Electronic Supplementary Information

Carbonate Phosphonium Salts as Catalysts for the Transesterification of Dialkyl Carbonates with Diols. The Competition between Cyclic Carbonates and Linear Dicarbonate Products

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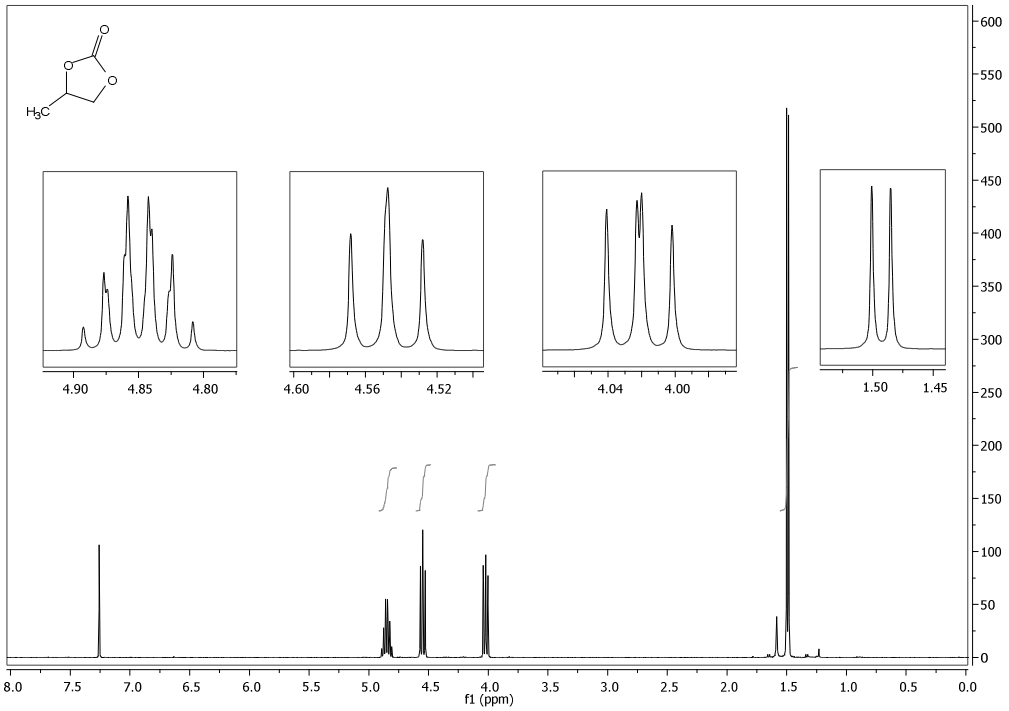

Figure S1. ^{1}H NMR spectrum of **2a**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.90-4.80 (m, 1H); 4.55 (dd, J_1 = 8.3, J_2 = 7.8 Hz, 1H); 4.02 (dd, , J_1 = 8.4,J_2 7.2 Hz, 1H); 1.49 (d, J = 6.2 Hz, 3H).

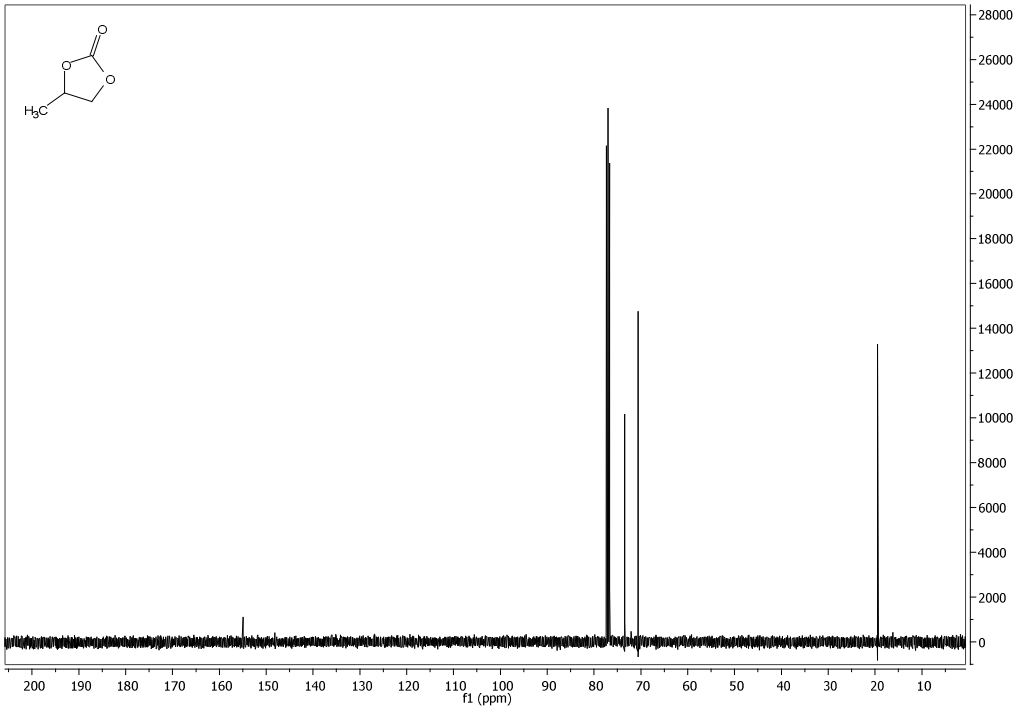

Figure S2. ^{13}C NMR spectrum of **2a**.

^{13}C NMR ($CDCl_3$, 400 MHz) δ (ppm): 154.9, 73.4, 70.7, 19.5.

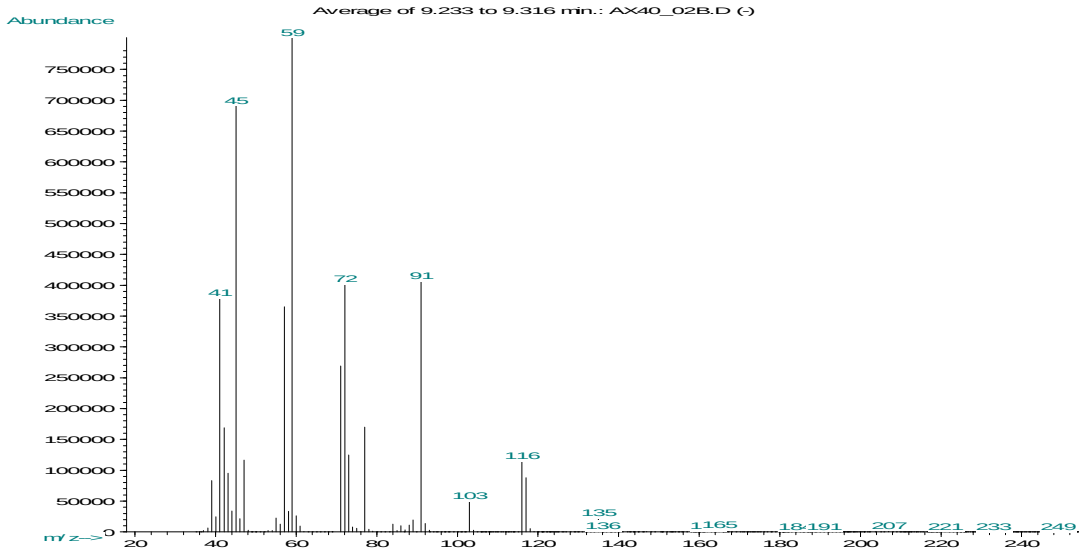

Figure S3. MS spectrum of **2a**.

MS (70 eV) m/z: 102 (M^+, 8%), 87 (30), 58 (16), 57 (100).

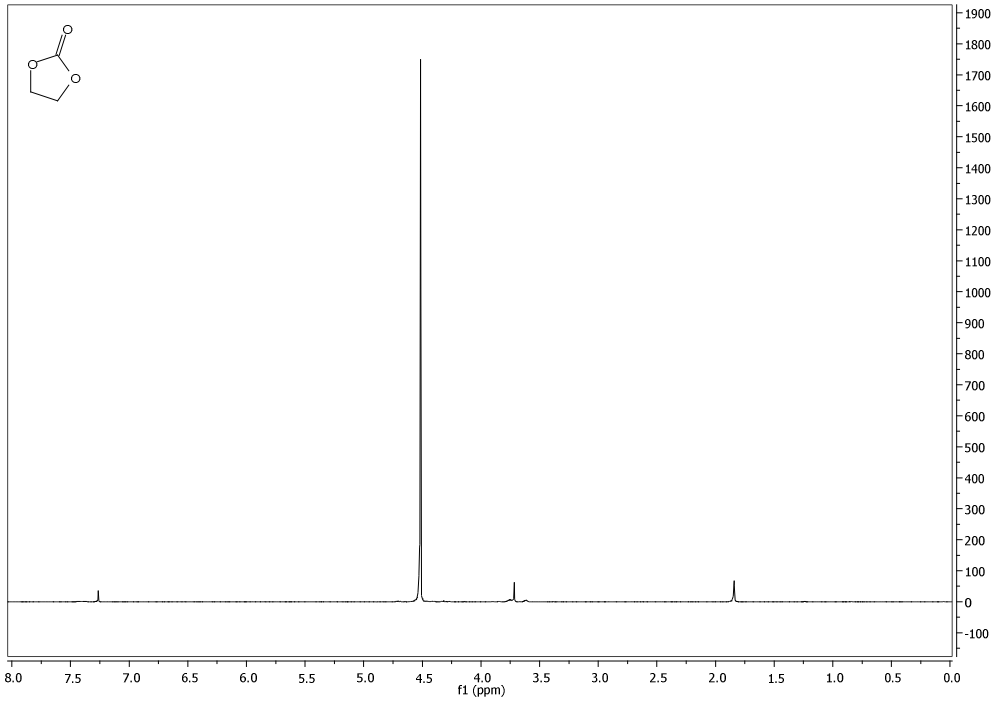

Figure S4. ^{1}H NMR spectrum of **3a**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.5 (s, 4H).

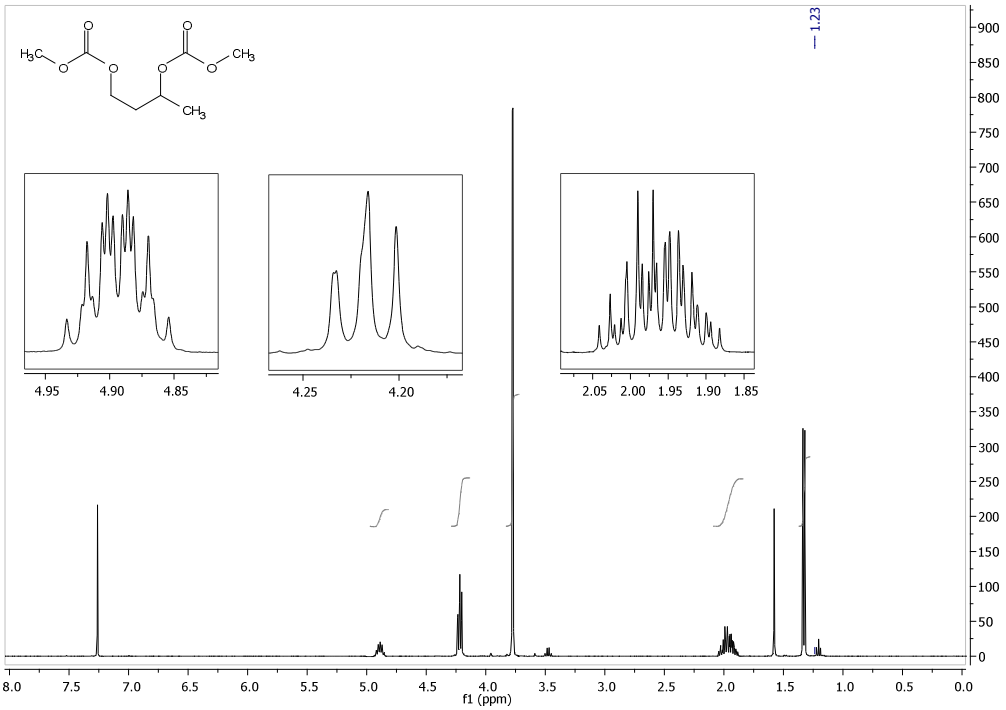

Figure S5. ^{1}H NMR spectrum of **4c**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.94-4.84 (m, 1H), 4.21 (t, *J* = 6.3 Hz, 2H), 3.78 (s+s, 6H), 2.05-1.87 (m, 2H), 1.32 (d, *J* = 6.3 Hz, 3H).

