Electronic Supplementary Material (ESI) for Catalysis Science & Technology

ELECTRONIC SUPPLEMENTARY INFORMATION:

Easily accessible bifunctional Zn(salpyr) catalysts for the formation of organic carbonates

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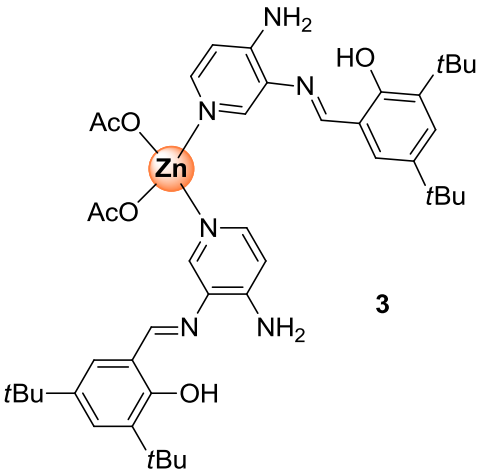

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Figure 1. ^{1}H NMR spectrum of monoimine salt **3** in $CDCl_3$ (500 MHz) at RT.

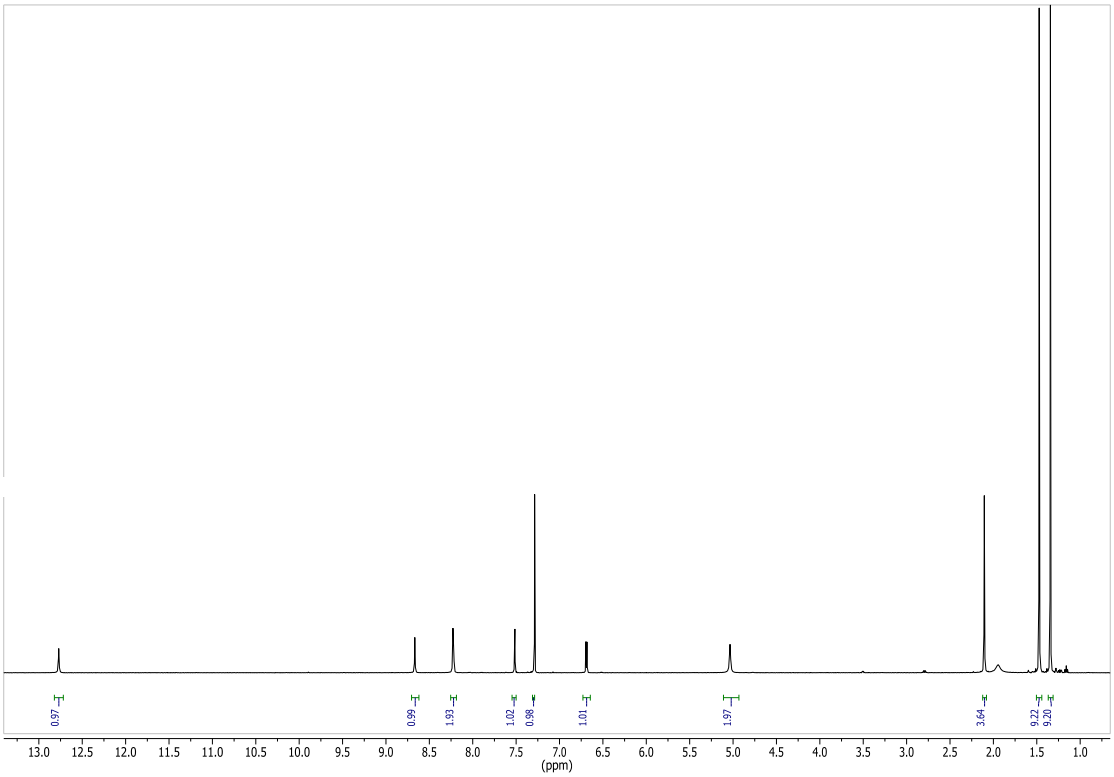


Figure 2. ^{13}C NMR spectrum of monoimine salt **3** in $CDCl_3$ (126 MHz) at RT.

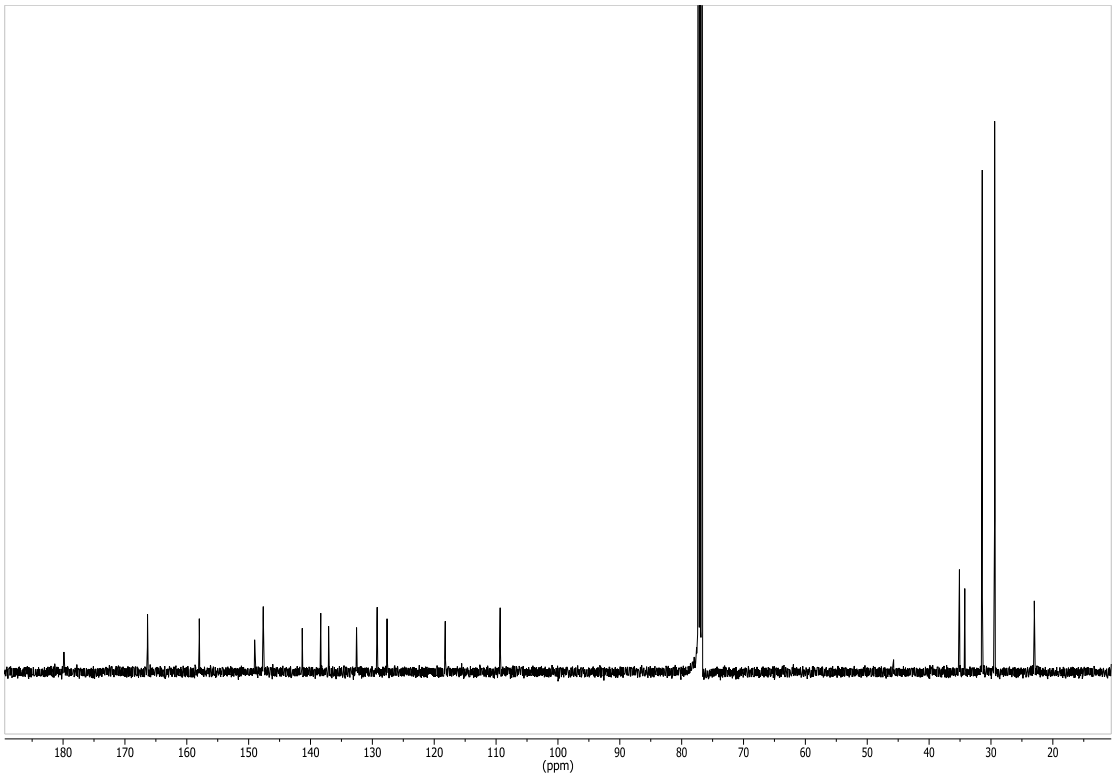


Figure 3. Mass spectrum (ESI+, MeOH) of monoimine salt **3**.

