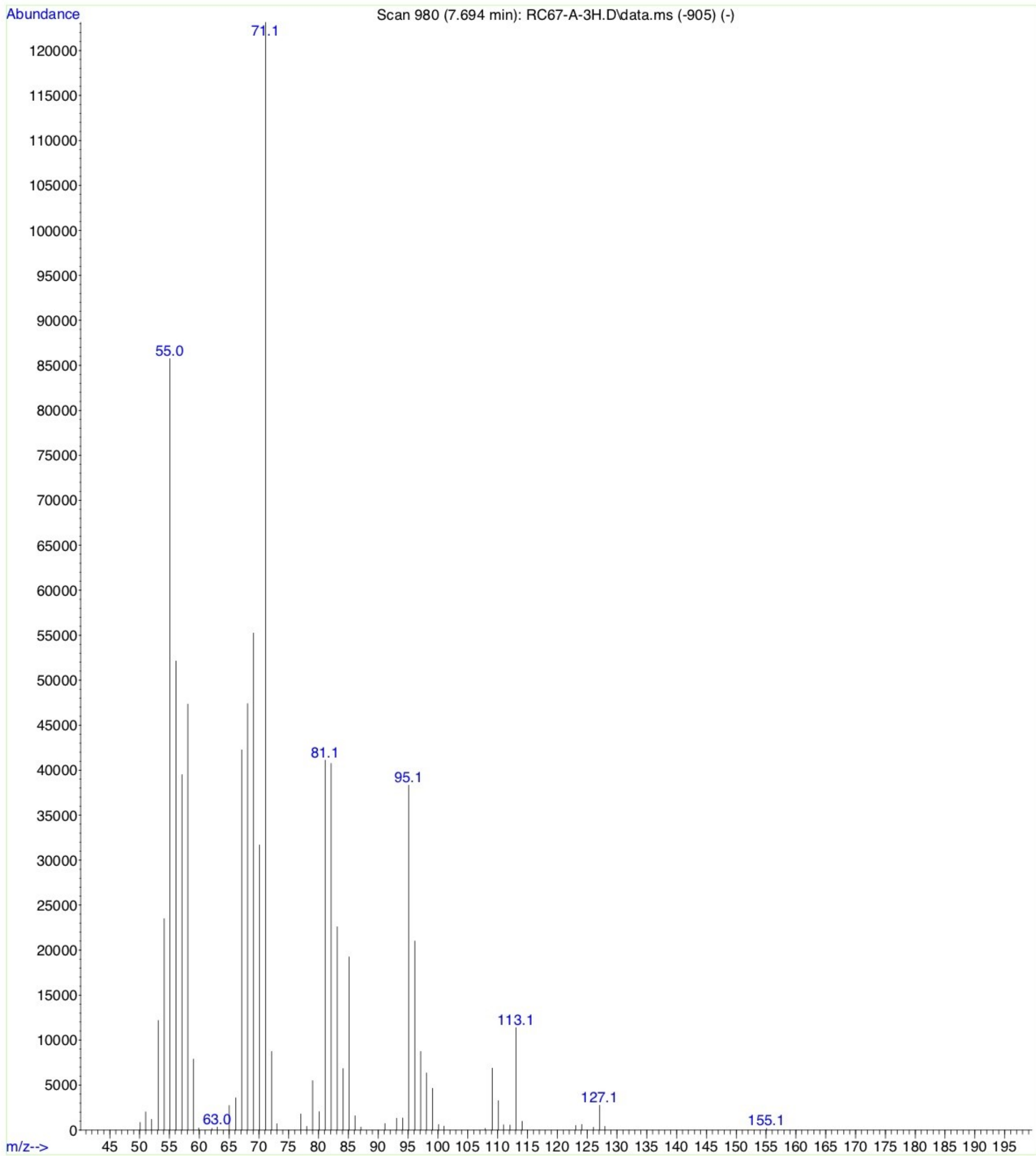

Figure S11. MS of **2a** (EI, 70 eV). m/z (70 eV): 156 (M^+, 0), 113 (9), 96 (17), 95 (31), 85 (16), 83 (18), 82 (33), 81 (33), 71 (100), 70 (26), 69 (45=, 68 (38), 67 (34), 58 (38), 57 (32), 56 (42), 55 (70), 54 (19), 53 (10)

4-Octyl-1,3-dioxolan-2-one (1-decene carbonate) (**3**)

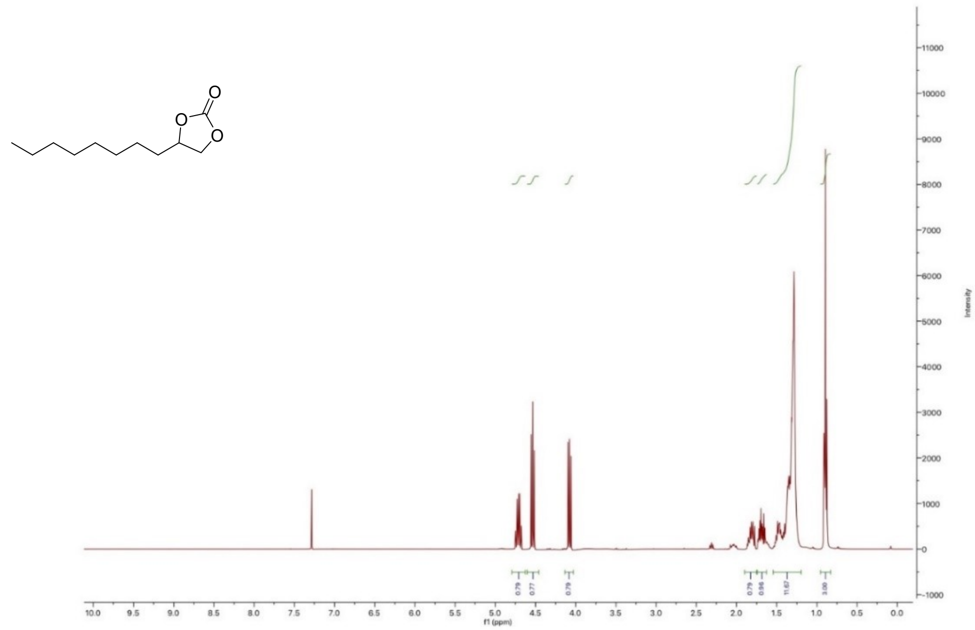

Figure S12. ^{1}H-NMR of **3** (400 MHz, 298 K, $CDCl_3$). δ (ppm): 4.81-4.64 (m, 1H), 4.59-4.46 (dd, 1H), 4.16-3.97 (dd, 1H), 1.90-1.75 (m, 1H), 1.75-1.60 (m, 1H), 1.55-1.16 (m, 12H), 1.02-0.74 (m, 3H).

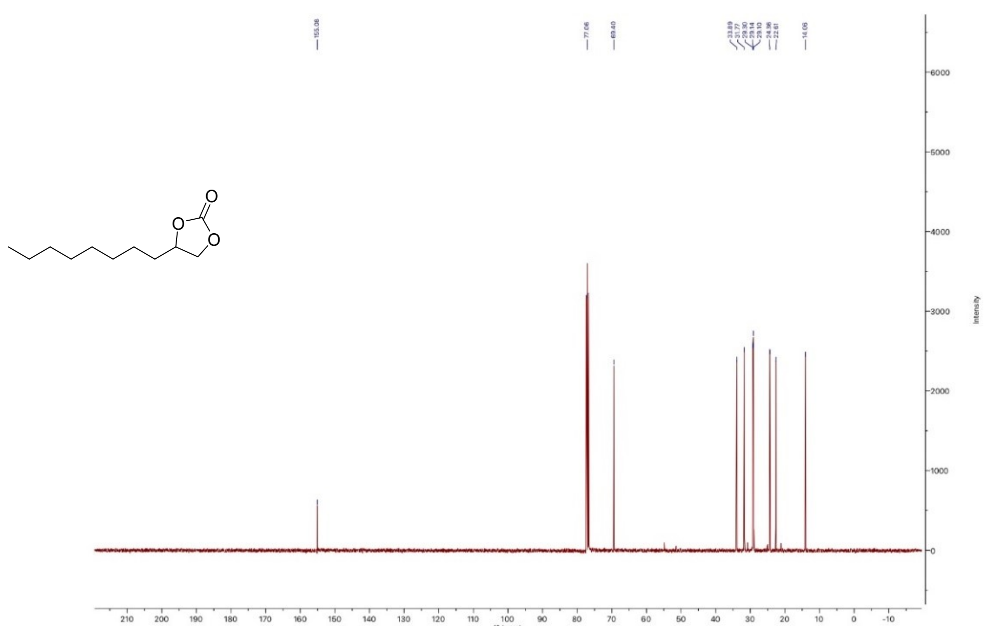

Figure S13. ^{13}C-NMR of **3** (100 MHz, 298 K, $CDCl_3$). δ (ppm): 155.08, 77.06, 69.40, 33.89, 31.77, 29.30, 29.14, 29.10, 24.36, 22.61, 14.06.