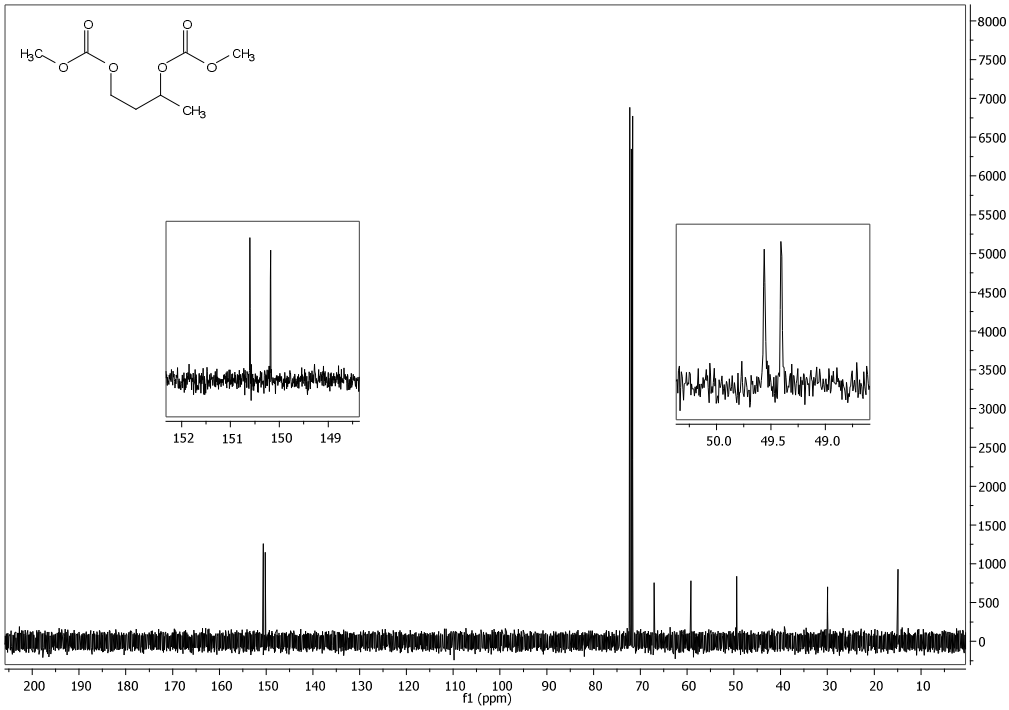

Figure S6. ^{13}C NMR spectrum of **4c**.

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 150.6, 150.1, 67.0, 59.2, 49.6, 49.4, 30.0, 14.9.

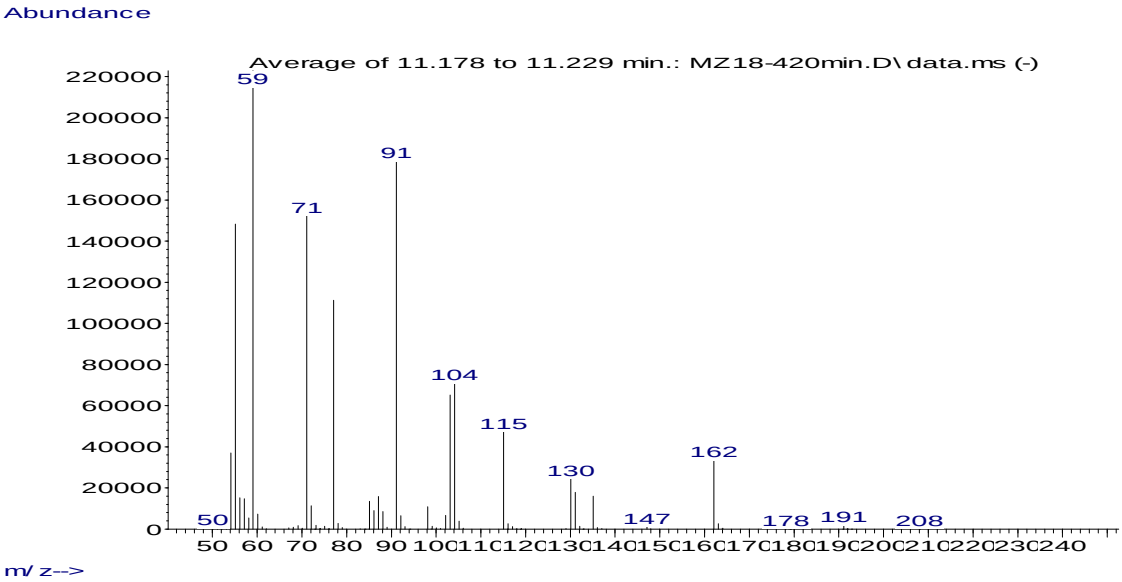

Figure S7. MS spectrum of **4c**.

MS (70 eV) m/z: 206 (M^+ <1%), 162 (15), 135 (7), 131 (8), 130 (11), 115 (21), 104 (32), 103 (29), 98 (5), 91 (80), 87 (7), 85 (6), 77 (50), 72 (5), 71 (68), 59 (100), 57 (7), 56 (7), 55 (66), 54 (17).

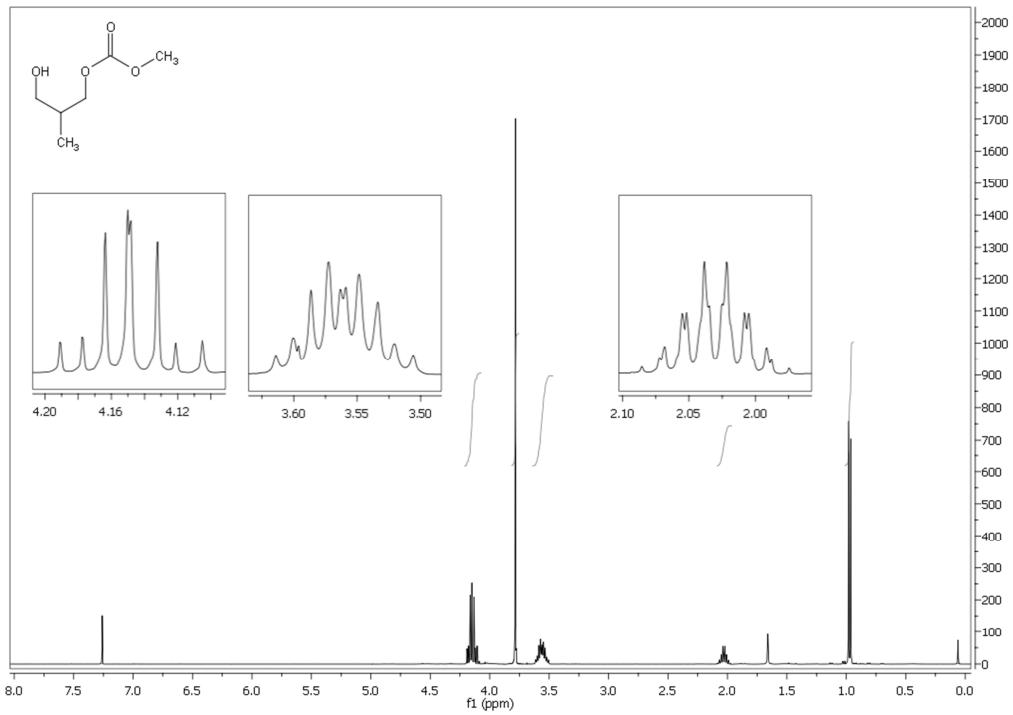

Figure S8. ^{1}H NMR spectrum of **5b**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.22-4.06 (m, 2H), 3.78 (s, 3H), 3.63-3.48 (m, 2H), 2.10-1.97 (m, 1H), 0.97 (d, *J* = 7.0 Hz, 1H).

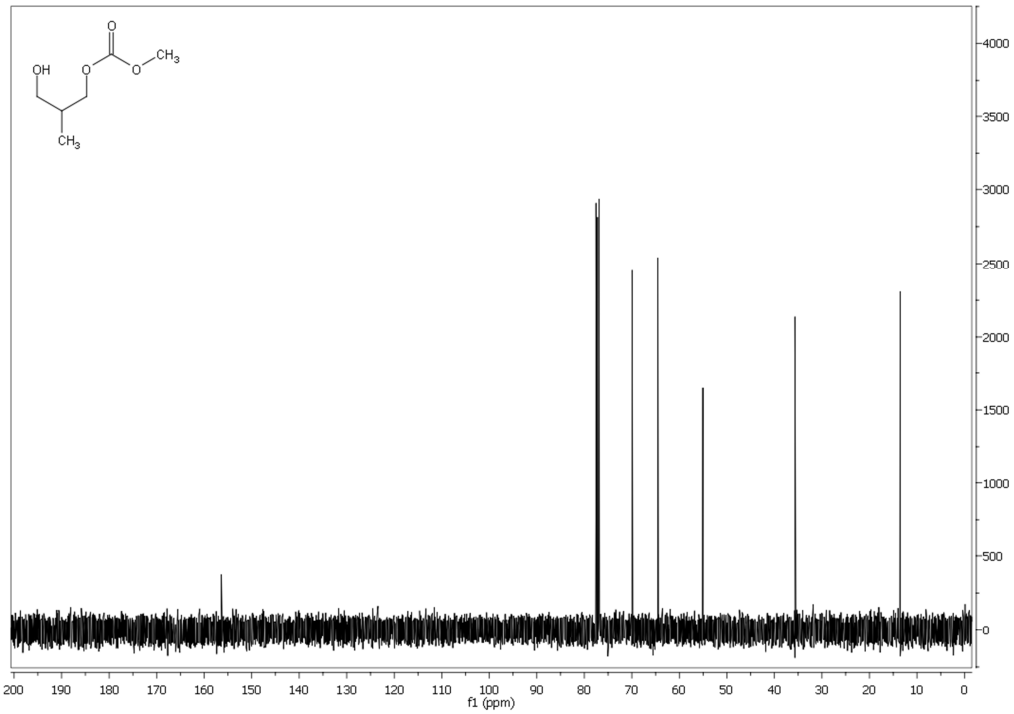

Figure S9. ^{13}C NMR spectrum of **5b**.

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 156.1, 69.8, 64.1, 54.7, 35.4, 13.3.

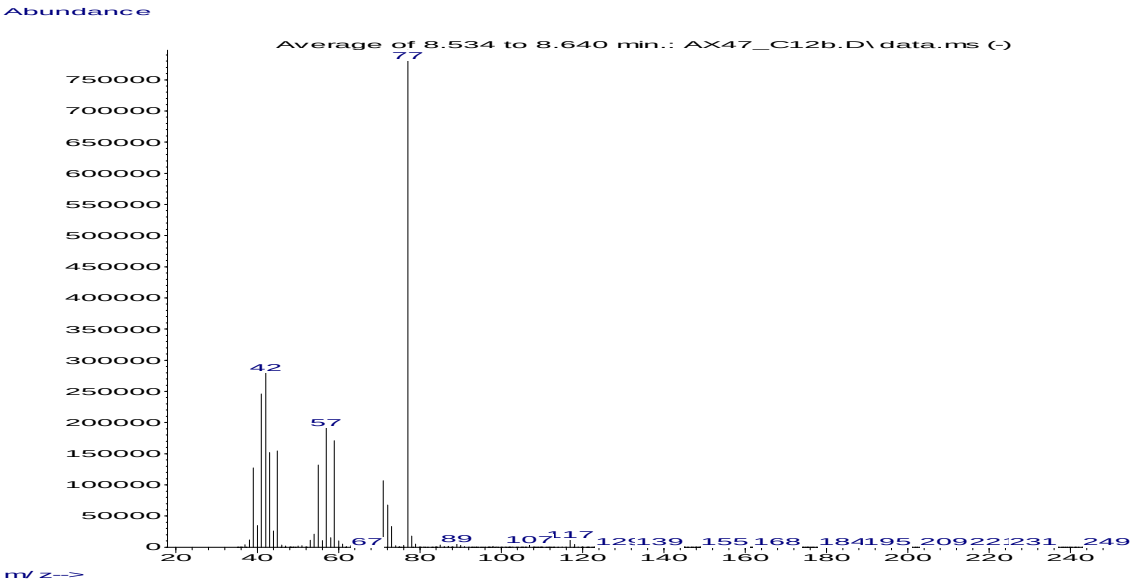

Figure S10. MS spectrum of **5b**.