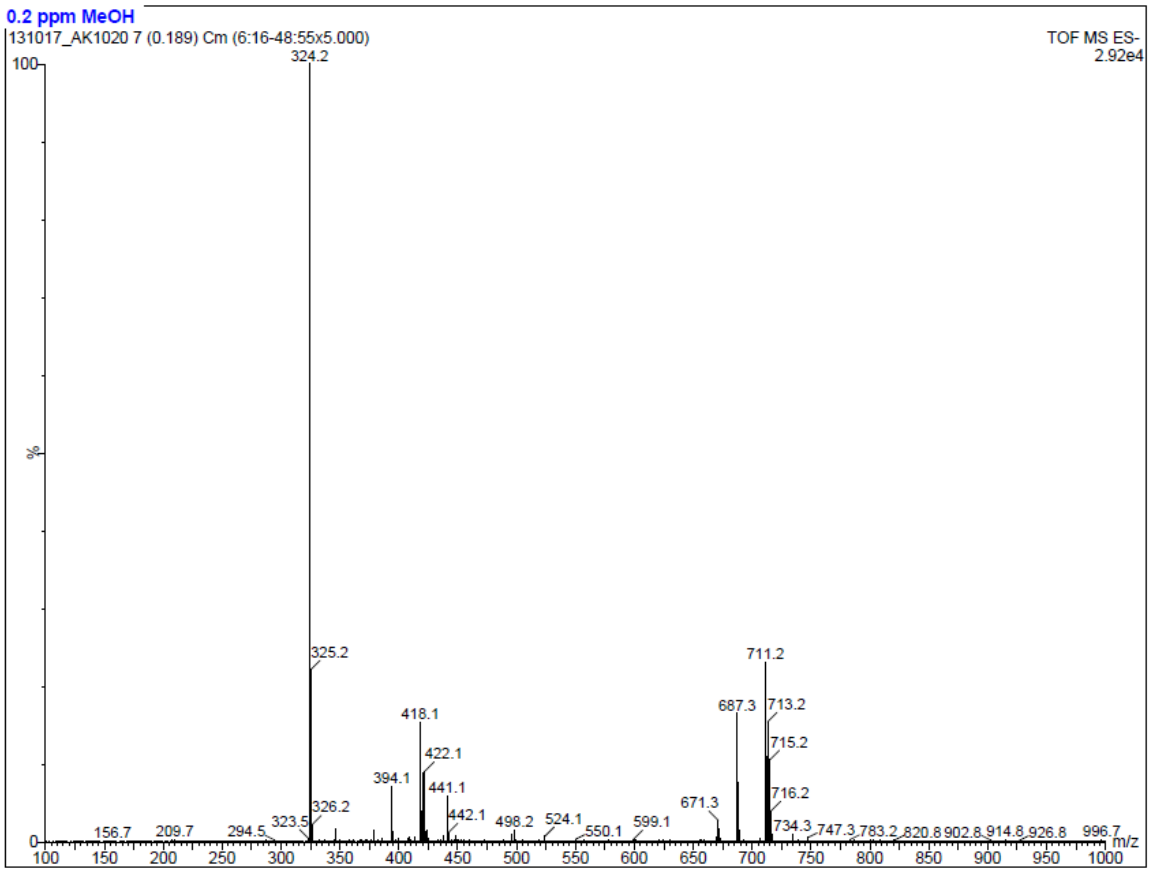
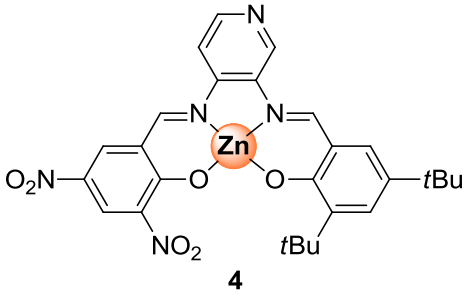


Figure 4. ^{1}H NMR spectrum of nonsymmetrical Zn(salpyr) complex **4** in DMSO-d_6 (500 MHz) at RT.



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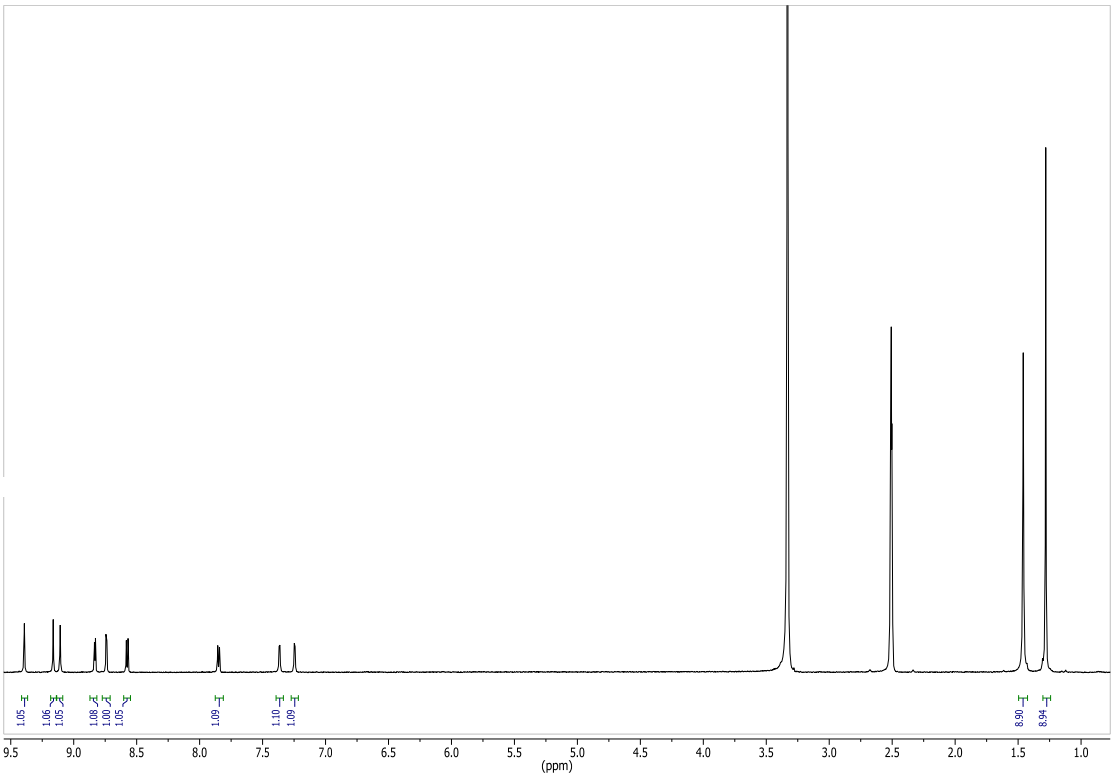


Figure 5. ^{13}C NMR spectrum of nonsymmetrical Zn(salpyr) complex **4** in DMSO-d_6 (126 MHz) at RT.