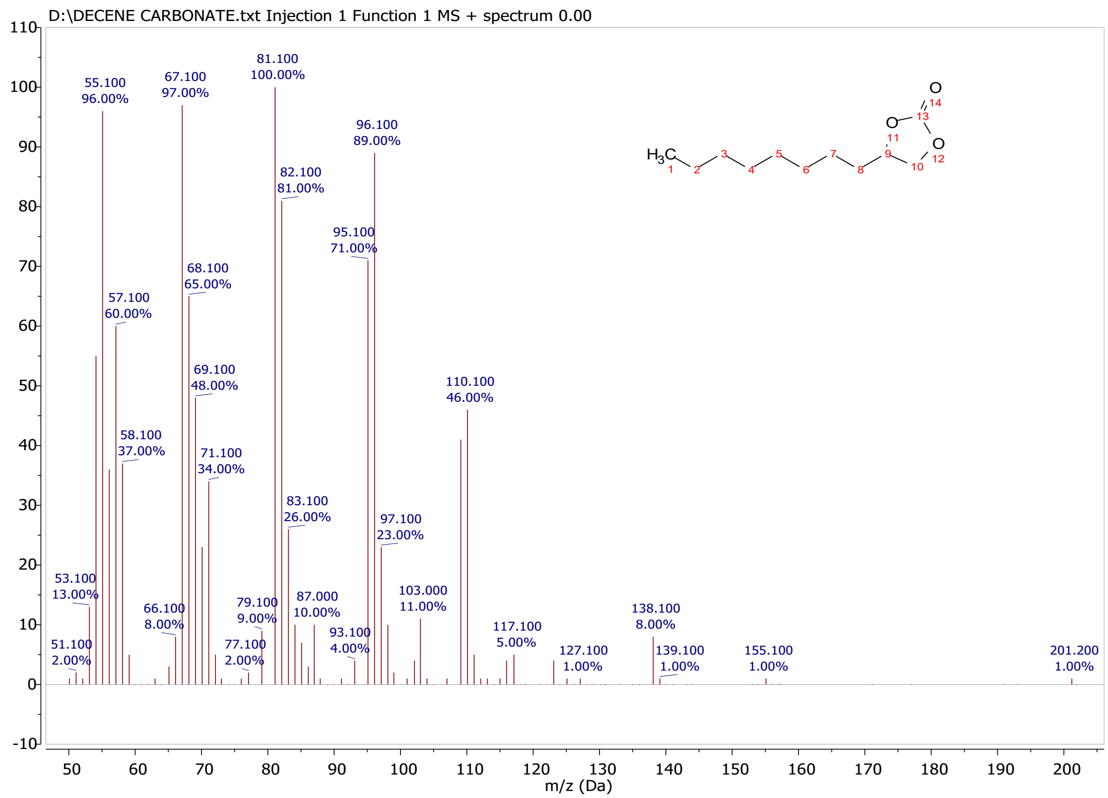

Figure S14. MS of **3** (EI, 70 V). m/z (70 eV): 201 (MH^+, 1), 110 (46), 96 (89), 81 (100), 67 (97), 55 (96).

<u>4-Butyl-1,3-dioxolan-2-one (1-hexene carbonate) (**3a**)</u>

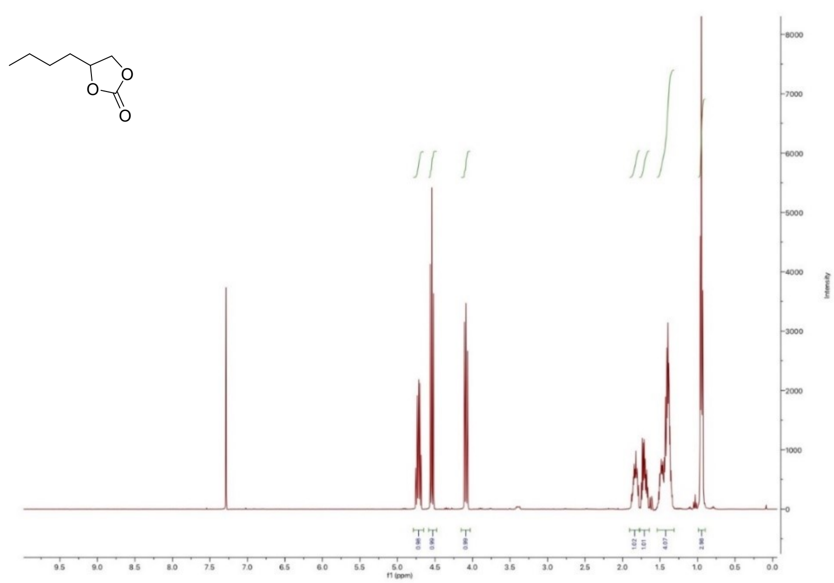

Figure S15. ^{1}H-NMR of **2c** (400 MHz, 298 K, $CDCl_3$). δ (ppm): 4.80-4.65 (m, 1H), 4.61-4.48 (dd, 1H), 4.13-4.03 (dd, 1H), 1.92-1.76 (m, 1H), 1.77-1.64 (m, 1H), 1.55-1.30 (m, 4H), 1.00-0.89 (t, 3H).

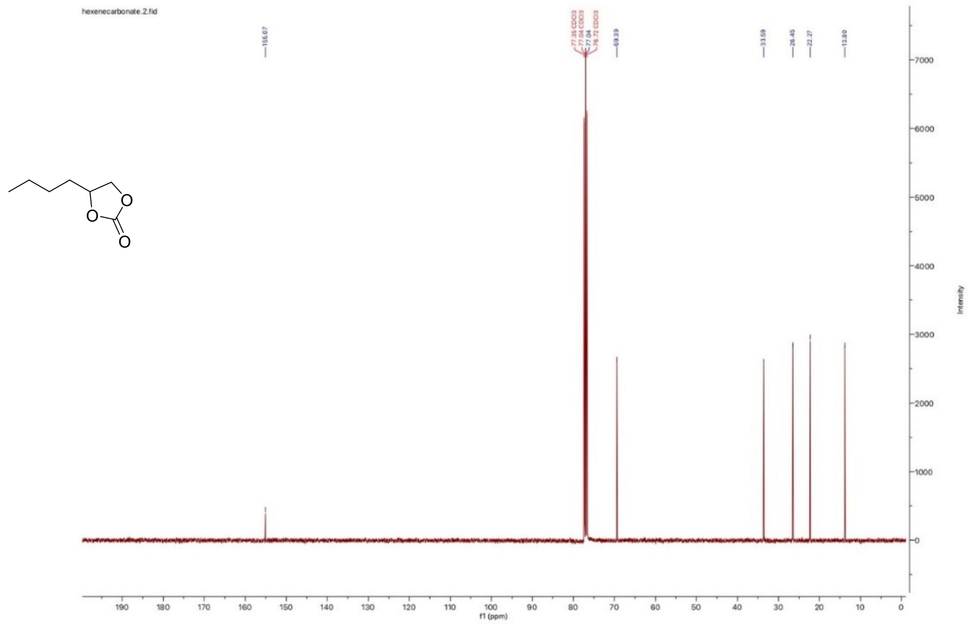

Figure S16. ^{13}C-NMR of **2c** (100 MHz, 298 K, $CDCl_3$). δ (ppm): 155.07, 77.04, 69.39, 33.59, 26.45, 22.27, 13.80.

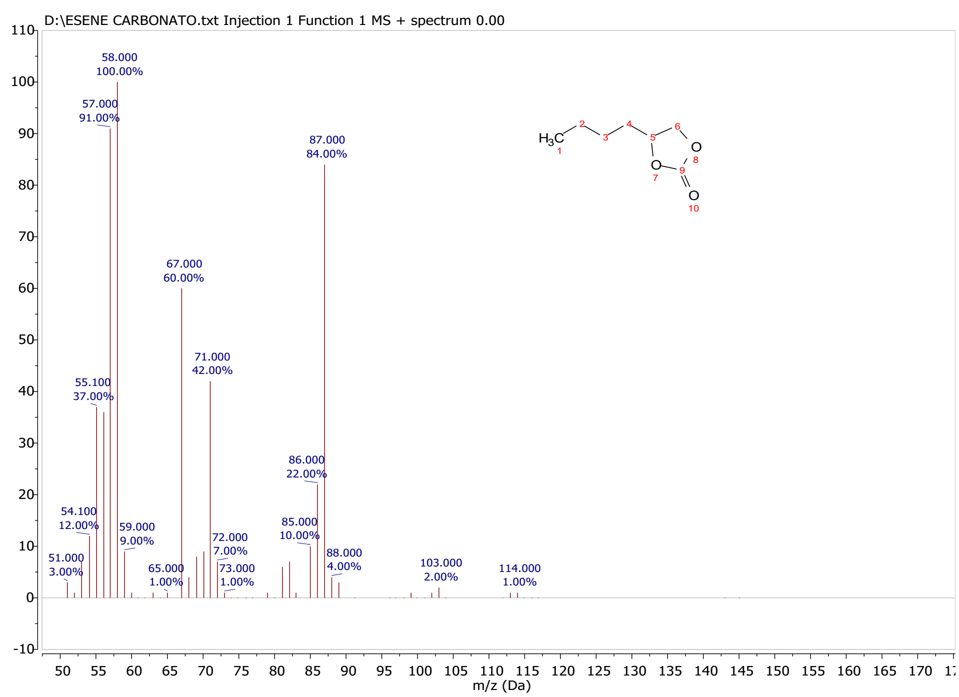

Figure S17. MS of **3a** (EI, 70 V). m/z (70 eV): 114 (1), 87 (84), 71 (42), 67 (70), 58 (100), 57 (91), 55 (37).