MS (70 eV) m/z: 148 (M+ <1%) 77 (100%), 73 (4), 72 (8), 71 (13), 59 (21), 57 (24), 55 (17), 45 (19), 43 (19), 42 (35), 41 (31), 40 (4), 39 (16).

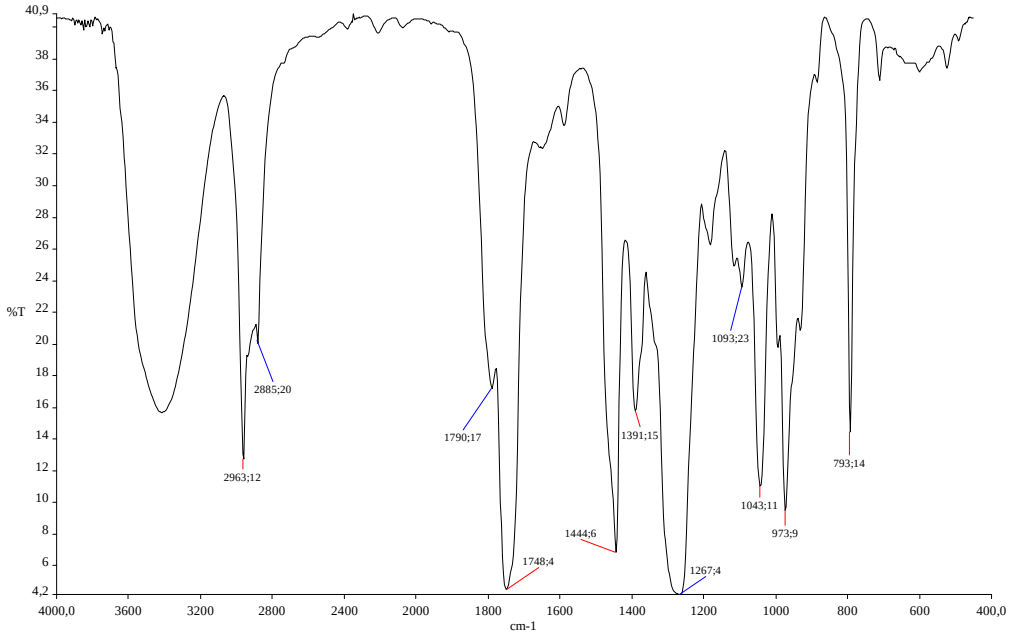

Figure S11. IR spectrum of **5b**.

IR (neat) ν = 2963, 2885, 1790, 1748, 1445, 1391, 1267, 1093, 1043, 974, 793 cm^{-1}.

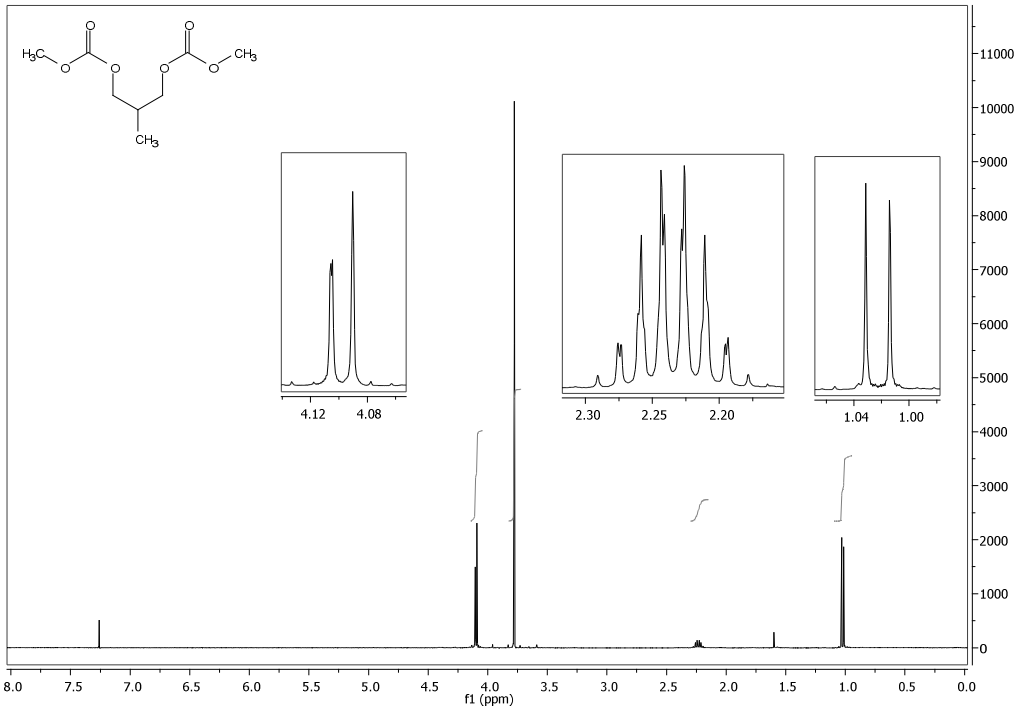

Figure S12. ^{1}H NMR spectrum of **5c**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.11-4.08 (m, 4H), 3.78 (s, 6H), 2.31-2.16 (m, 1H), 1.02 (d, *J* = 7.0 Hz, 3H).

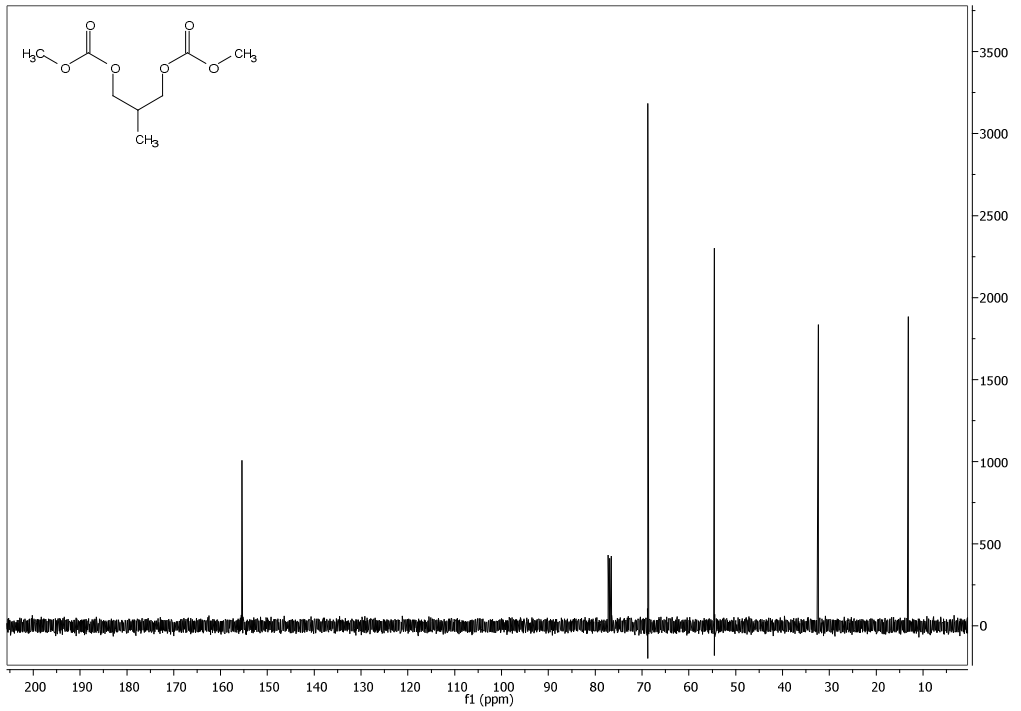

Figure S13. ^{13}C NMR spectrum of **5c**.

^{13}C NMR (CDCl3, 100 MHz) δ (ppm): 155.5, 68.8, 54.5, 32.4, 13.2.

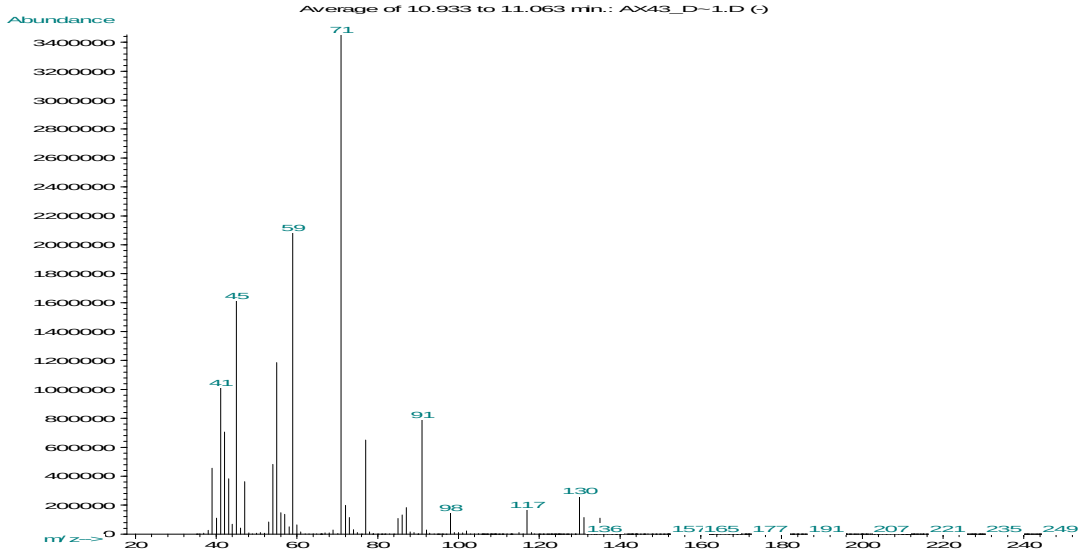

Figure S14. MS spectrum of **5c**.

MS (70 eV) m/z: 206 (M^+ <1%), 135 (3), 130 (8), 117 (5), 102 (1), 98 (4), 91 (23), 87 (5), 86 (4), 85 (3), 77 (19), 73 (3), 72 (6), 71 (100), 59 (60), 57 (4), 56 (4), 55 (35), 54 (14), 47 (11), 45 (47), 43 (11), 42 (20), 41 (29), 39 (13).

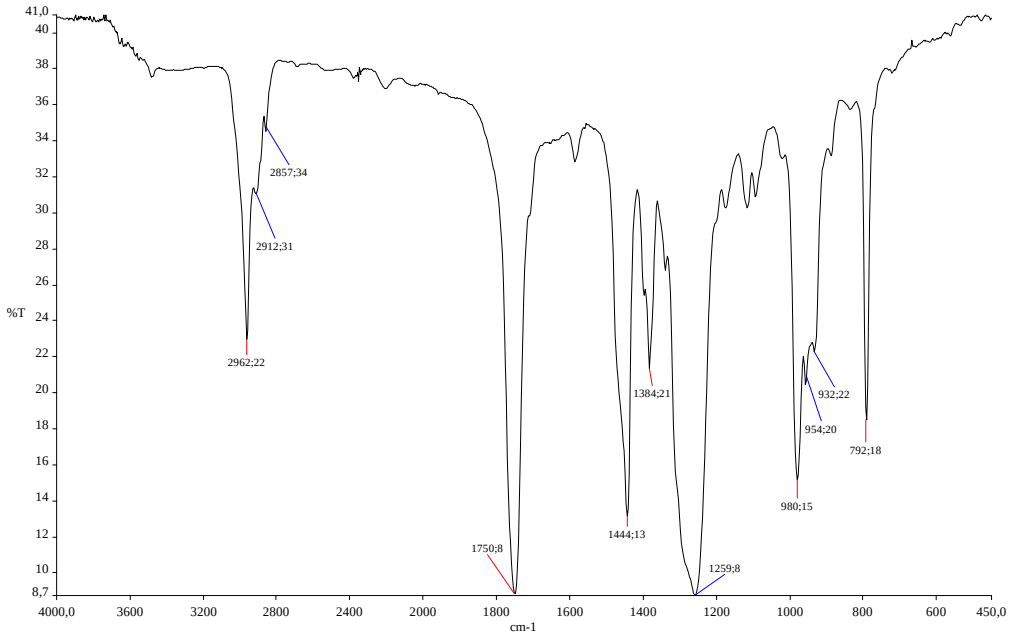

Figure S15. IR spectrum of **5c**.