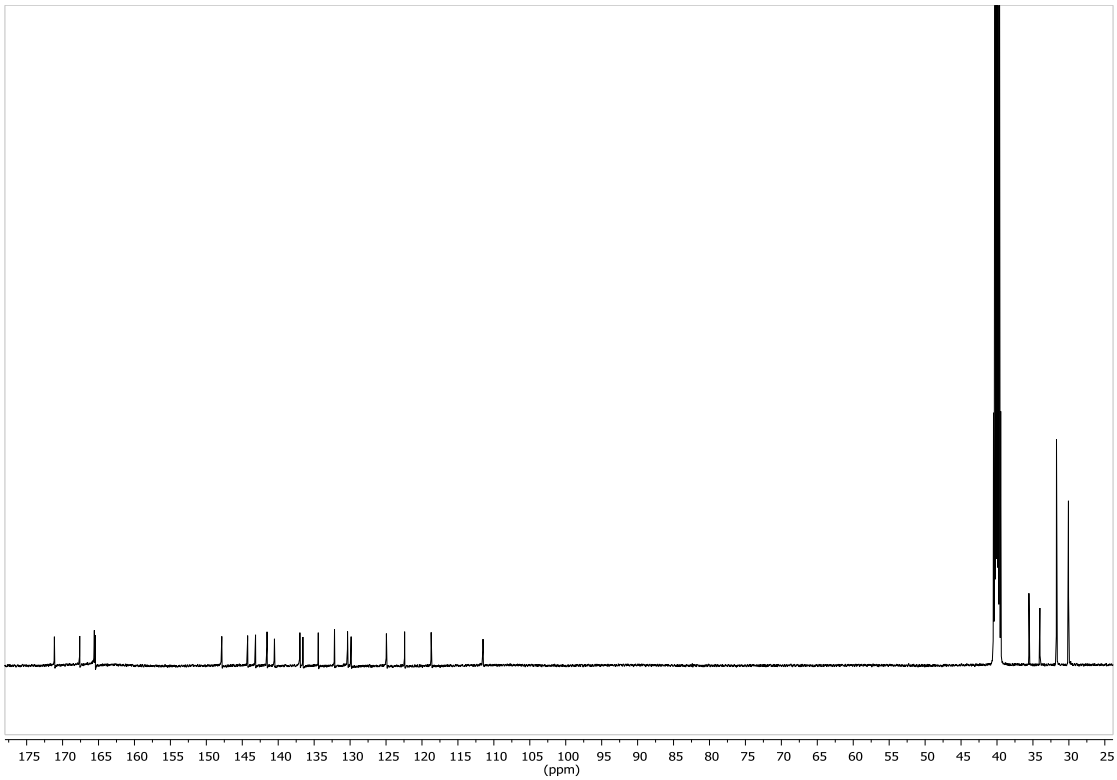


Figure 6. Mass spectrum (MALDI+, pyrene) of nonsymmetrical Zn(salpyr) complex **4**.

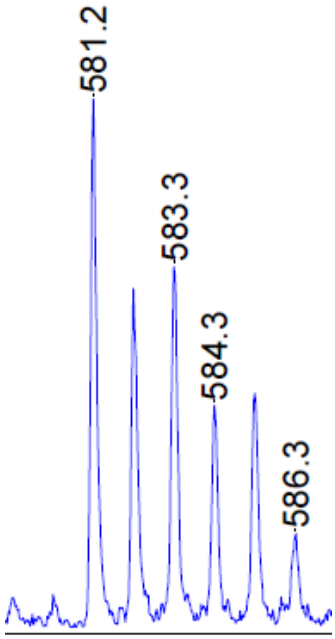
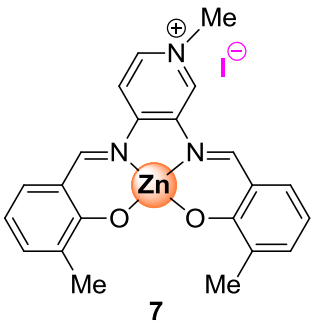


Figure 7. ^{1}H NMR spectrum of alkylated Zn(salpyr) complex **7** in DMSO-d_6 (500 MHz) at RT.



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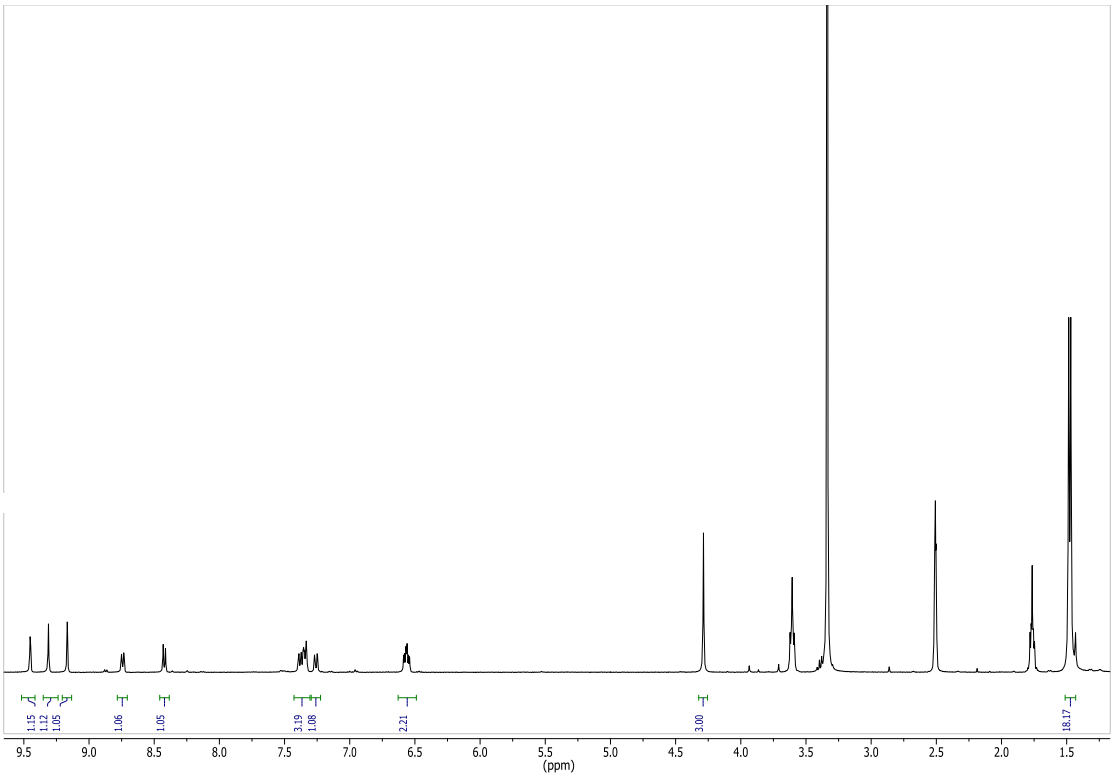


Figure 8. ^{13}C NMR spectrum of alkylated Zn(salpyr) complex **7** in DMSO-d_6 (126 MHz) at RT.