4-Dodecyl-1,3-dioxolan-2-one (1-tetradecene carbonate) (**3b**)

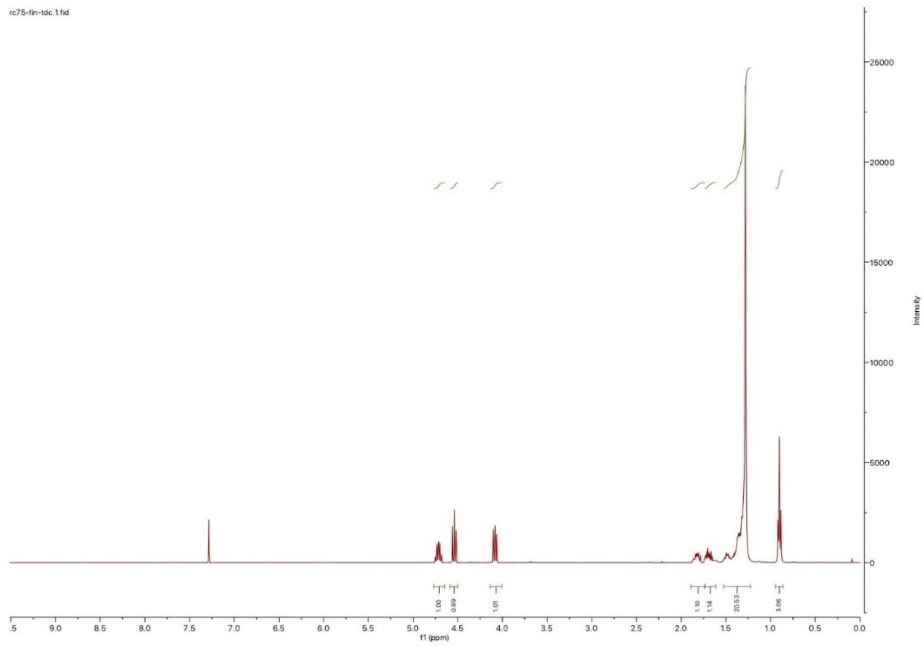

Figure S18. ^{1}H-NMR of **3b** (400 MHz, $CDCl_3$) δ = 4.83 – 4.60 (dd, 1H), 4.60 – 4.45 (t, 1H), 4.16 – 3.94 (dd, 1H), 1.90 – 1.73 (m, 1H), 1.75 – 1.59 (m, 1H), 1.54 – 1.18 (m, 20H), 1.03 – 0.70 (m, 3H).

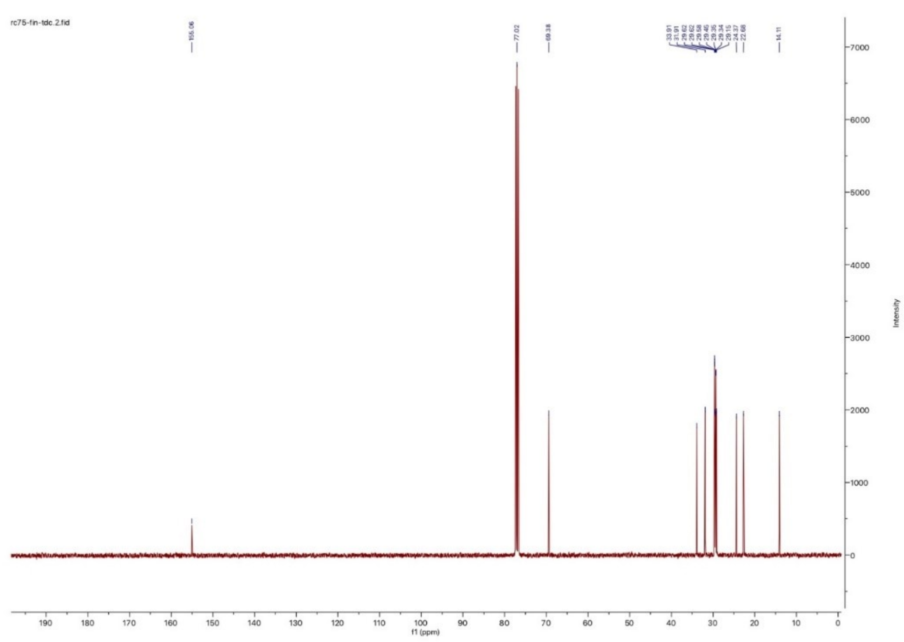

Figure S19. ^{13}C-NMR of **3b** (101 MHz, $CDCl_3$) δ 155.06, 77.02, 69.38, 33.91, 31.91, 29.63, 29.62, 29.58, 29.45, 29.35, 29.34, 29.15, 24.37, 22.68, 14.11.

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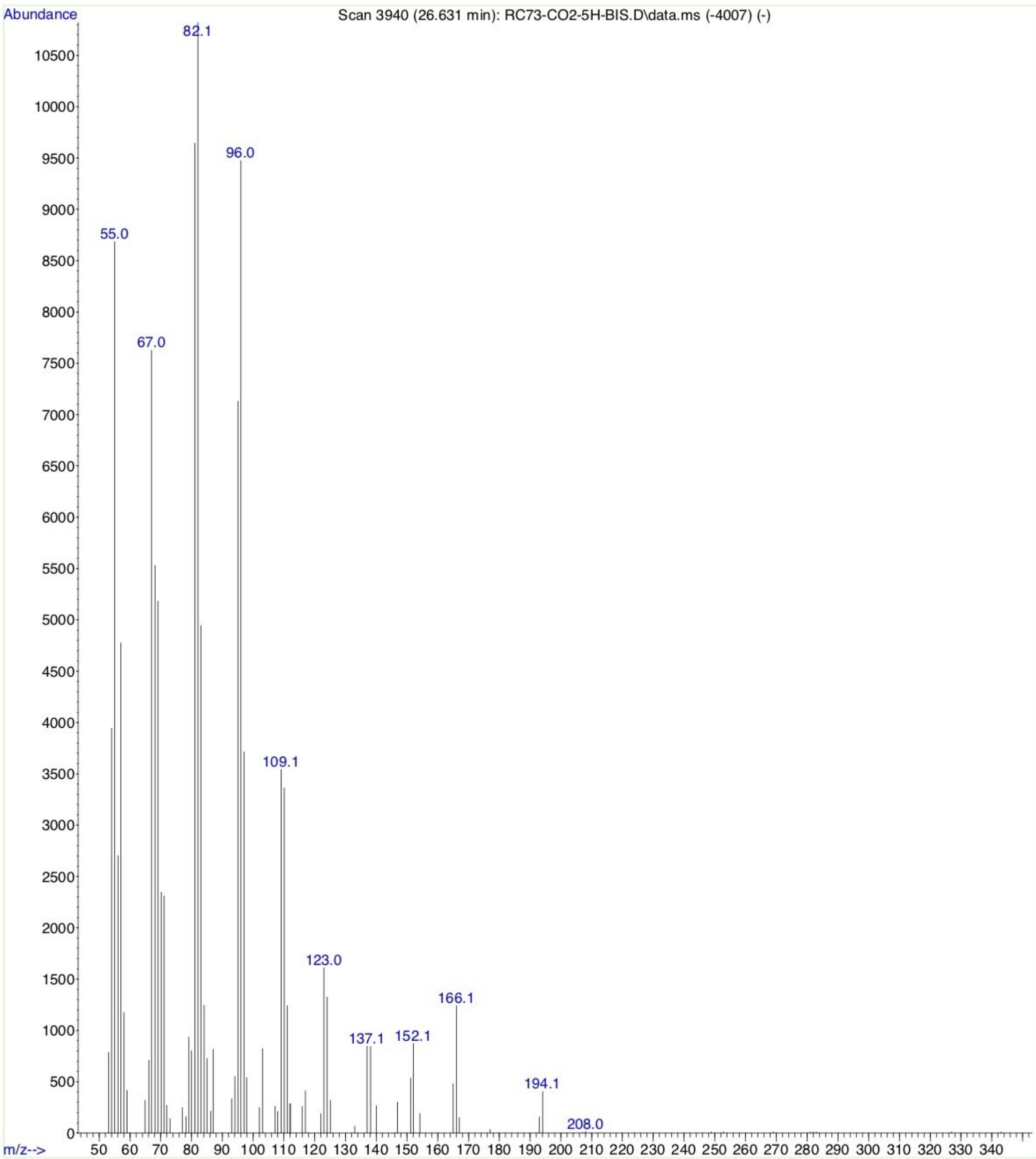

Figure S20. MS of **3b** (EI, 70 V). m/z (70 eV): 194 (1), 166 (13), 124 (17), 123 (15), 111 (13), 110 (30), 109 (36), 97 (34), 96 (97), 95 (76), 83 (44), 82 (100), 81 (100), 71 (22), 70 (19), 69 (57), 68 (55), 67 (81), 57 (50), 56 (28), 55 (87), 54 (38).