IR (neat) ν = 2962, 2912, 2857, 1751, 1444, 1384, 1260, 980, 954, 932, 792 cm^{-1}.

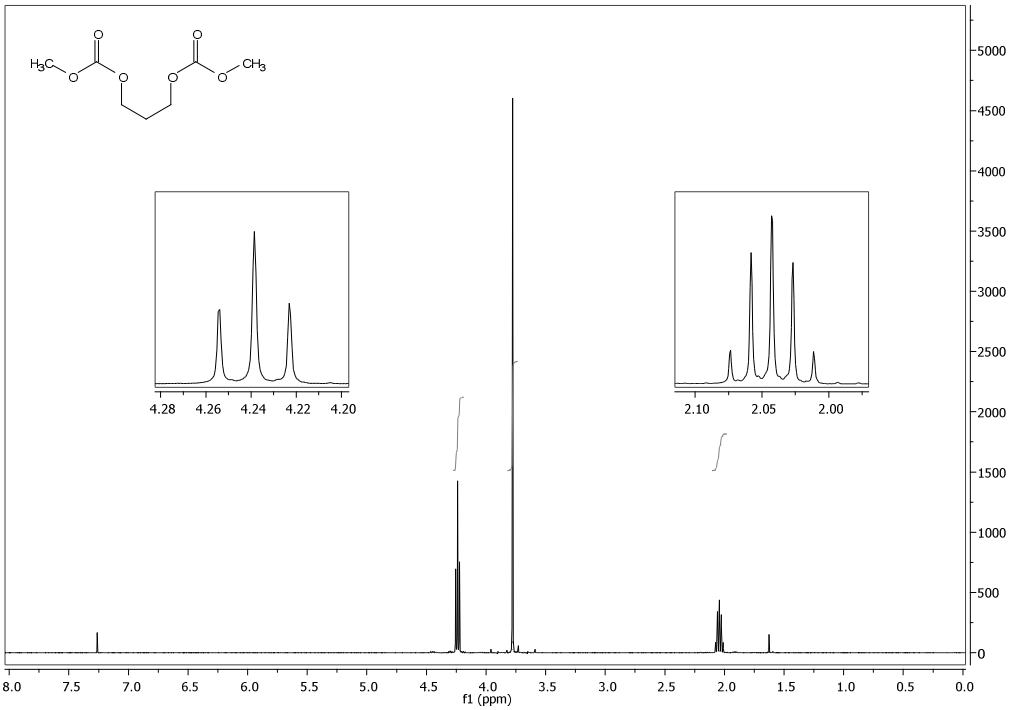

Figure S16. ^{1}H NMR spectrum of **6c**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.24 (t, *J* = 6.2 Hz, 4H), 3.78 (s, 6H), 2.04 (p, *J* = 6.2 Hz, 2H).

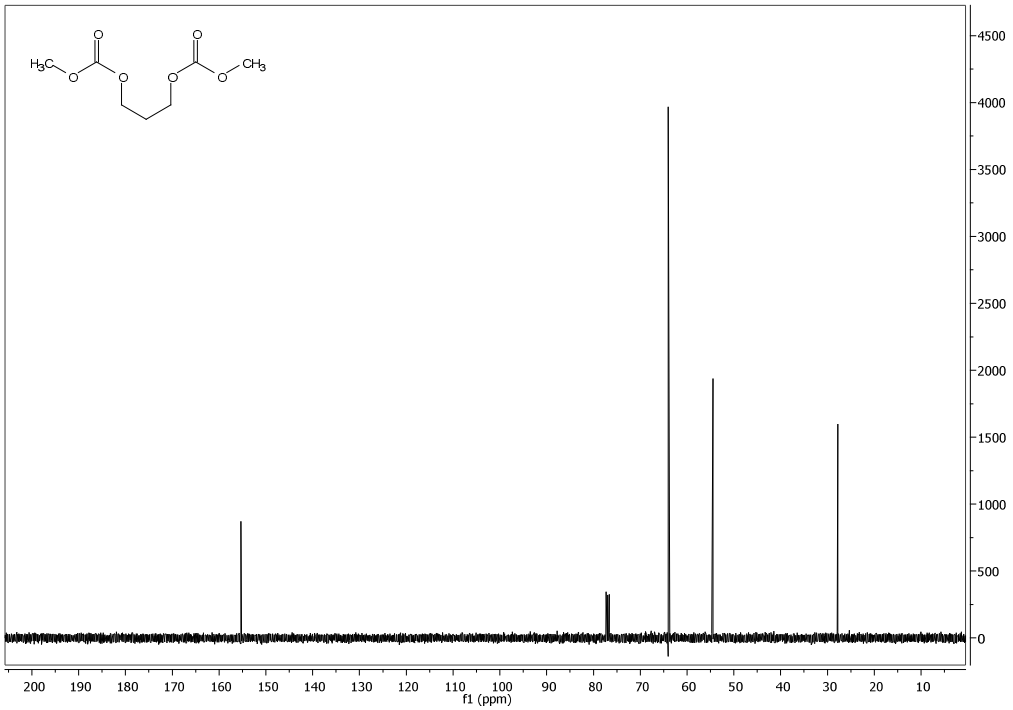

Figure S17. ^{13}C NMR spectrum of **6c**.

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.4, 64.0, 54.5, 27.8.

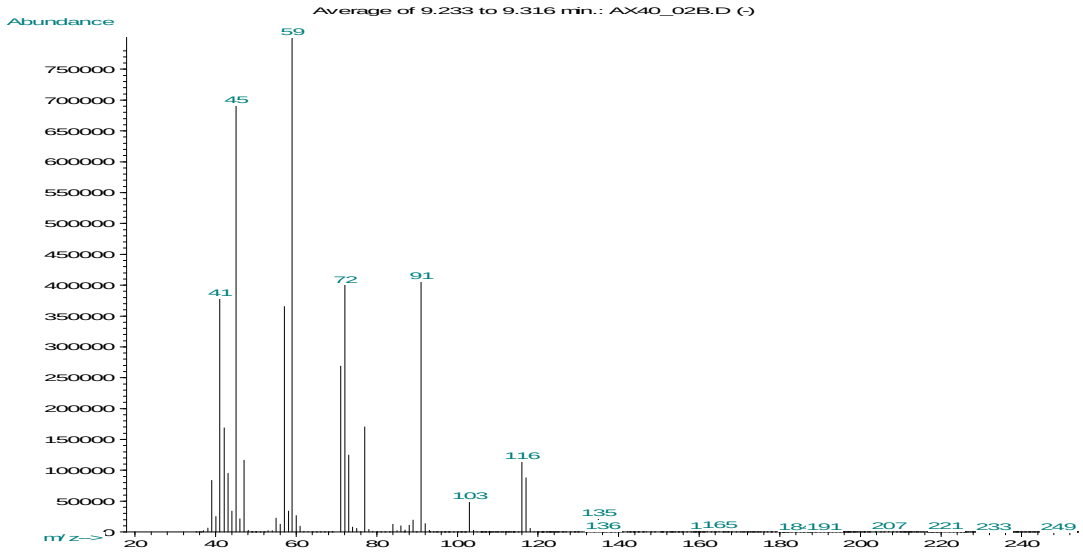

Figure S18. MS spectrum of **6c**.

MS (70 eV) m/z: 192 (M^+ <1%) 135 (3), 117 (11), 116 (14), 103 (6), 91 (51), 77 (21), 73 (16), 72 (50), 71 (34), 59 (100), 58 (4), 57 (46),55 (3), 47 (15), 45 (86), 44 (4), 43 (12), 42 (21), 41 (47), 39 (10).

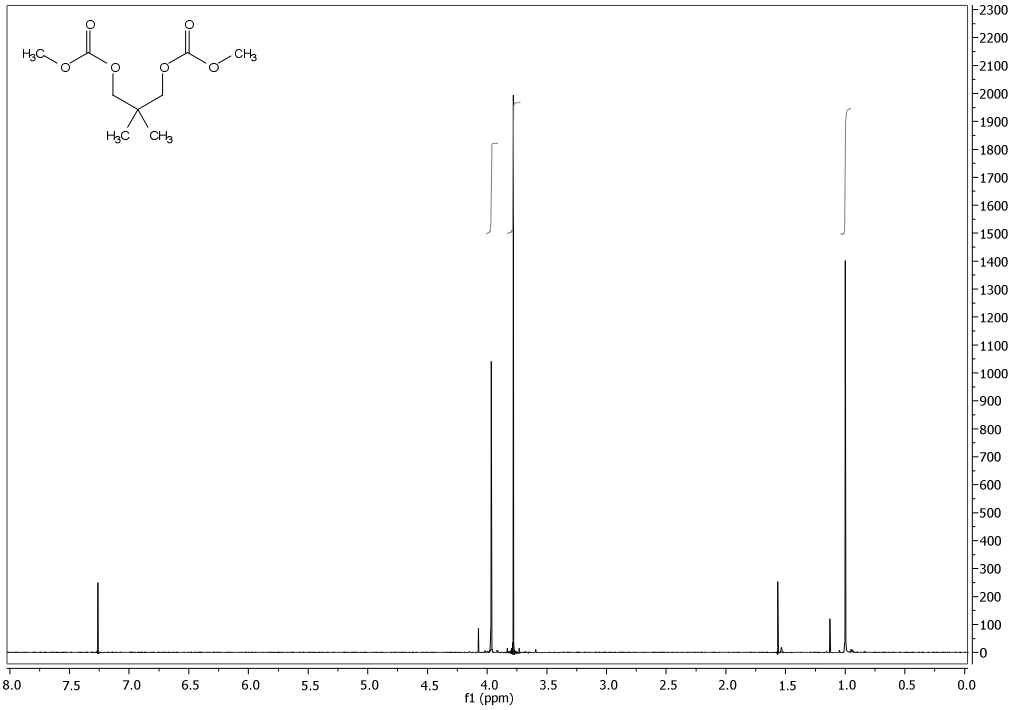

Figure S19. ^{1}H NMR spectrum of **7c**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 3.97 (s, 4H), 3.78 (s, 6H), 1.00 (s, 6H).