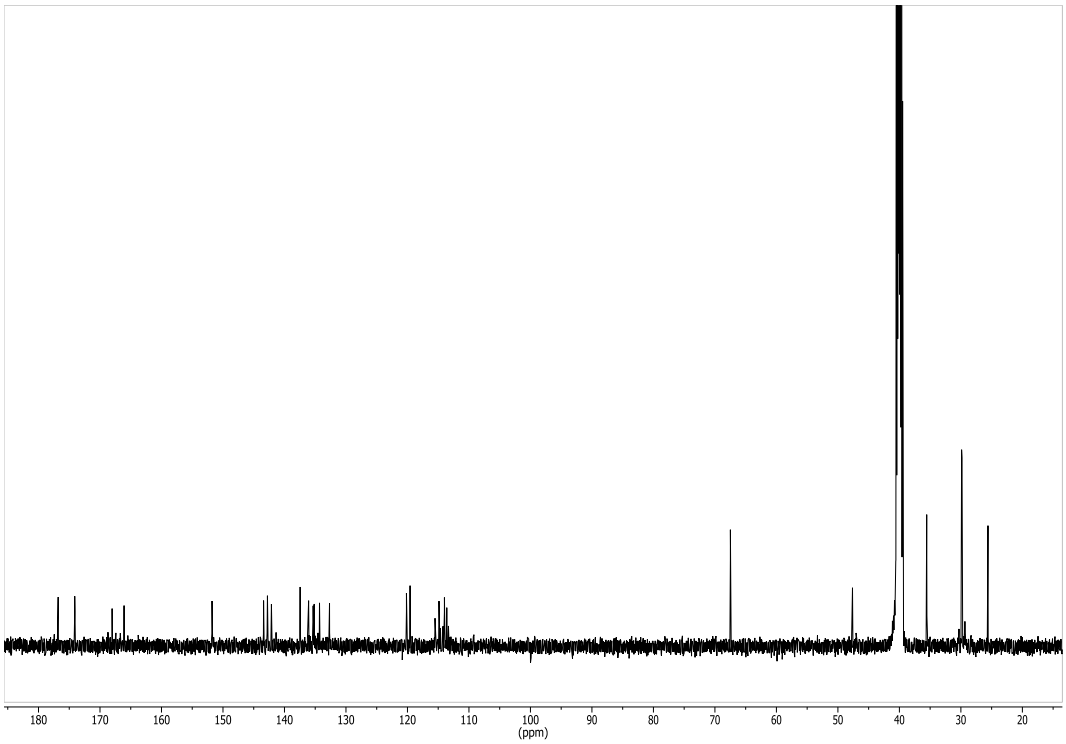


Figure 9. Mass spectrum (MALDI(+), dctb) of alkylated Zn(salpyr) complex **7**.

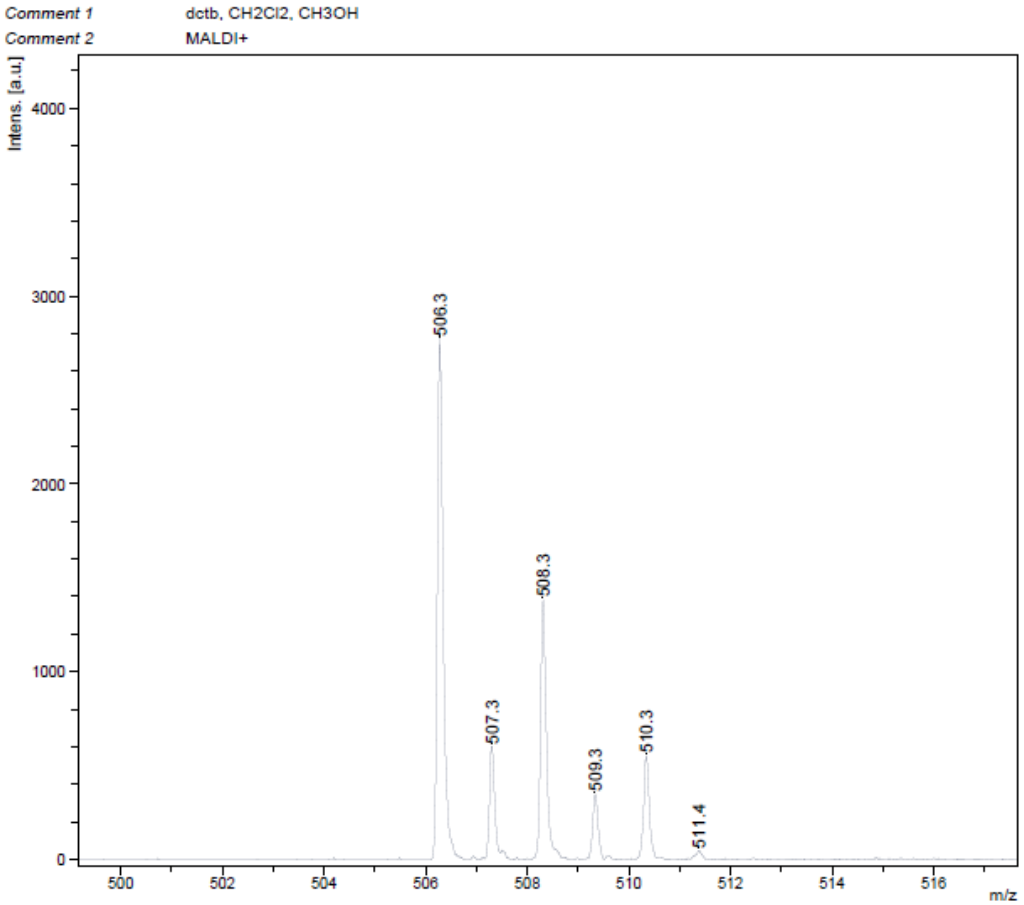
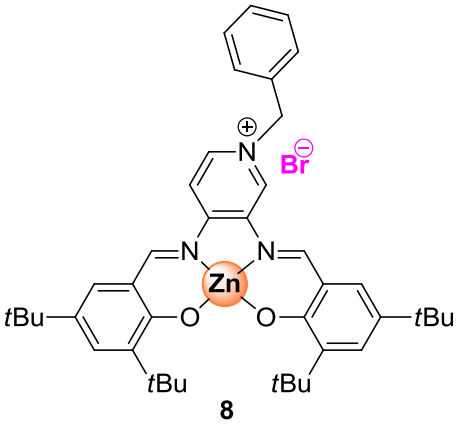


Figure 10. ^{1}H NMR spectrum of benzylated Zn(salpyr) complex **8** in DMSO-d_6 (500 MHz) at RT.