4-Tetradecyl-1,3-dioxolan-2-one (1-hexadecene carbonate) (**3c**)

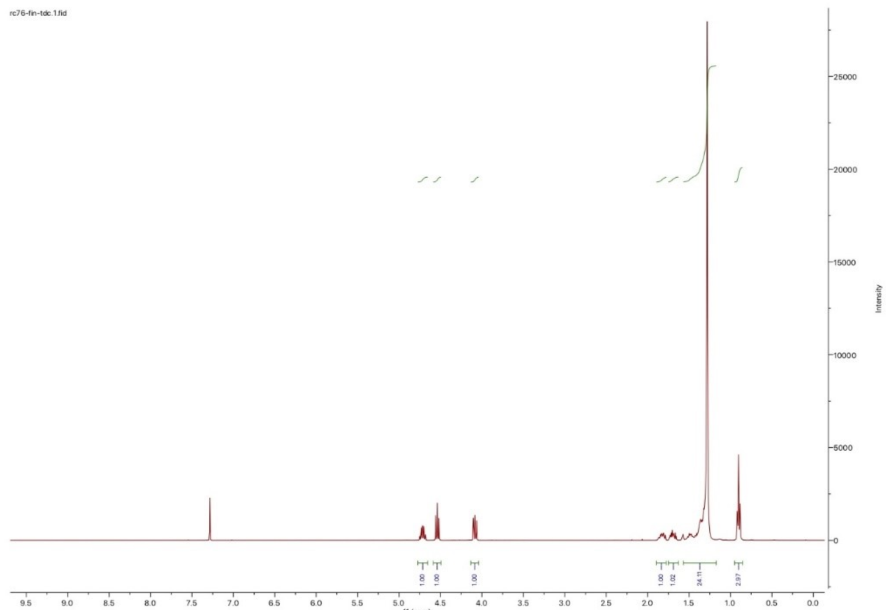

Figure S21. ^{1}H-NMR of **3c** (400 MHz, $CDCl_3$) δ = 4.79 – 4.61 (dd, 1H), 4.59 – 4.48 (t, 1H), 4.16 – 3.91 (dd, 1H), 1.91 – 1.74 (m, 1H), 1.76 – 1.60 (m, 1H), 1.54 – 1.15 (m, 24H), 0.99 – 0.80 (m, 3H).

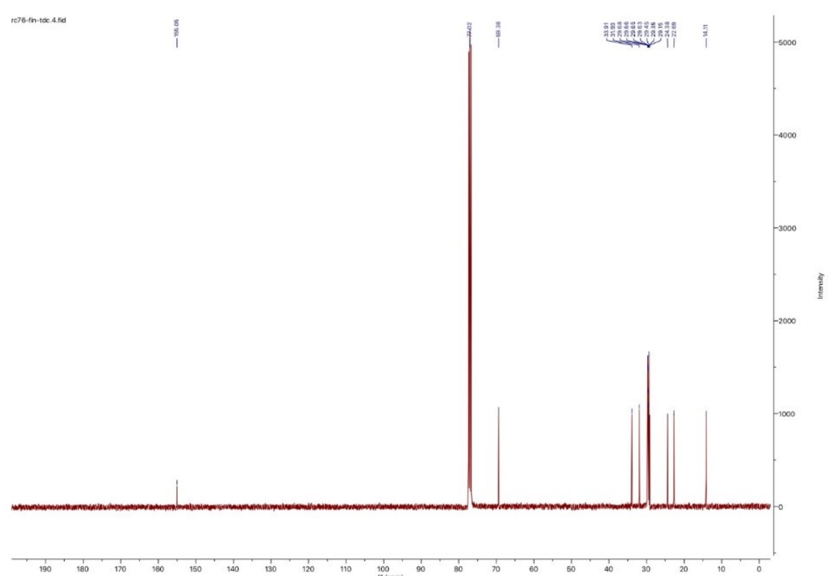

Figure S22. ^{13}C-NMR of **3c** (101 MHz, $CDCl_3$) δ 155.05, 77.02, 69.38, 33.91, 31.93, 29.68, 29.66, 29.65, 29.63, 29.58, 29.45, 29.35, 29.34 29.15, 24.38, 22.69, 14.11.

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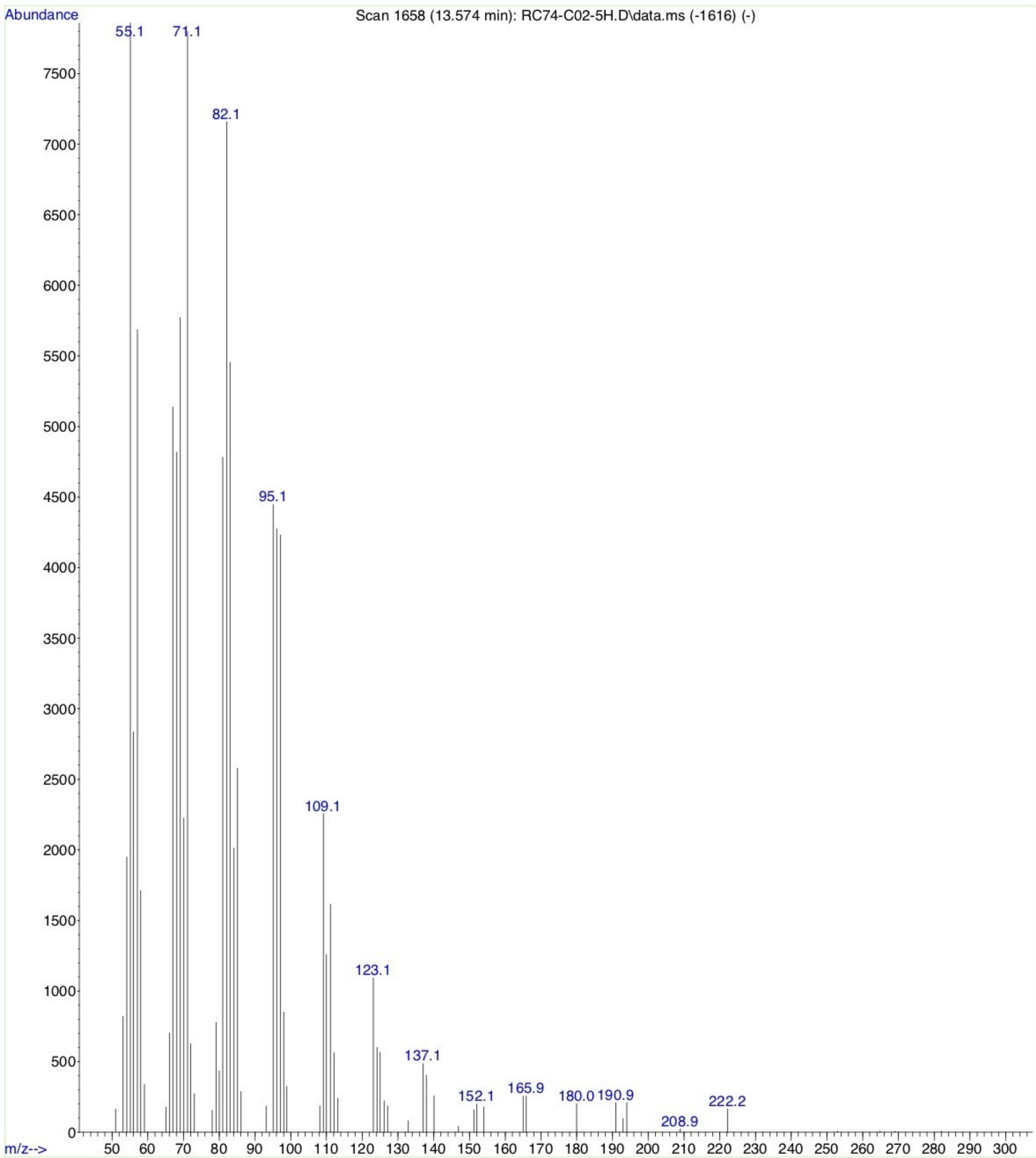

Figure S23. MS of **3c** (EI, 70 V). m/z (70 eV): 222 (2), 194 (3), 191 (4), 180 (3), 165 (6), 152 (2), 138 (10), 123 (14), 111 (21), 110 (16), 109 (29), 98 (11), 97 (54), 96 (54), 95 (57), 85 (33), 84 (26), 83 (69), 82 (91), 81 (61), 71 (99), 70 (28), 69 (73), 68 (61), 67 (65), 58 (22), 57 (72), 56 (36), 55 (100), 54 (25), 53 (10).