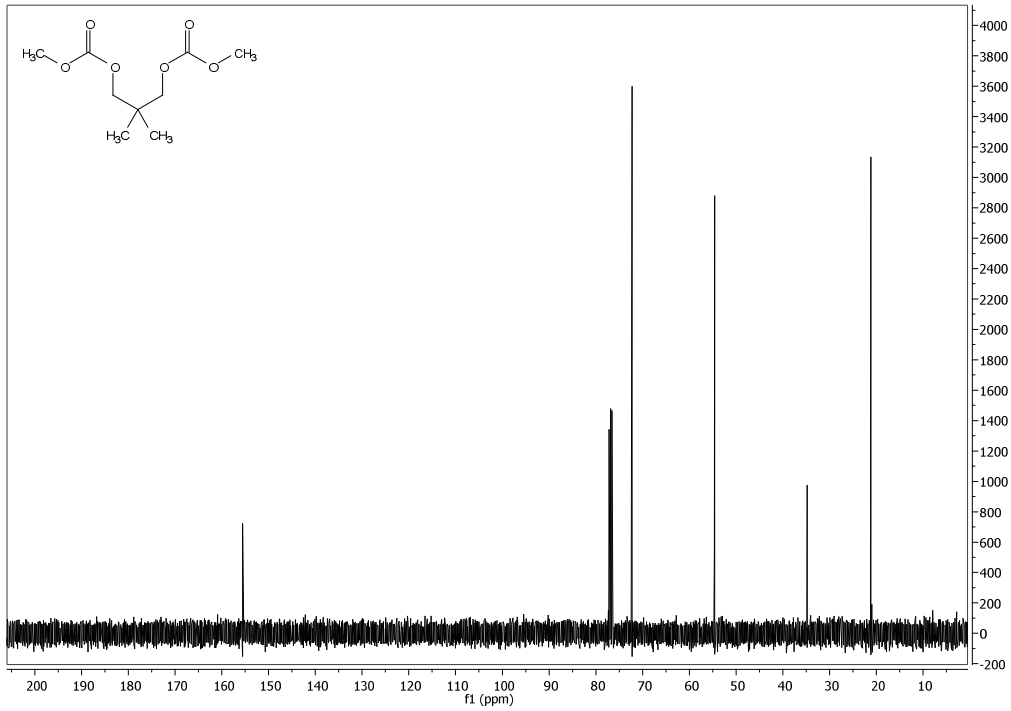

Figure S20. ^{13}C NMR spectrum of **7c**.

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.5, 72.3, 54.6, 34.8, 21.2.

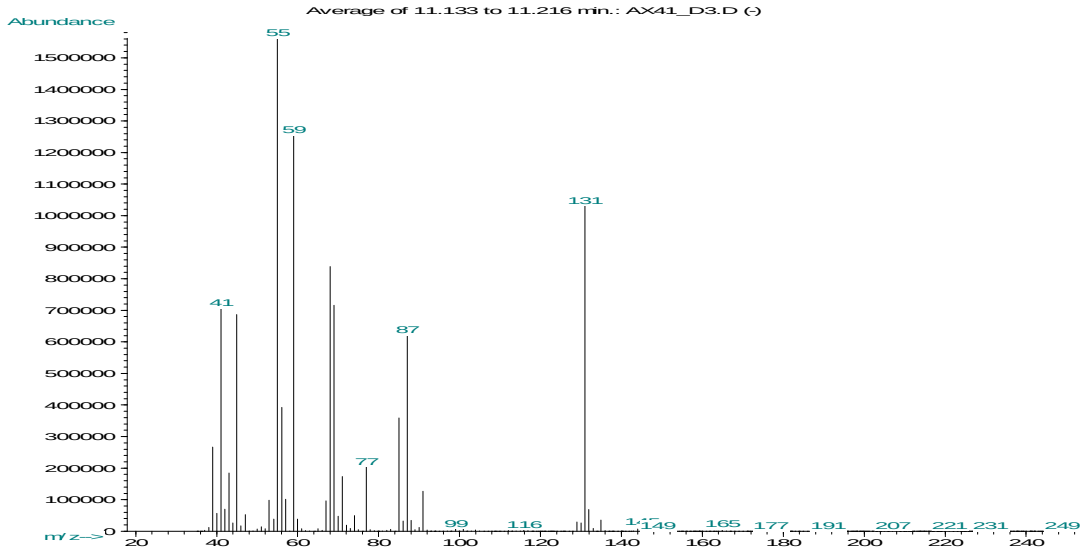

Figure S21. MS spectrum of **7c**.

MS (70 eV) m/z: 220 (M^+ <1%), 135 (3), 132 (6), 131 (84), 91 (9), 87 (44), 85 (25), 77 (14), 74 (4), 71 (11), 69 (51), 68 (64), 67 (6), 59 (68), 57 (6), 56 (22), 55 (100), 53 (5), 45 (38), 43 (10), 41 (35), 39 (12).

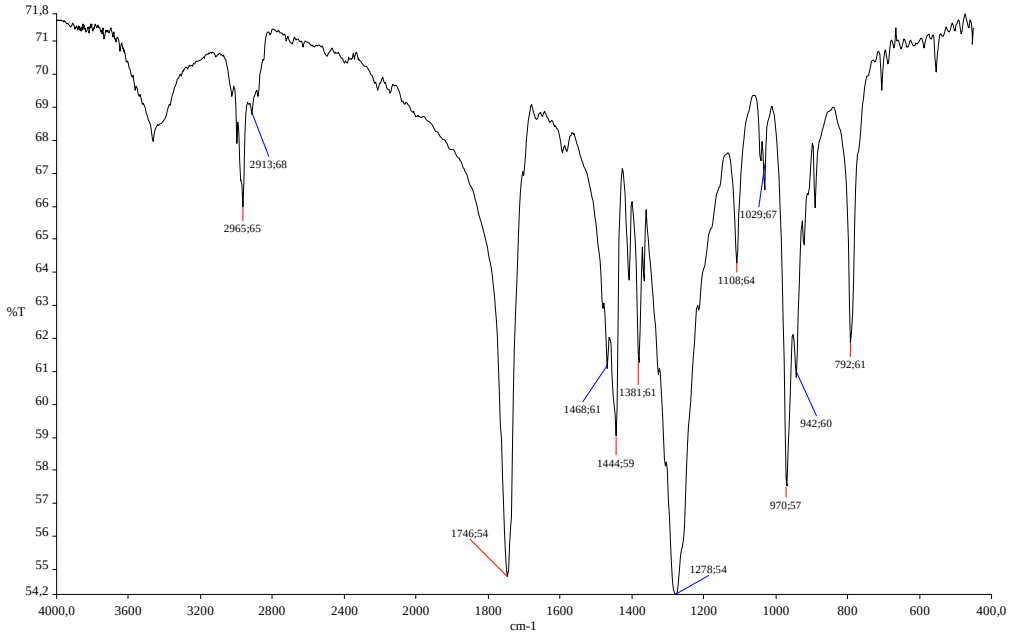

Figure S22. IR spectrum of **7c**.

IR (neat) ν = 2966, 2914, 1746, 1469, 1445, 1382, 1278, 1109, 1030, 971, 943, 793 cm^{-1}.

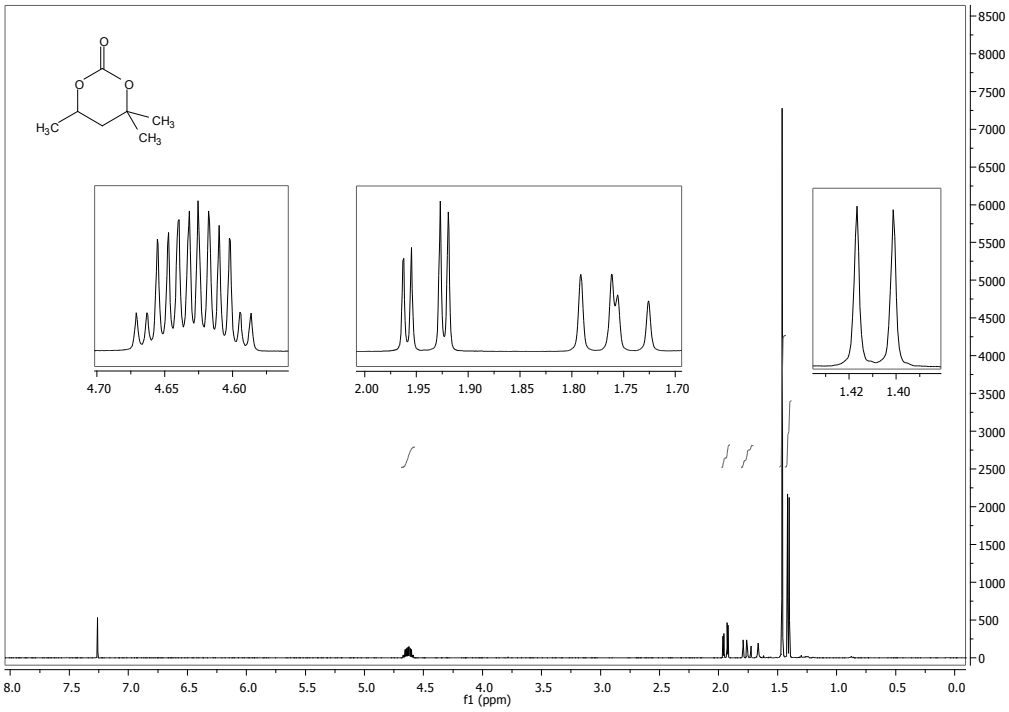

Figure S23. ^{1}H NMR spectrum of **8a**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.63 (dqd, J_1 = 12.4, J_2 = 6.2, J_3 = 3.2 Hz, 1H), 1.85 (ddd, J_1 = 26.1, J_2 = 14.2, J_3 = 7.6 Hz, 2H); 1.46 (s, 6H); 1.41 (d, J = 6.2 Hz, 3H).

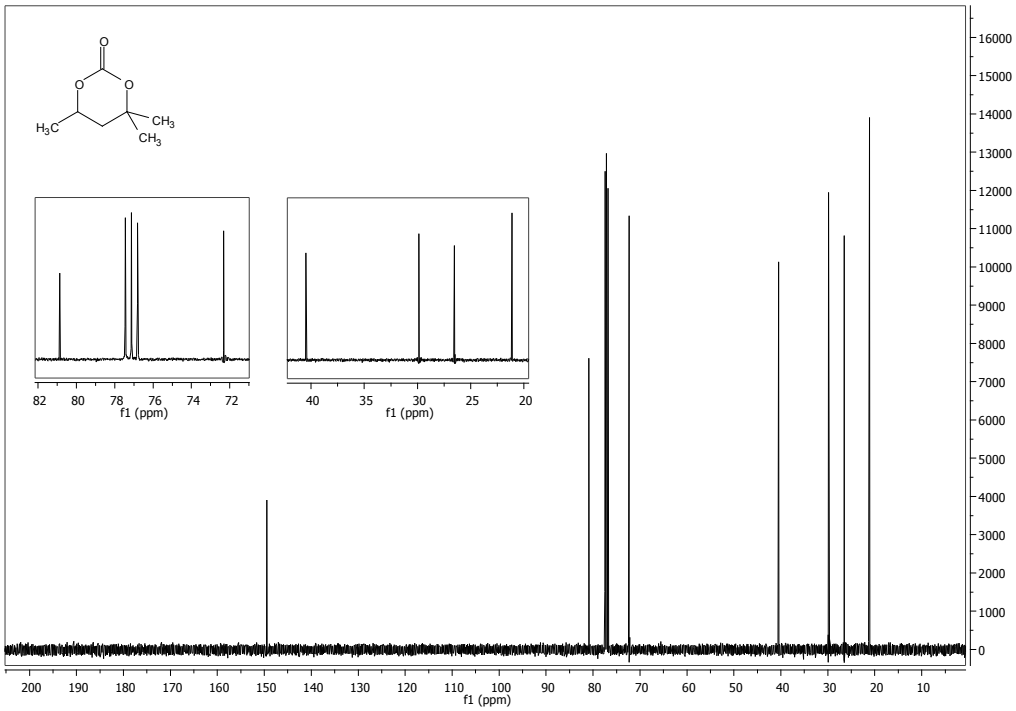

Figure S24. ^{13}C NMR spectrum of **8a**.

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 149.5, 80.9, 72.3, 40.5, 29.9, 26.5, 21.1.