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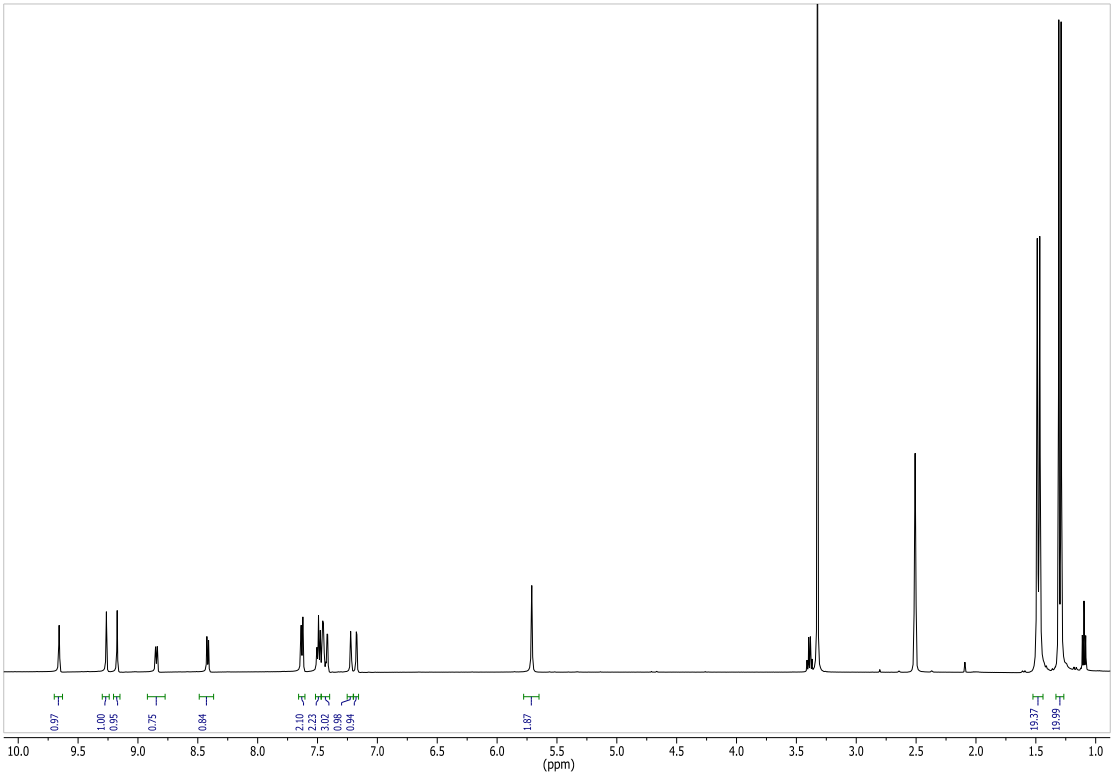


Figure 11. ^{13}C NMR spectrum of benzylated Zn(salpyr) complex **8** in DMSO-d_6 (126 MHz) at RT.

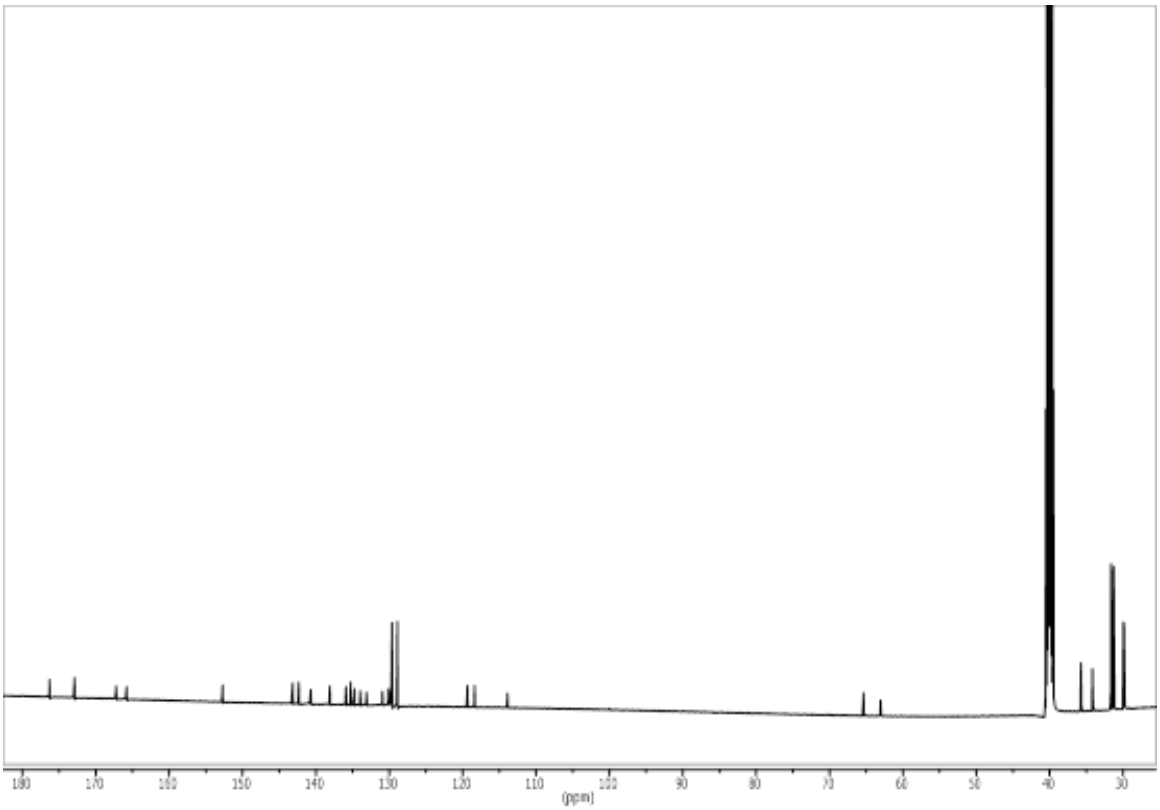


Figure 12. MALDI(+) mass spectra (dctb) of benzylated Zn(salpyr) complex **8**.