Allylbenzene carbonate (**3d**)

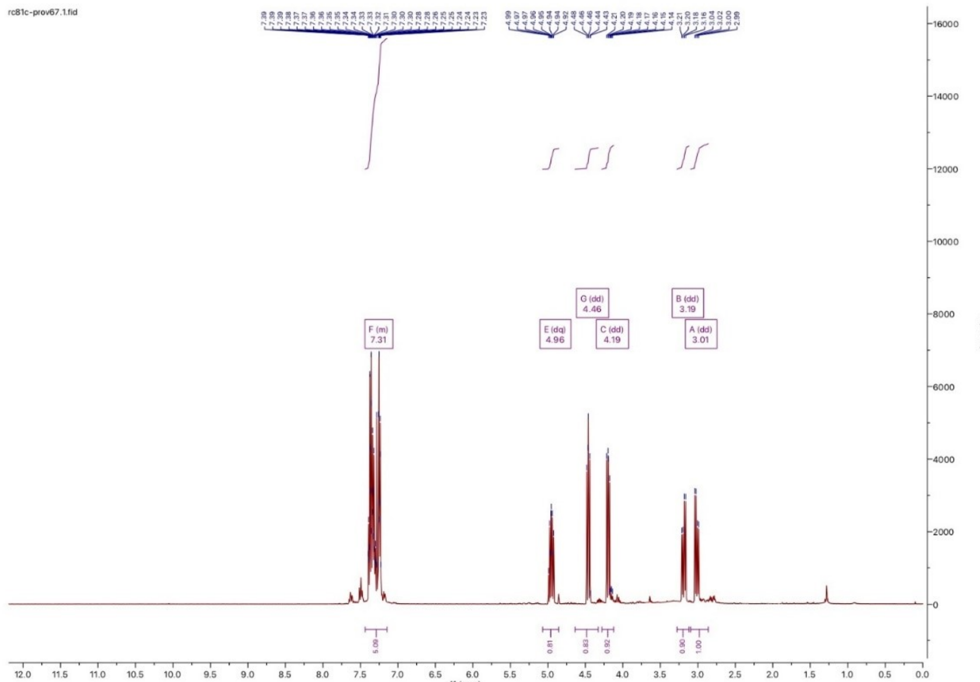

Figure S24. ^{1}H-NMR of **3d** (400 MHz, $CDCl_3$) δ = 7.44 – 7.15 (m, 5H), 5.07 – 4.85 (m, 1H), 4.54 – 4.38 (dd, 1H), 4.28 – 4.12 (dd, 1H), 3.28 – 3.12 (dd, 1H), 3.09 – 2.86 (dd, 1H).

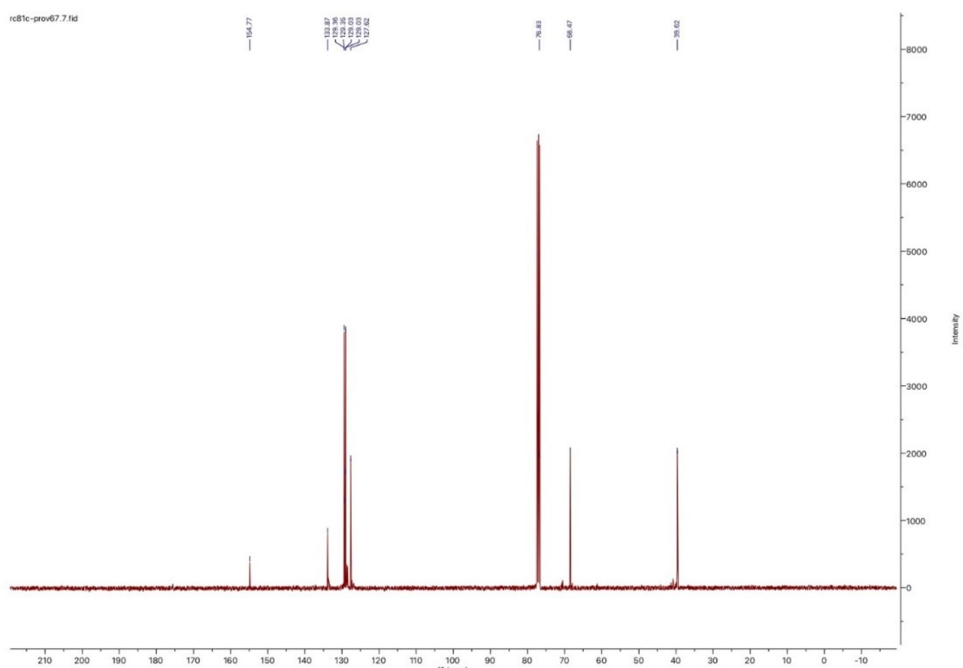

Figure S25. ^{13}C-NMR of **3d** (101 MHz, $CDCl_3$) δ 154.77, 133.87, 129.36, 129.35, 129.03, 129.03, 127.62, 76.83, 68.47, 39.62.

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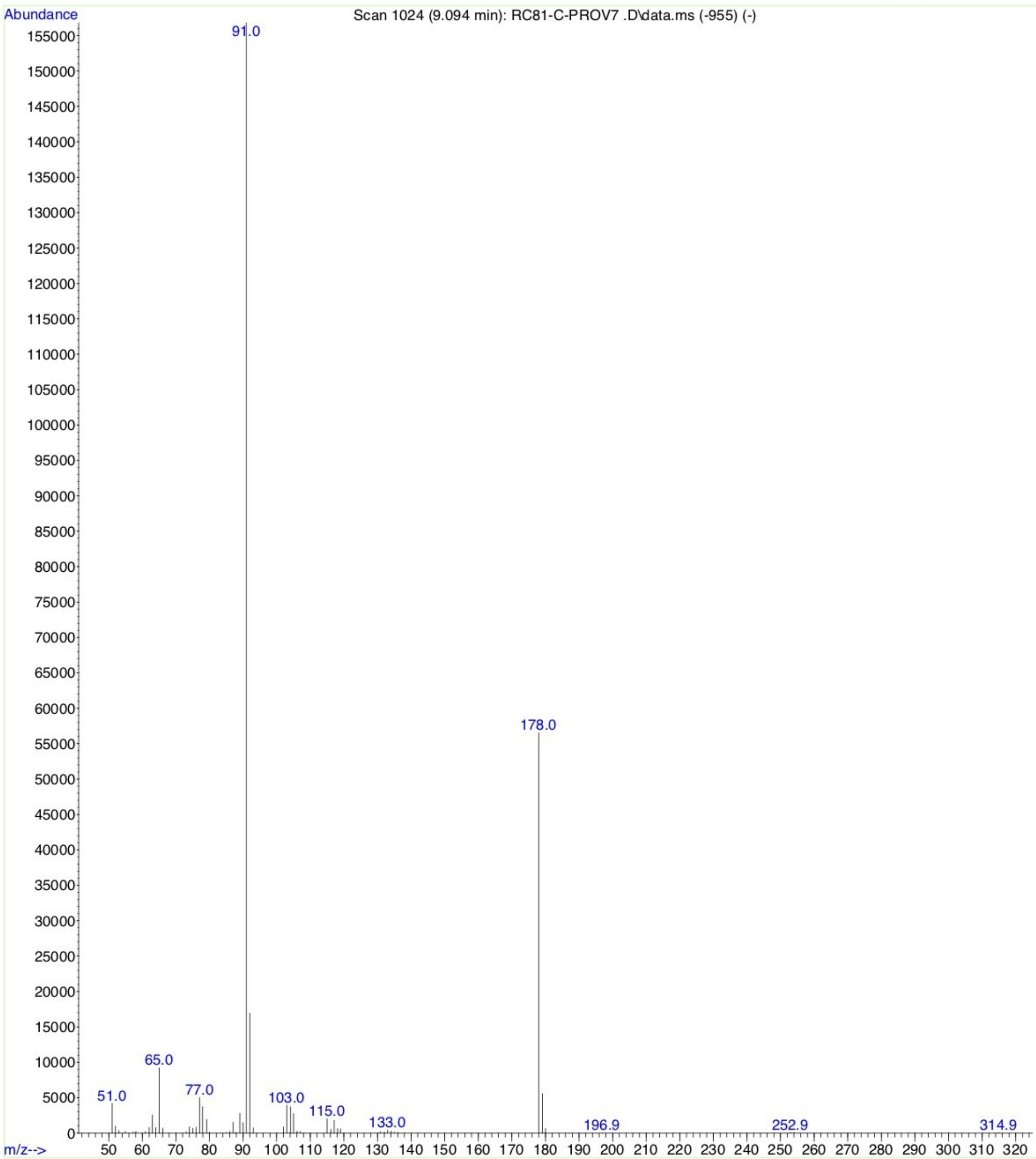

Figure S26. MS of **3d** (EI, 70 V). m/z: 178 (30), 105(2), 103(3), 92 (11), 91 (100), 77 (3), 65 (6), 51 (3).