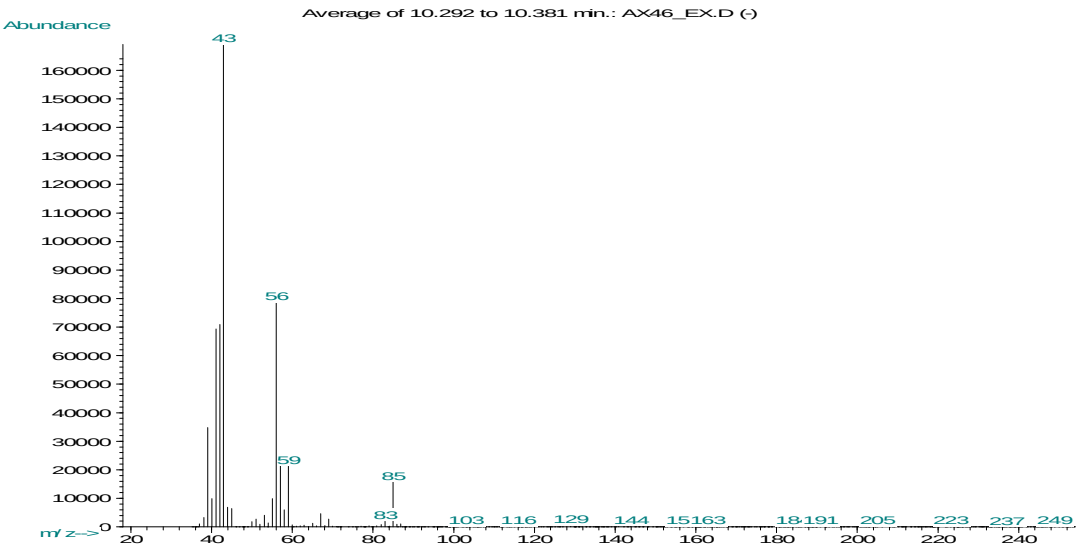

Figure S25. MS spectrum of **8a**.

MS (70 eV) m/z: 144 (M^+ <1%), 87 (2), 86 (2), 85 (37), 83 (4), 69 (3), 67 (6), 59 (35), 58 (9), 57 (28), 56 (100), 55 (12), 53 (4).

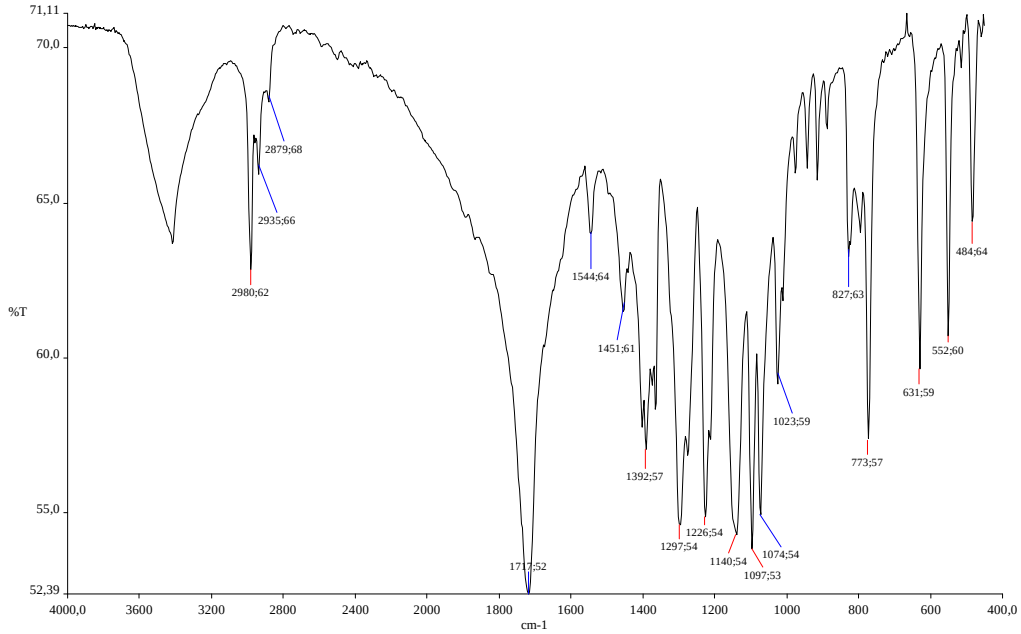

Figure 26. IR spectrum of **8a**.

IR (KBr) ν = 2966, 2914, 1746, 1469, 1445, 1382, 1278, 1109, 1030, 971, 943, 793 cm^{-1}.

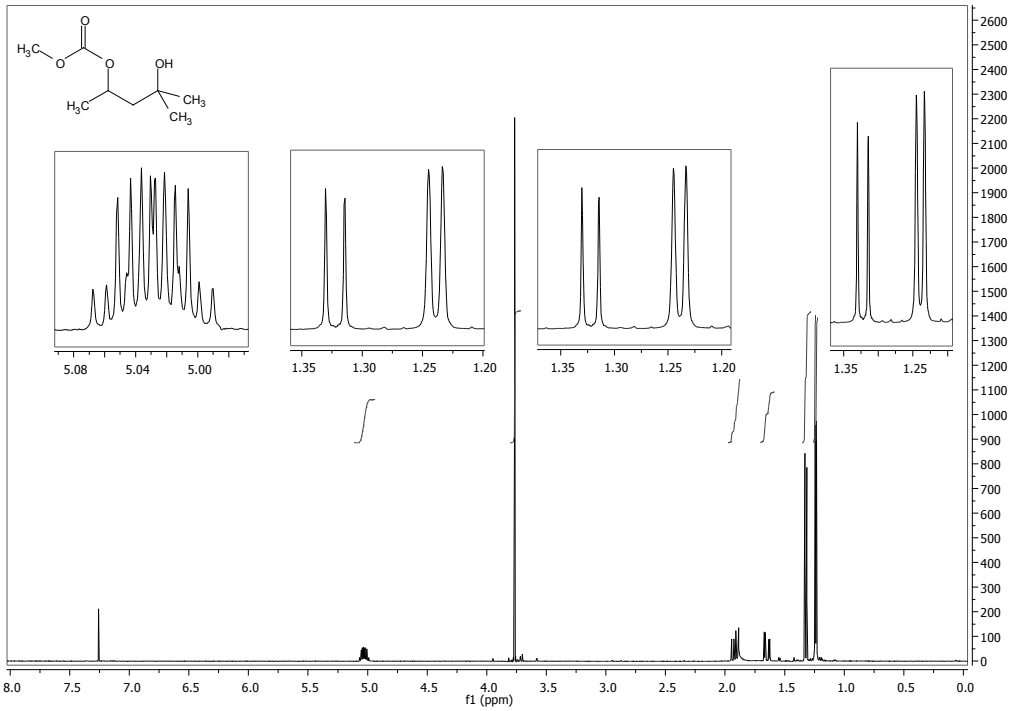

Figure S27. ^{1}H NMR spectrum of **8b**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.07-4.98 (m, 1H), 3.77 (s, 3H), 1.92 (dd, *J* = 15.0, 8.6 Hz, 1H), 1.65 (dd, *J* = 15.0, 3.4 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.25 (s, 3H), 1.24 (s, 3H).

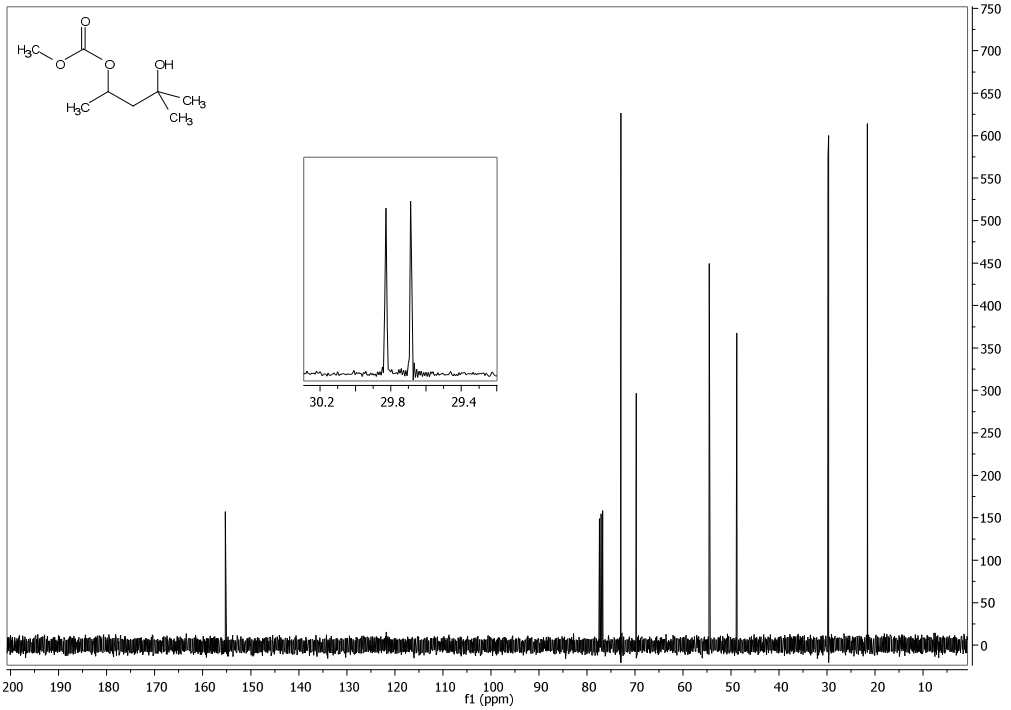

Figure S28. ^{13}C NMR spectrum of **8b**.

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.28, 72.96, 69.76, 54.53, 48.77, 29.83, 29.69, 21.59.

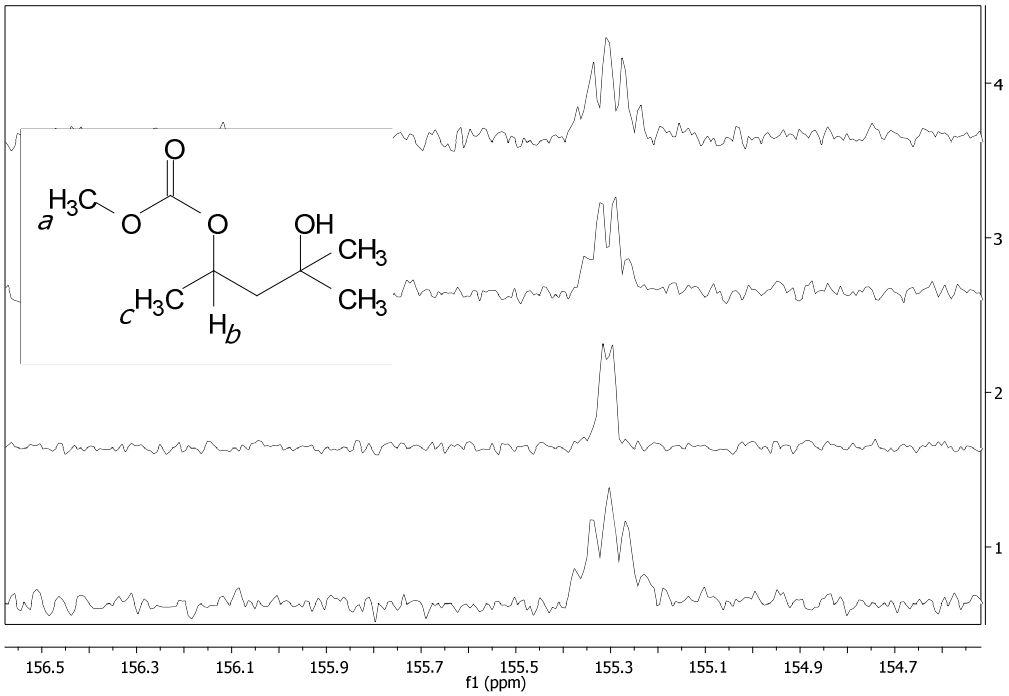

Figure S29. Stacked ^{13}C NMR spectra of **8b** with varies ^{1}H decoupling schemes for comparision. With no 1H decoupling (Spectrum 1), the spectrum showed a quintet for C=O. With continuous wave decoupling at the frequency of Ha (Spectrum 2) the same signal appeared as a doublet, because of the coupling with proton Hb. When decoupling was set at the frequency of Hb (Spectrum 3), the carbonyl carbon appeared as a quartet. Finally decoupling at the frequency of Hc had no effect.