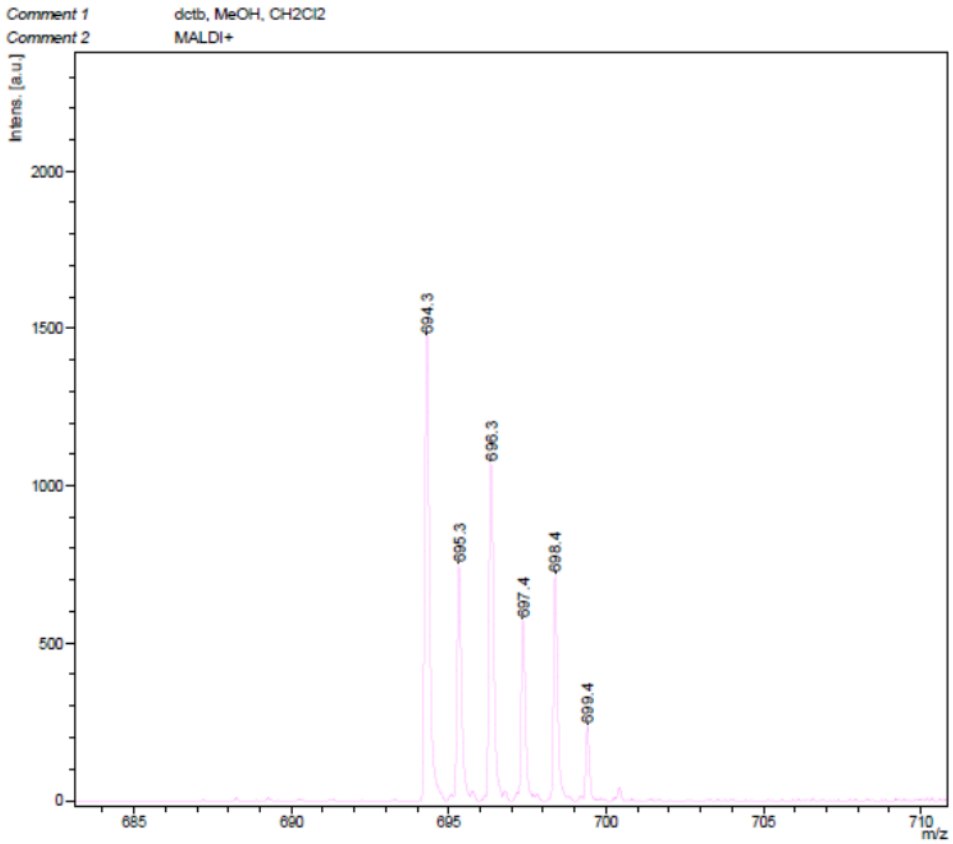
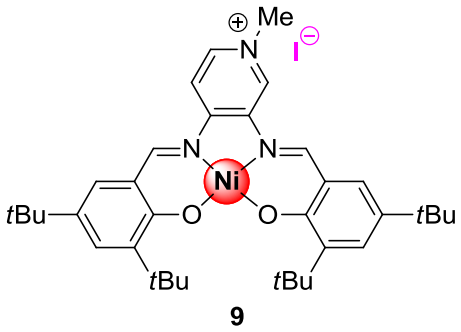


Figure 13. ^{1}H NMR spectrum of alkylated Ni(salpyr) complex **9** in DMSO-d_6 (500 MHz) at RT.



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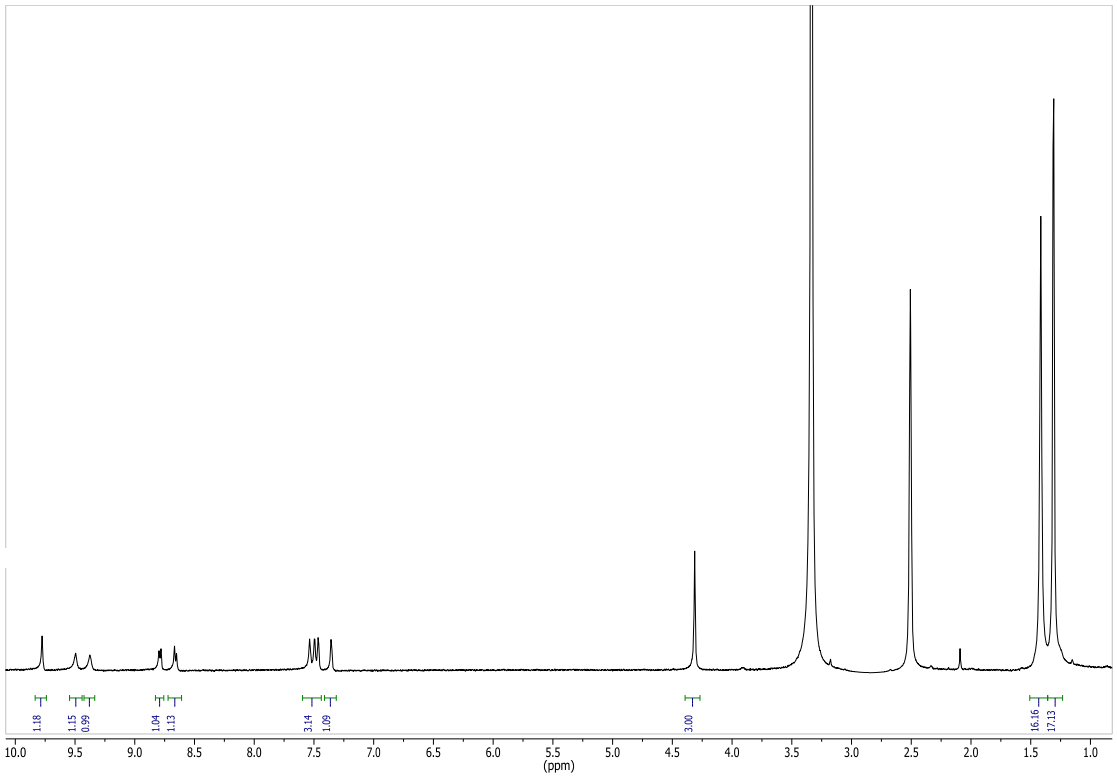


Figure 14. ^{13}C NMR spectrum of alkylated Ni(salpyr) complex **9** in DMSO-d_6 (126 MHz) at RT.