Allyltoluene carbonate (**3e**)

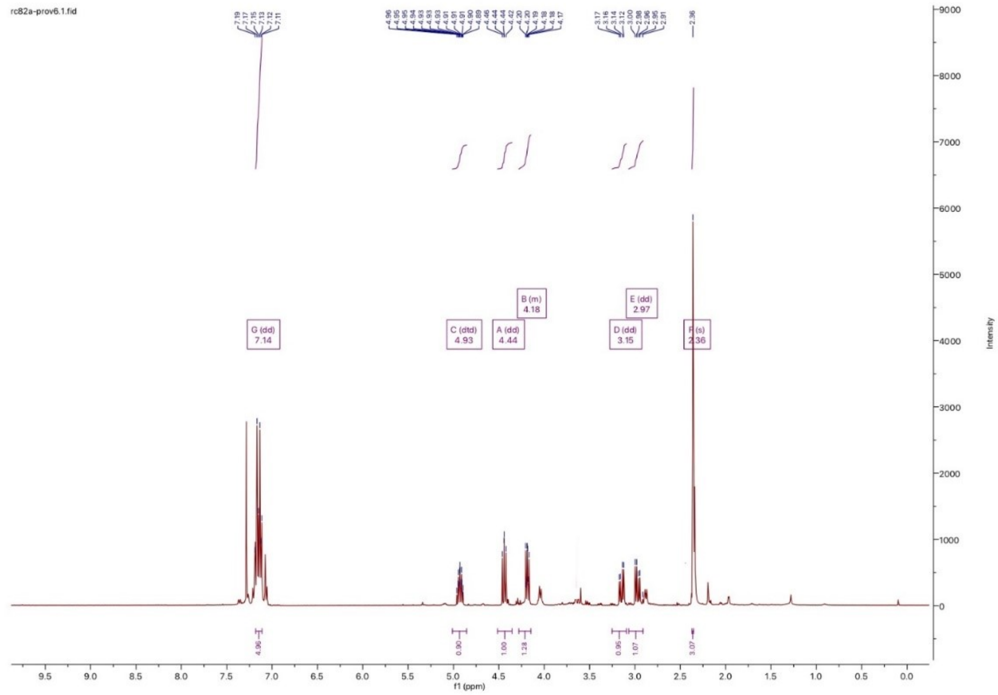

Figure S27. ^{1}H-NMR of **3e** (400 MHz, $CDCl_3$) δ = 7.24 – 7.07 (m, 5H), 4.97-4.85 (dd, 1H), 4.48 – 4.35 (dd, 1H), 4.24 – 4.12 (dd, 1H), 3.23 – 3.09 (dd, 1H), 3.00 – 2.86 (dd, 1H), 2.37-2.28 (s, 3h)

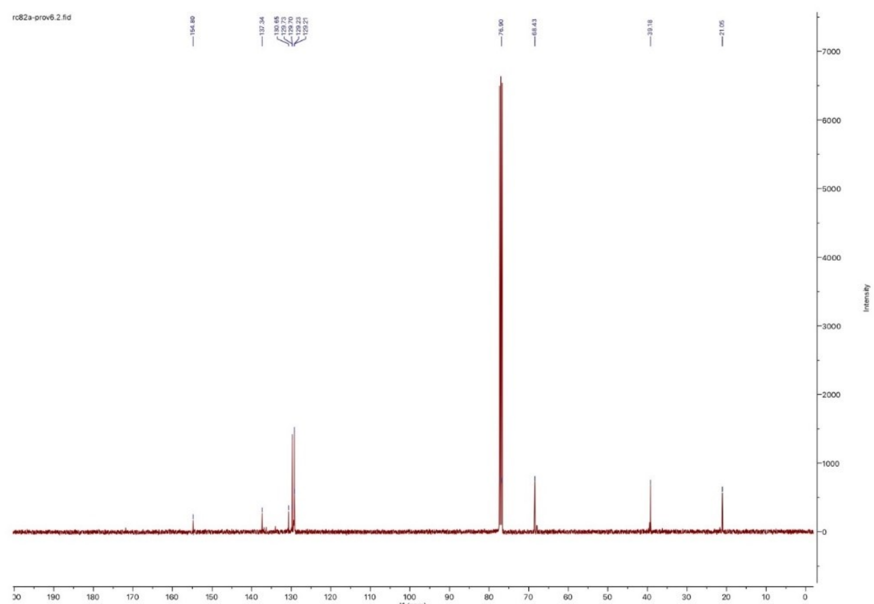

Figure S28. ^{13}C-NMR of **3e** (101 MHz, $CDCl_3$) δ 154.48, 137.34, 130.29, 129.73, 129.70, 129.23, 129.21, 76.90, 68.43, 39.18, 21.05

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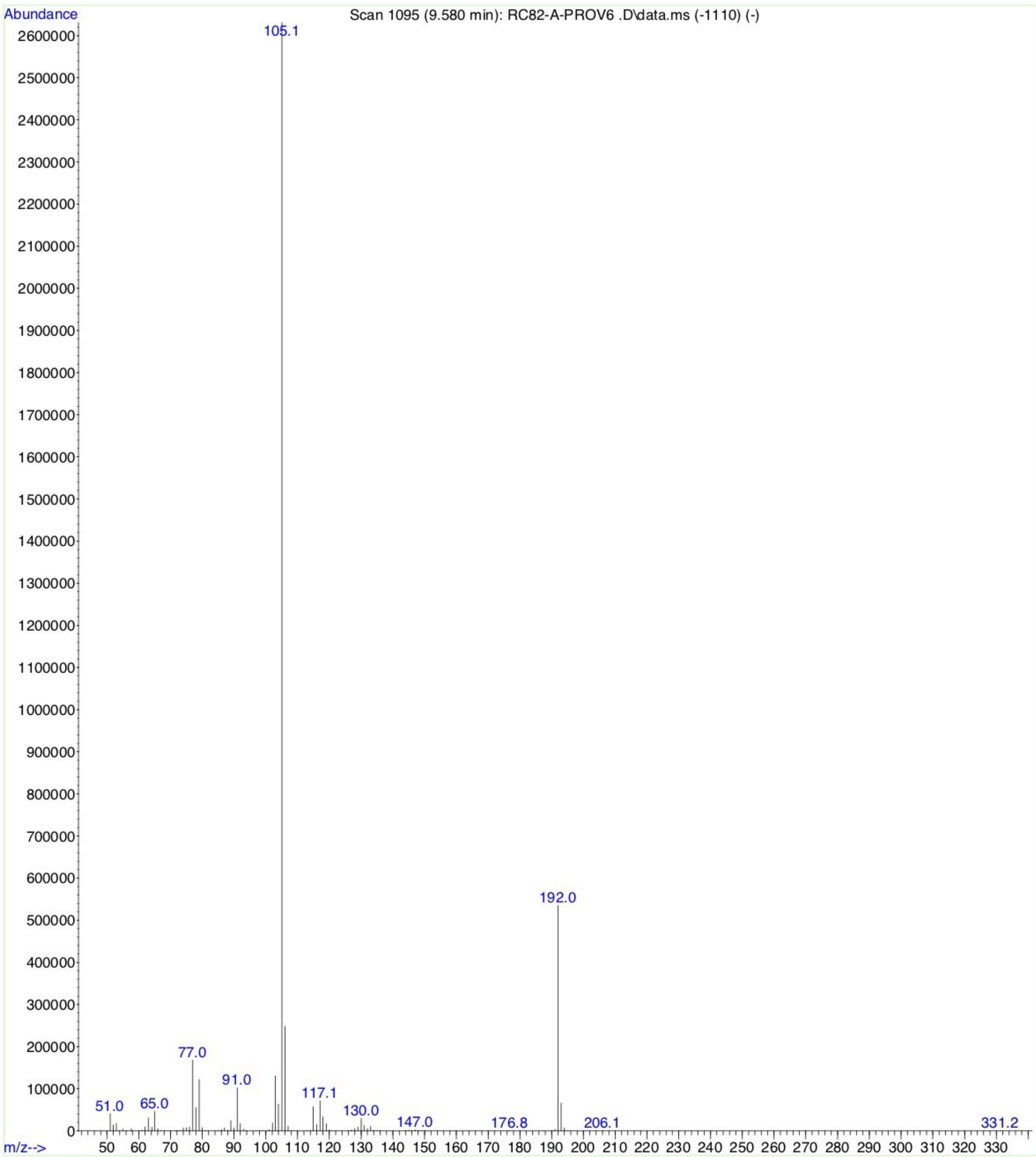

Figure S29. MS of **3e** (EI, 70 V). m/z: 192 (25), 106 (9), 105(100), 91 (4), 91, 77 (6), 65 (2), 51 (2).