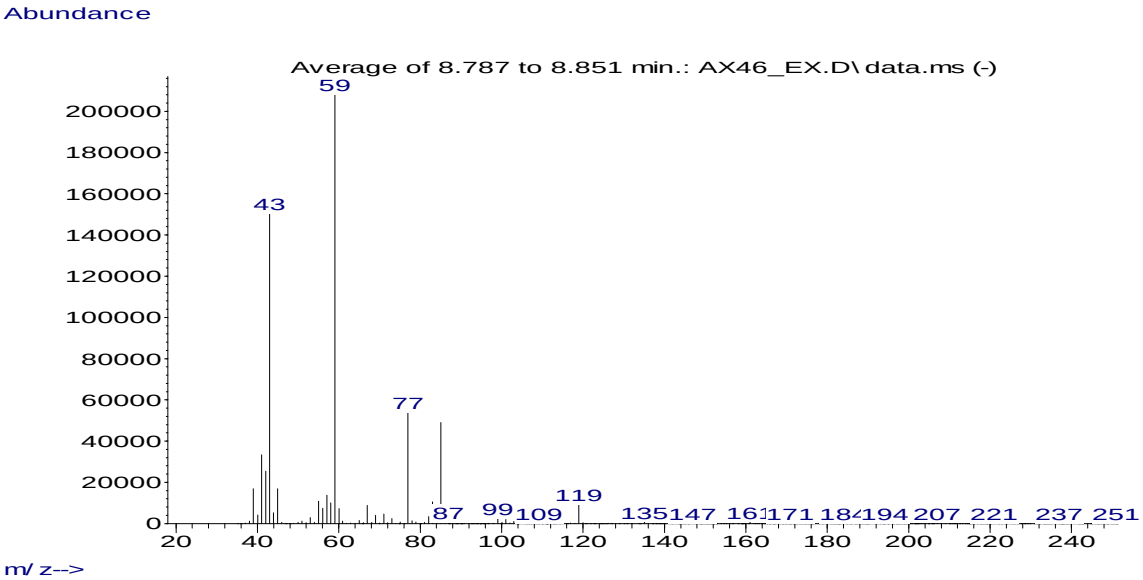

Figure S30. MS spectrum of **8b**.

MS (70 eV) m/z: 176 (M^+ <1%), 119 (4), 85 (23), 83 (5), 77 (25), 67 (4), 59 (100), 58 (5), 57 (6), 55 (5), 45 (8), 43 (69), 42 (12), 41 (15).

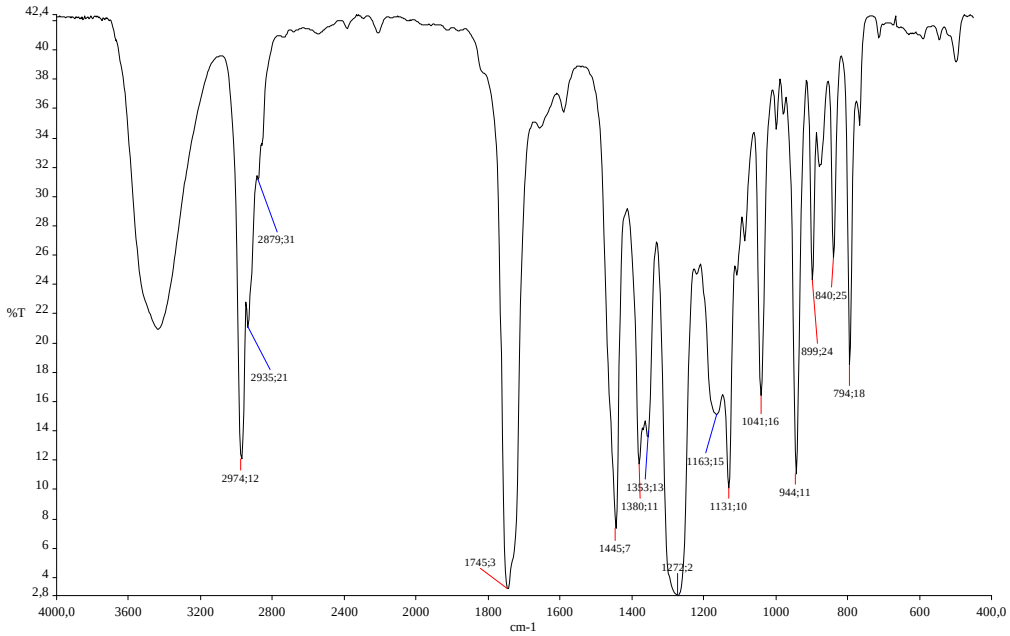

Figure S31. IR spectrum of **8b**.

IR (neat) ν = 2974, 2935, 1745, 1446, 1380, 1353, 1272, 1163, 1131, 1041, 944, 899, 840, 794 cm^{-1}.

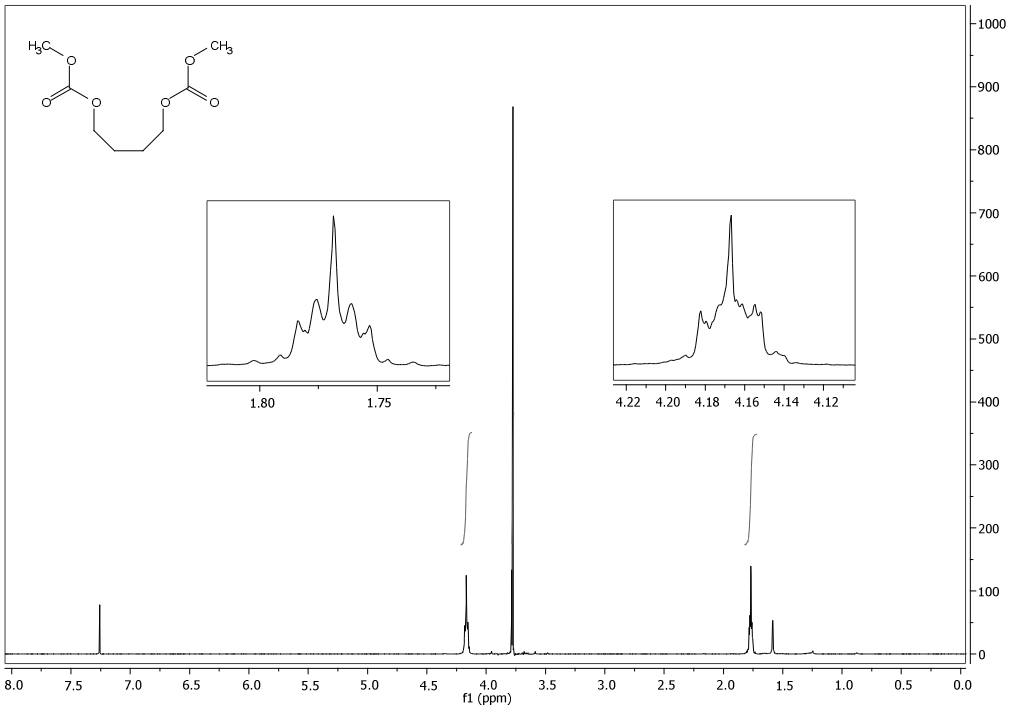

Figure S32. ^{1}H NMR spectrum of **9c**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.20-4.13 (m, 4H), 3.77 (s, 6H), 1.79-1.74 (m, 4H).

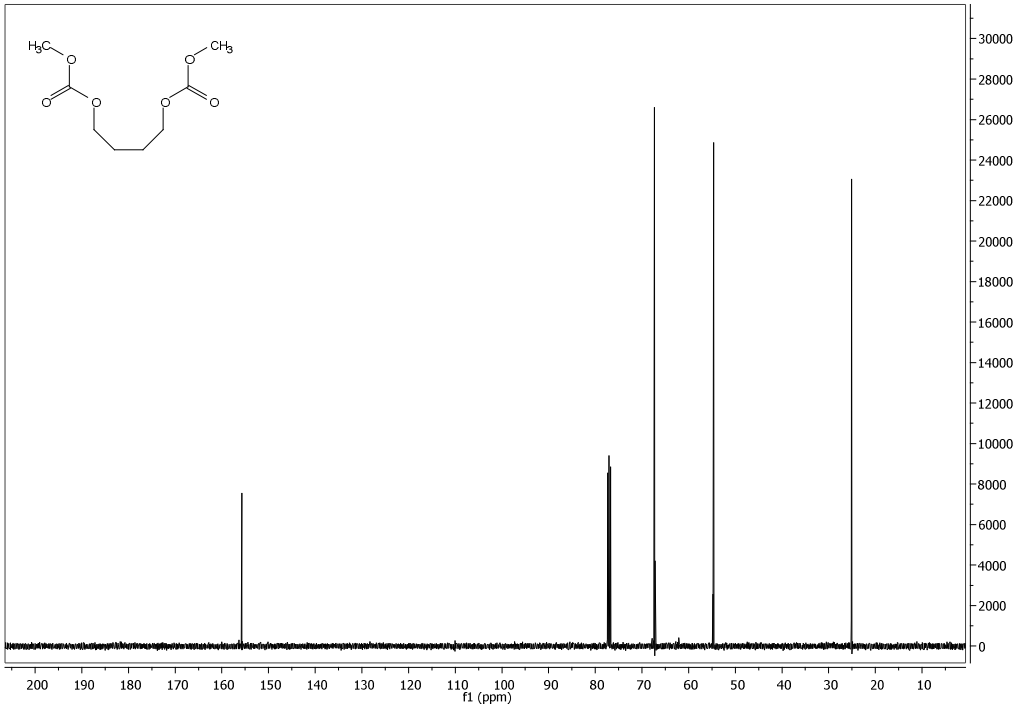

Figure S33. ^{13}C NMR spectrum of **9c**.

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.7, 67.3, 54.7, 25.1.

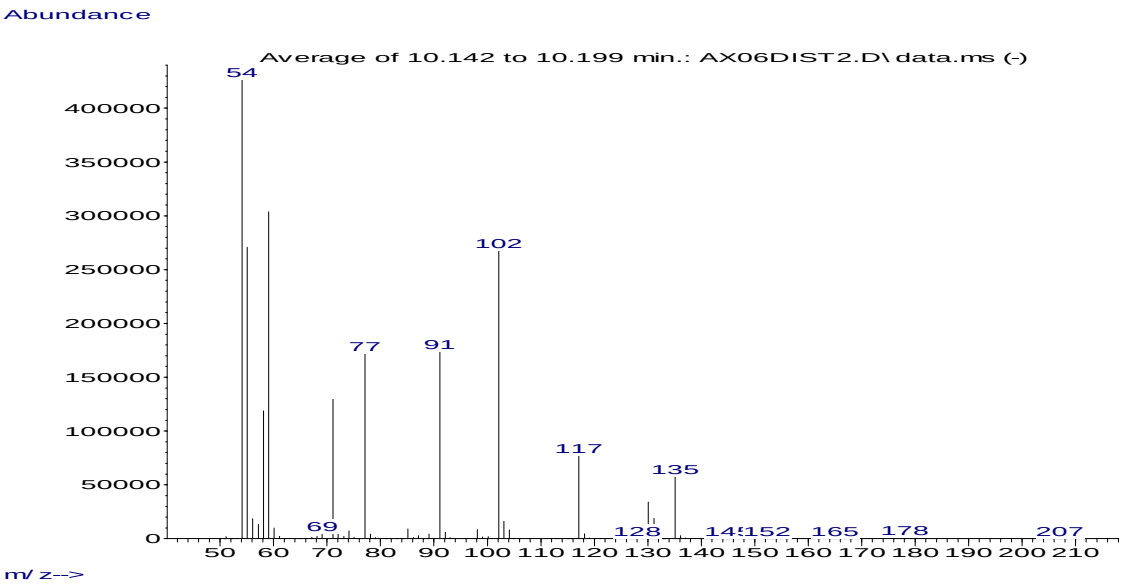

Figure S34. MS spectrum of **9c**.

MS (70 eV) m/z: 206 (M^+ <1%)135 (14), 131 (5), 130 (8), 117 (19), 103 (4), 102 (66), 91 (42), 77 (41), 71 (31), 59 (73), 58 (28), 57 (4), 59 (73), 58 (28), 57 (4), 56 (4), 55 (63), 54 (100).