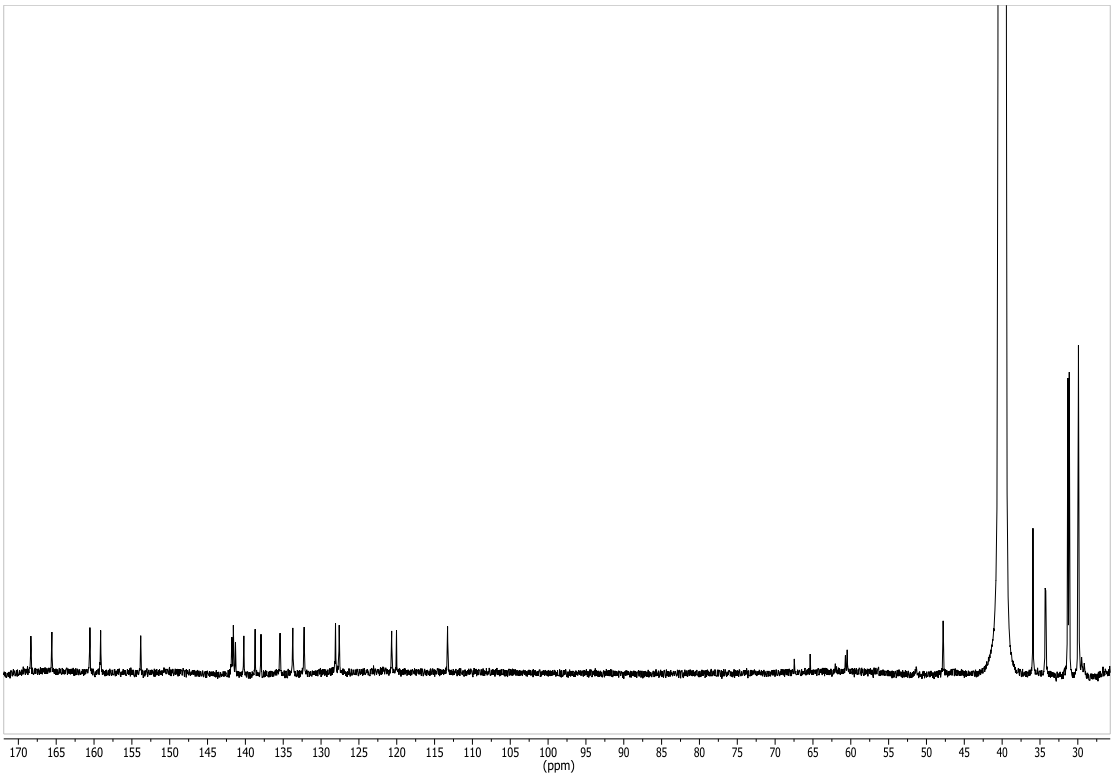
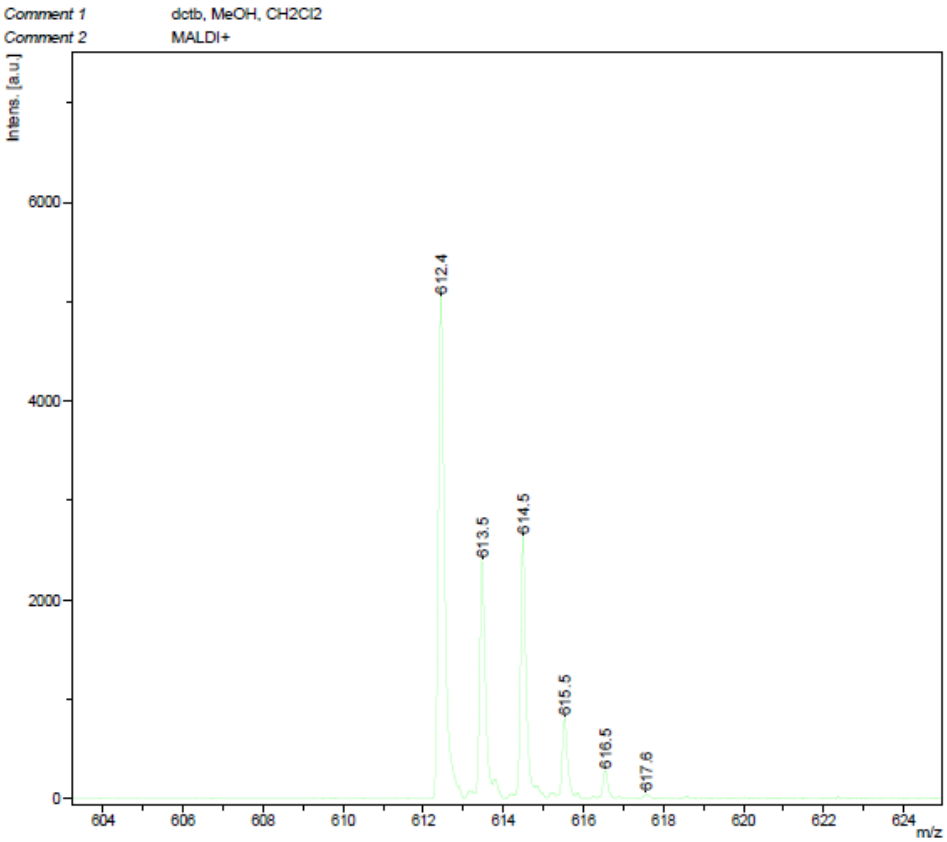
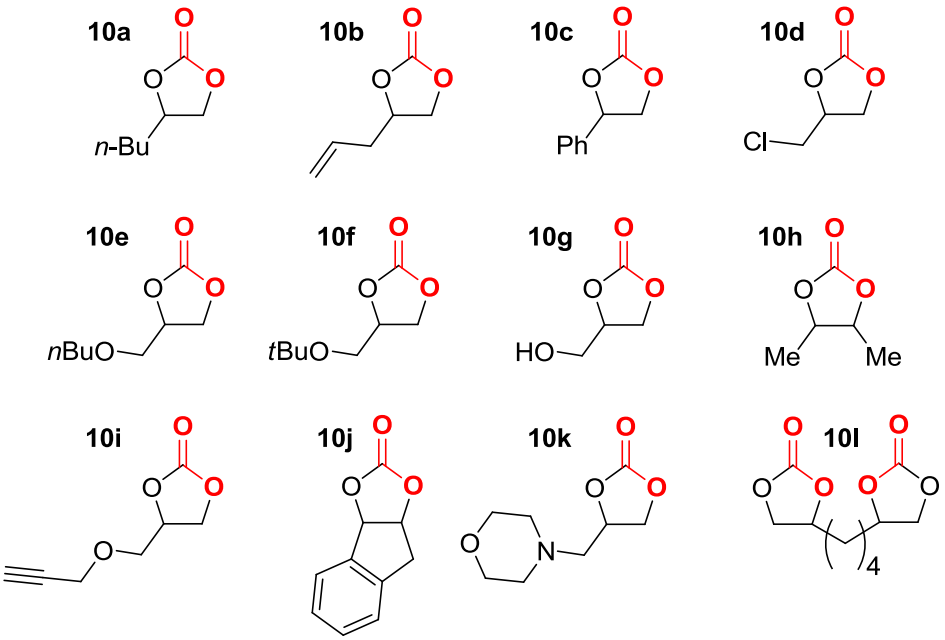


Figure 15. MALDI(+) mass spectrum (dctb) of alkylated Ni(salpyr) complex **9**.



SPECTROSCOPIC DATA AND NMR/IR SPECTRA OF CYCLIC CARBONATES 10a-10l:



[10a]: 4-butyl-1,3-dioxolan-2-one [1]

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.76 – 4.66 (m, 1H), 4.53 (dd, $^2J_{HH}$ = 8.2, $^3J_{HH}$ = 8.0 Hz, 1H), 4.08 (dd, $^2J_{HH}$ = 8.3, $^3J_{HH}$ = 7.3 Hz, 1H), 1.90 – 1.61 (m, 2H), 1.53 – 1.30 (m, 4H), 0.94 (t, $^3J_{HH}$ = 7.1 Hz, 3H). IR Neat: 1786 cm^{-1} (C=O).

[10b]: 4-(but-3-en-1-yl)-1,3-dioxolan-2-one [2]

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.80 (m,1H), 5.10 (m, 1H), 5.06 (m, 1H), 4.74 (m, 1H), 4.54 (dd, $^2J_{HH}$ = 8.6, $^3J_{HH}$ = 8.6 Hz, 1H), 4.09 (dd, $^2J_{HH}$ = 8.4, $^3J_{HH}$ = 7.2 Hz, 1H), 2.35 – 2.12 (m, 2H), 2.02 – 1.88 (m, 1H), 1.86 – 1.72 (m, 1H). IR Neat: 1784 cm^{-1} (C=O).