Allylanisole carbonate (**3f**)

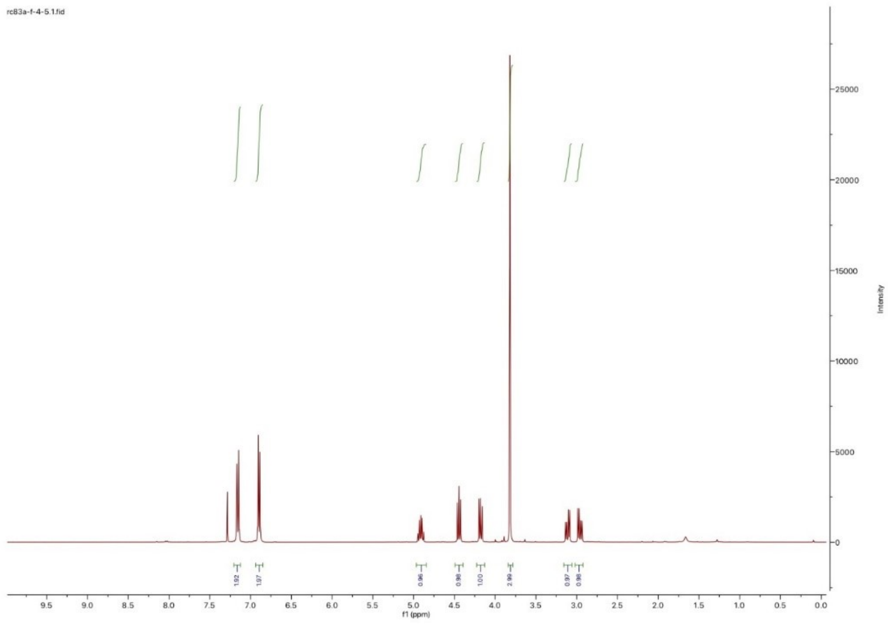

Figure S30. ^{1}H-NMR of **3f** (400 MHz, $CDCl_3$) δ = 7.21 – 7.10 (m, 2H), 6.96 – 6.79 (m, 2H), 5.00 – 4.83 (dtd, 1H), 4.50 – 4.39 (dd, 1H), 4.24 – 4.13 (dd, 1H), 3.85 – 3.79 (s, 3H), 3.18 – 3.06 (dd, 1H), 3.02 – 2.87 (dd, 1H).

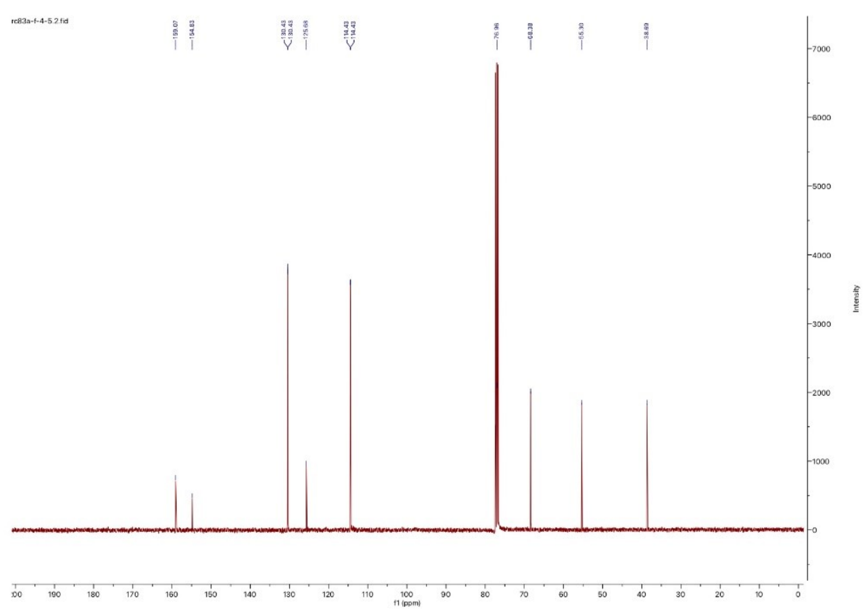

Figure S31. ^{13}C-NMR of **3f** (101 MHz, $CDCl_3$) δ 159.07, 154.83, 130.43, 130.43, 125.68, 114.43, 114.43, 76.96, 68.38, 55.30, 38.69.

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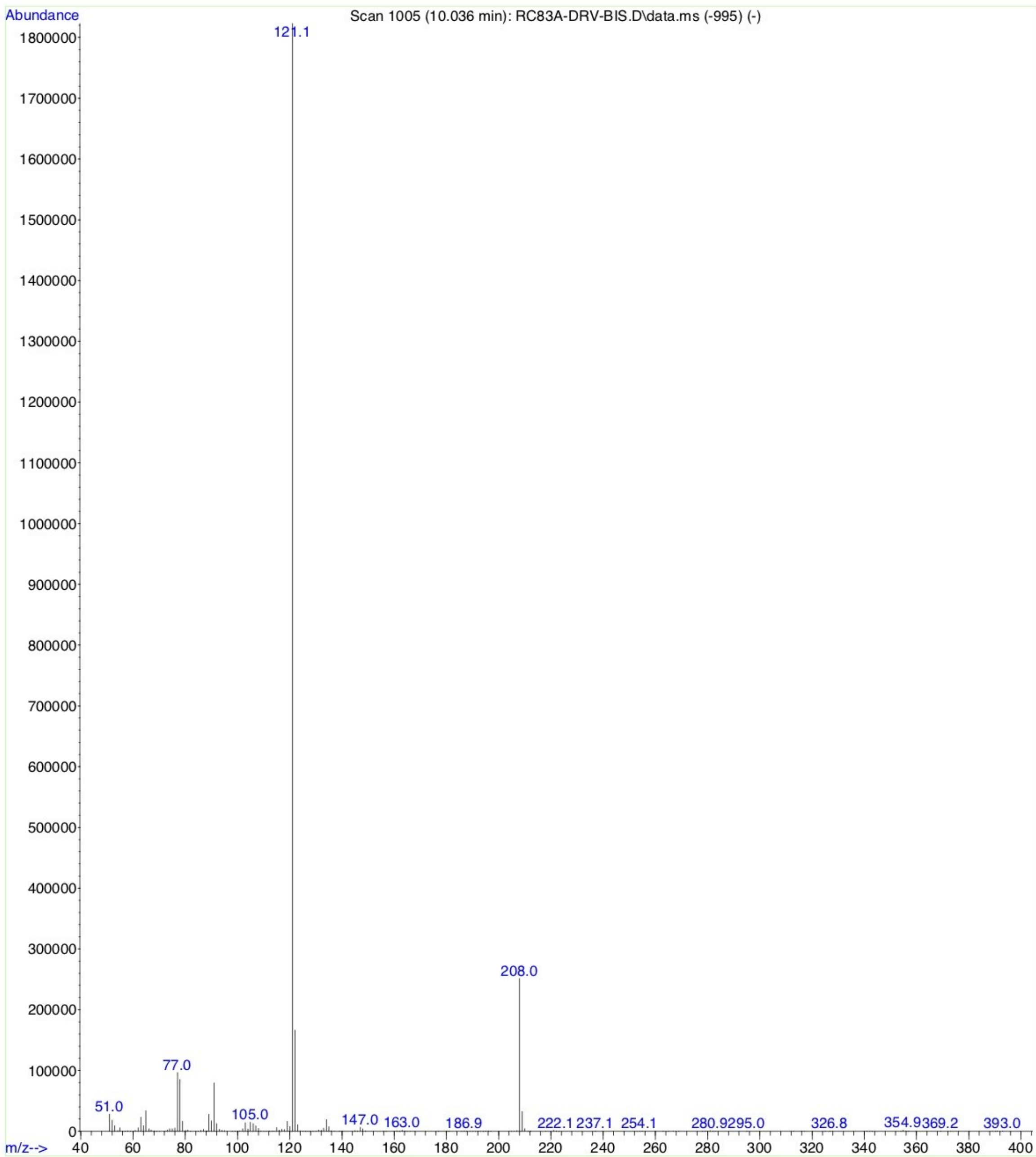

Figure S32. MS of **3f** (EI, 70 V). m/z: 208 (15), 122 (9), 121 (100), 91 (4), 91, 77 (5), 65 (2), 51 (1).