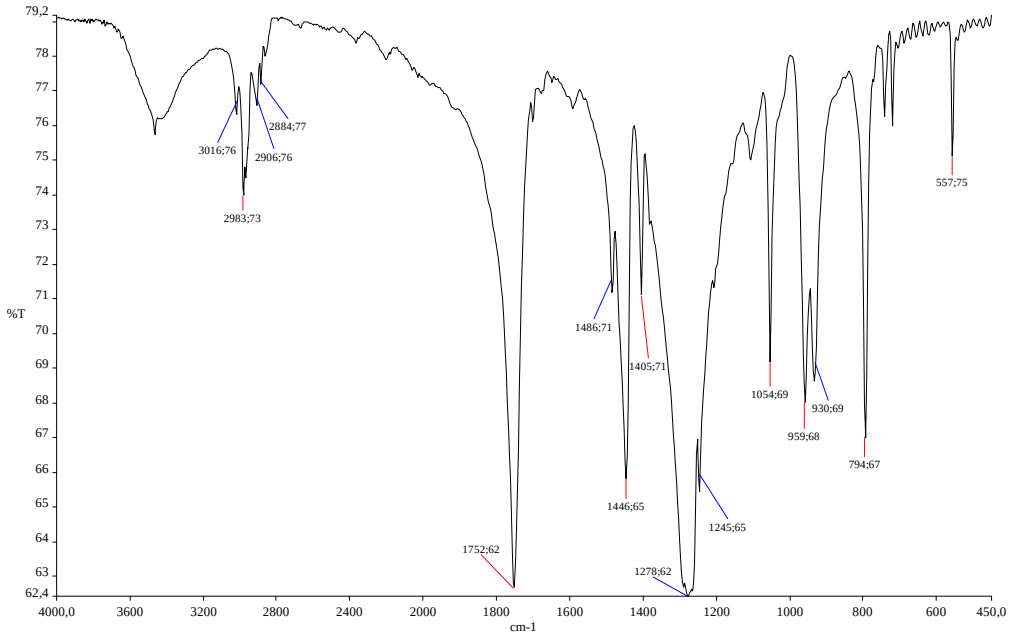

Figure S35. IR spectrum of **9c**.

IR (KBr) ν = 3017, 2984, 2907, 2885, 1753, 1487, 1447, 1406, 1279, 1246, 1055, 960, 931, 795, 558 cm^{-1}.

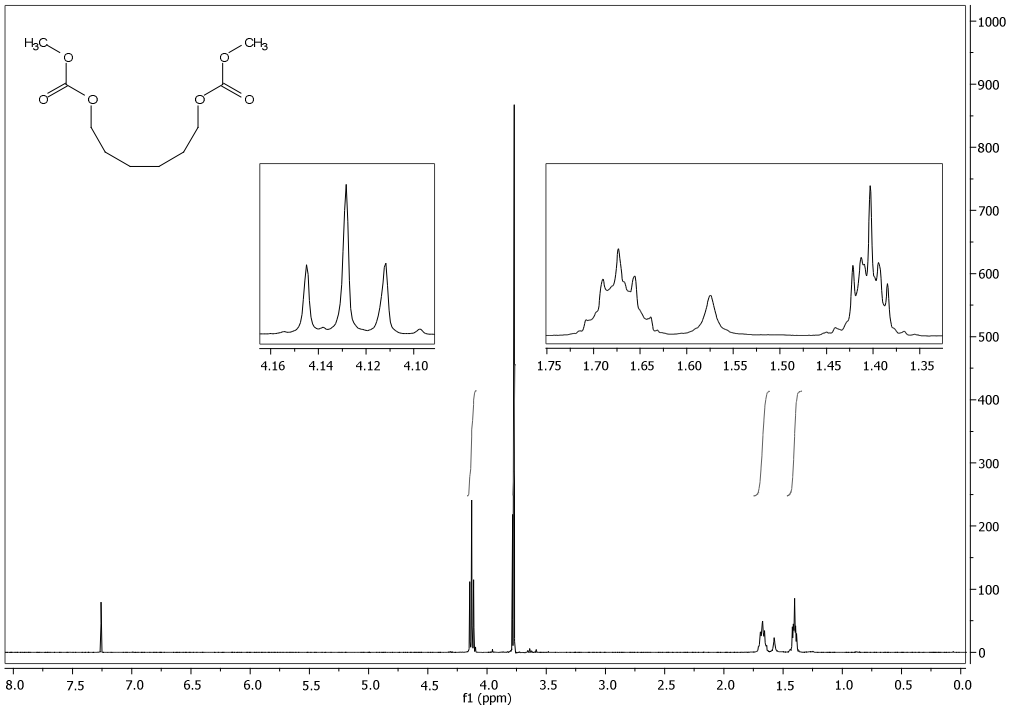

Figure S36. ^{1}H NMR spectrum of **10c**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.13 (t, *J* = 6.6 Hz, 4H), 3.77 (s, 6H), 1.72-1.62 (m, 4H), 1.45-1.36 (m, 4H).

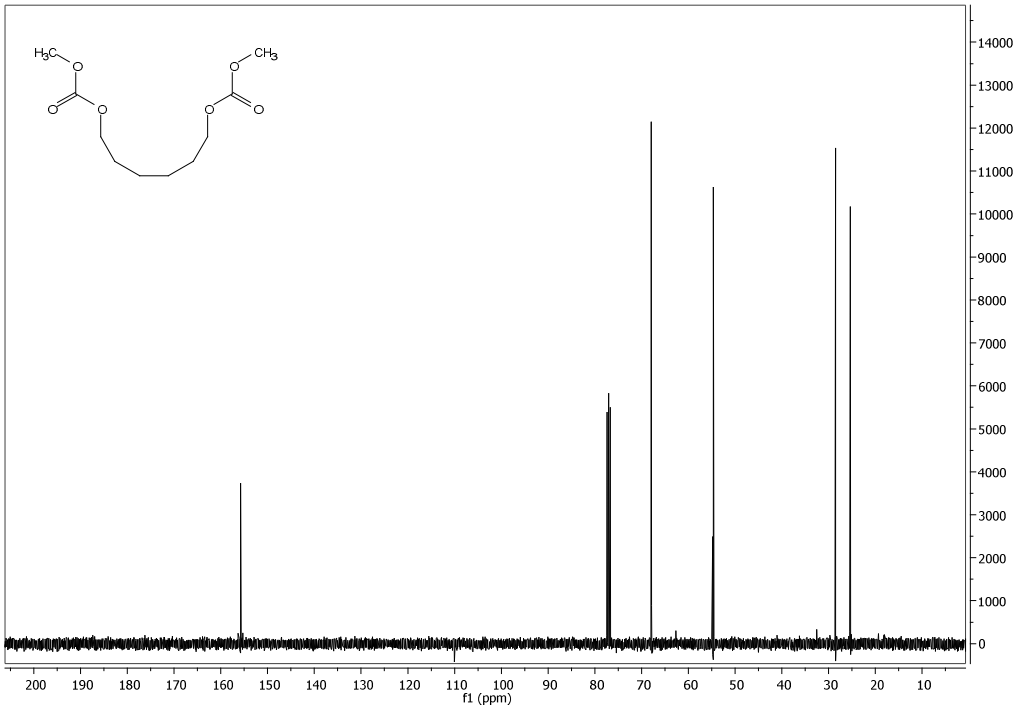

Figure S37. ^{13}C NMR spectrum of **10c**.

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.8, 67.9, 54.6, 28.5, 25.3.

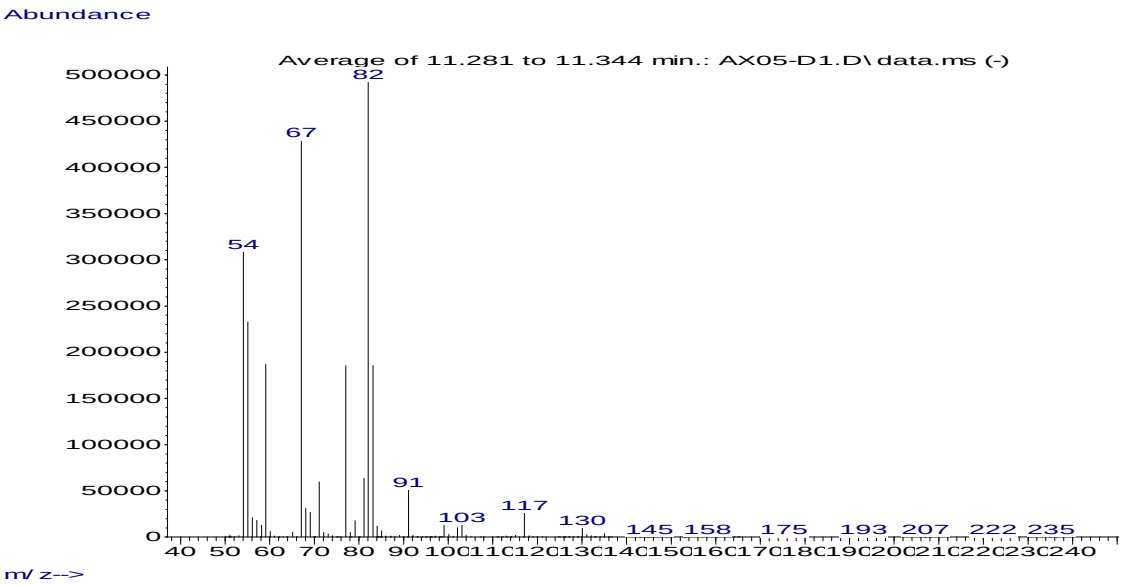

Figure S38. MS spectrum of **10c**.

MS (70 eV) m/z: 234 (M^+ <1%)130 (2), 117 (5), 99 (4), 91 (9), 83 (35), 82 (100), 81 (11), 79 (3), 77 (34), 71 (11), 69 (5), 68 (6), 67 (82), 59 (32), 58 (4), 56 (4), 55 (45), 54 (67), 53 (4).

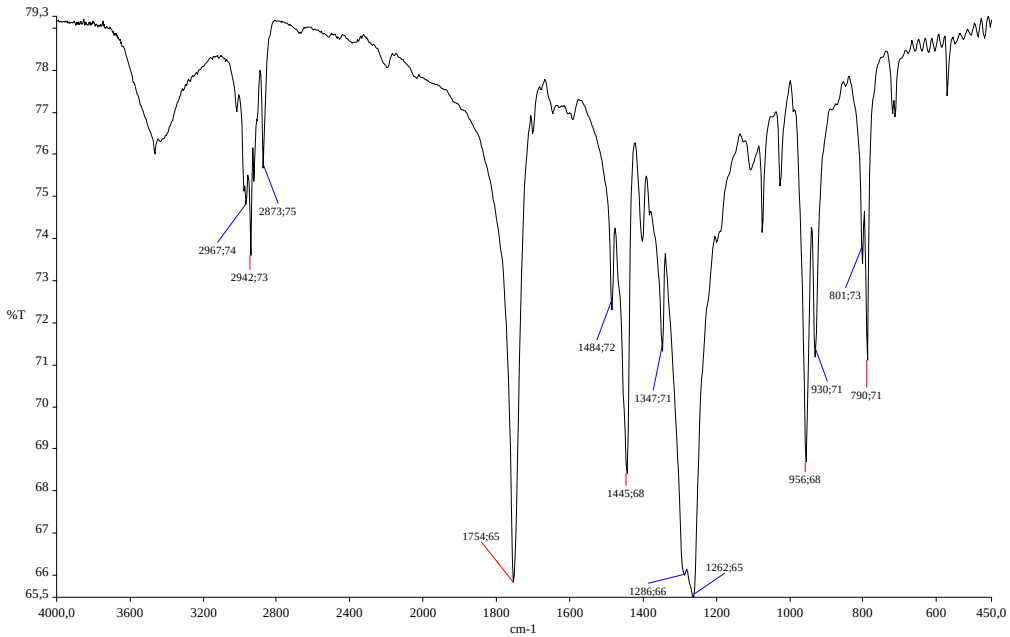

Figure S39. IR spectrum of **10c**.

IR (KBr) ν = 2968, 2943, 2874, 1755, 1485, 1446, 1348, 1287, 1263, 957, 931, 802, 791 cm-1.