Benzy glycidil carbonate (**3g**)

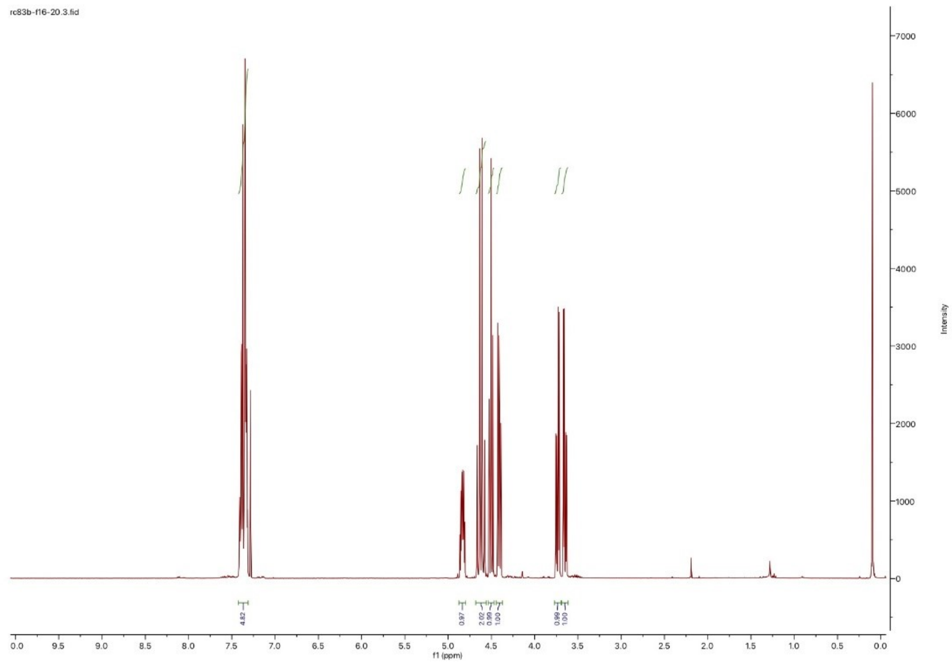

Figure S33. ^{1}H-NMR of **3g** (400 MHz, $CDCl_3$) δ = 7.46 – 7.30 (m, 5H), 4.91 – 4.77 (ddt, 1H), 4.69 – 4.55 (m, 2H), 4.55 – 4.47 (t, 1H), 4.45 – 4.37 (dd, 1H), 3.79 – 3.67 (dd, 1H), 3.69 – 3.59 (dd, 1H).

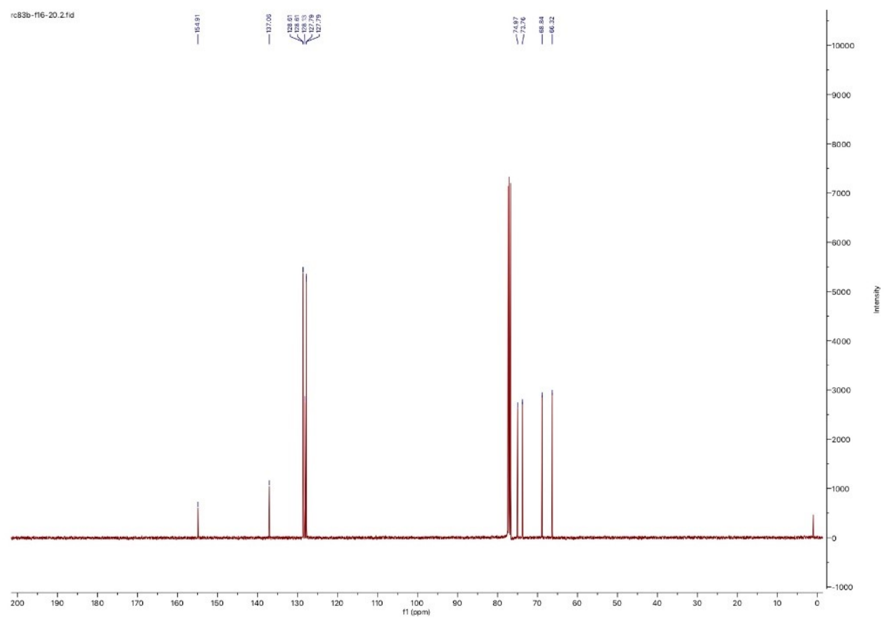

Figure S34. ^{13}C-NMR of **3g** (101 MHz, $CDCl_3$) δ 154.91, 137.06, 128.61, 128.61, 128.13, 127.79, 127.79, 74.97, 73.76, 68.84, 66.32.

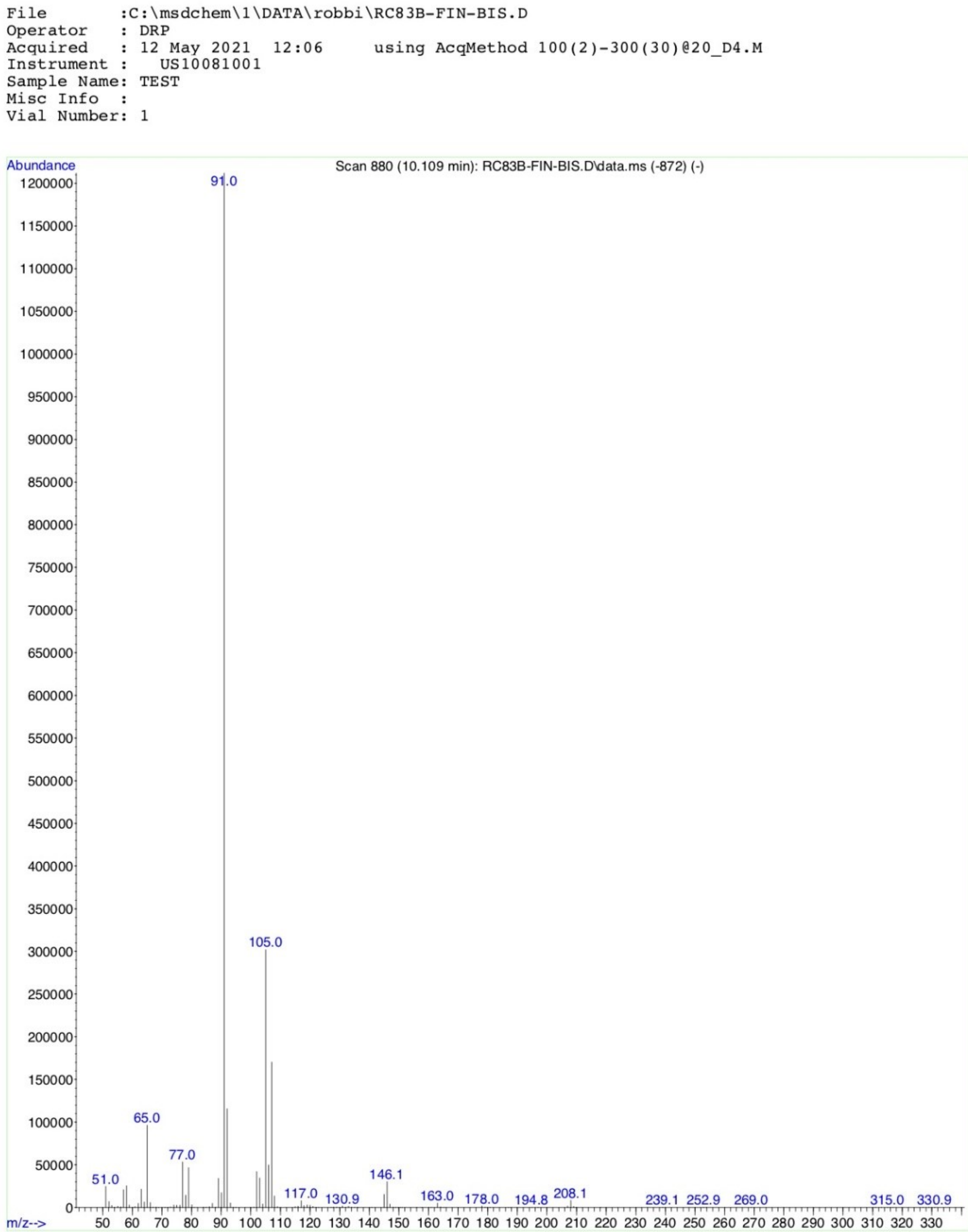

Figure S35. MS of **3g** (EI, 70 V). m/z: 208 (1), 146 (2), 107 (14), 105(25), 92(10), 91 (100), , 77 (4), 65 (8), 51 (2).

[1] L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Doremieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.M. Bregeault, Inorganic Chemistry, 1994, **33**, 871-878;