[10c]: 4-phenyl-1,3-dioxolan-2-one [3]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 – 7.42 (m, 3H), 7.40 – 7.34 (m, 2H), 5.68 (dd, $^3J_{HH}$ = 8.3, $^2J_{HH}$ = 7.5 Hz, 1H), 4.82 (dd, $^2J_{HH}$ = 8.5, $^3J_{HH}$ = 8.2 Hz, 1H), 4.36 (dd, $^2J_{HH}$ = 8.6, $^3J_{HH}$ = 7.9 Hz, 1H). IR Neat: 1775 cm^{-1} (C=O).

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[1] J.-L. Jiang, F. Gao, R. Hua, X. Qiu, *J. Org. Chem*., 2005, **70**, 381.

[2] Z. Zhu, A. G. Einset, C.-Y. Yang, W.-Y. Chen, G. E. Wnek, *Macromolecules*, 1994, **27**, 4076.

[3] Y. Ren, J.-J. Shim, *ChemCatChem*, 2013, **5**, 1344.

[10d]: 4-chloromethyl-1,3-dioxolan-2-one [4]

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.02 – 4.94 (m, 1H), 4.61 (dd, $^2J_{HH}$ = 8.9, $^3J_{HH}$ = 8.6 Hz, 1H), 4.43 (dd, $^2J_{HH}$ = 8.8, $^3J_{HH}$ = 8.8 Hz, 1H), 3.83 – 3.71 (m, 1H). IR Neat: 1780 cm^{-1} (C=O).

[10e]: 4-butoxymethyl-1,3-dioxolan-2-one [3]

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.86 – 4.77 (m, 1H), 4.49 (dd, $^2J_{HH}$ = 8.4, $^3J_{HH}$ = 8.1 Hz, 1H), 4.39 (dd, $^2J_{HH}$ = 8.4, $^3J_{HH}$ = 8.4 Hz, 1H), 3.70 – 3.58 (m, 2H), 3.52 (t, $^3J_{HH}$ = 6.4 Hz, 2H), 1.65 – 1.51 (m, 2H), 1.37 (m, 2H), 0.92 (t, $^3J_{HH}$ = 7.4 Hz, 3H). IR Neat: 1787 cm^{-1} (C=O).

[10g]: 4-(hydroxymethyl)-1,3-dioxolan-2-one[5]

^{1}H NMR (300 MHz, DMSO): δ 5.25 (t, $^3J_{HH}$ = 5.6 Hz, 1H), 4.83 – 4.76 (m, 1H), 4.49 (dd, $^2J_{HH}$ = 8.3, $^3J_{HH}$ = 8.2 Hz, 1H), 4.28 (dd, $^2J_{HH}$ = 8.2, $^3J_{HH}$ = 5.9 Hz, 1H), 3.66 (ddd, $^2J_{HH}$ = 12.6, $^3J_{HH}$ = 5.3, $^3J_{HH}$ = 3.0 Hz, 1H), 3.50 (ddd, $^2J_{HH}$ = 12.7, $^3J_{HH}$ = 5.4, $^3J_{HH}$ = 3.4 Hz, 1H). IR Neat: 1766 cm^{-1} (C=O).

[10h]: 4,5-dimethyl-1,3-dioxolan-2-one[6]

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.38 – 4.27 (m, 2H), 1.45 (d, $^3J_{HH}$ = 5.9 Hz, 6H). IR Neat: 1796 cm^{-1} (C=O).

[10i]: 4-((prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one [7]

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.91 – 4.82 (m, 1H), 4.52 (dd, $^2J_{HH}$ = 8.4, $^3J_{HH}$ = 8.4 Hz, 1H), 4.40 (dd, $^2J_{HH}$ = 8.3, $^3J_{HH}$ = 6.1 Hz, 1H), 4.27 (dd, $^2J_{HH}$ = 15.9, $^4J_{HH}$ = 2.4 Hz, 1H), 4.20 (dd, $^2J_{HH}$ = 15.9, $^4J_{HH}$ = 2.4 Hz, 1H), 3.80 (dd, $^2J_{HH}$ = 10.7, $^3J_{HH}$ = 3.9 Hz, 1H), 3.73 (dd, $^2J_{HH}$ = 10.7, $^3J_{HH}$ = 3.9 Hz, 1H), 2.50 (t, $^4J_{HH}$ = 2.4 Hz, 1H). IR Neat: 1781 cm^{-1} (C=O).

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[4] J. Sun, L. Han, W. Cheng, J. Wang, X. Zhang, S. Zhang, *ChemSusChem*, 2011, **4**, 502.

[5] Y. Patel, J. George, S. M. Pillai, P. Munshi, *Green Chem.,* 2009, **11**, 1056.

[6] K. Matsumoto, Y. Sato, M. Shimojo, M. Hatanaka, *Tetraehedron: Asymmetry.,* 2000, **11**, 1965.

[7] C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, *J. Am. Chem. Soc.,* 2013, **135**, 1228.

[10j]: 8,8a-dihydro-3aH-indeno[1,2-d][1,3]dioxol-2-one [8]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 – 7.53 (m, 4H), 6.01 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 5.44 – 5.47 (m, 1H), 3.40 (m, 1H). IR Neat: 1773 cm^{-1} (C=O).

[10k]: 4-(morpholinomethyl)-1,3-dioxolan-2-one [7]

^{1}H NMR (300 MHz, $CDCl_3$): $\delta\delta$ 4.88 – 4.78 (m, 1H), 4.54 (dd, $^2J_{HH}$ = 8.5, $^3J_{HH}$ = 8.5 Hz, 1H), 4.25 (dd, $^2J_{HH}$ = 8.7, $^3J_{HH}$ = 7.2 Hz, 1H), 3.71 (t, $^3J_{HH}$ = 4.6 Hz, 1H), 2.71 (d, $^2J_{HH}$ = 1.2 Hz, 1H), 2.69 (d, $^2J_{HH}$ = 0.9 Hz, 1H), 2.61 – 2.54 (m, 4H). IR Neat: 1784 cm^{-1} (C=O).

[10l]: 1,4-di(oxiran-2-yl)butane: [7]

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.78 – 4.67 (m, 2H), 4.55 (dd, $^2J_{HH}$ = 8.5, $^3J_{HH}$ = 8.5 Hz, 2H), 4.08 (dd, $^2J_{HH}$ = 8.9, $^3J_{HH}$ = 7.2 Hz, 2H), 1.90 – 1.40 (m, 4H). IR Neat: 1775 cm^{-1} (C=O).

[8] J.-L. Wang, J.-Q. Wang, L.-N. He, X.-Y. Dou, F. Wu, *Green Chem.*, 2008, **10**, 1218.

Figure 16. ^{1}H NMR spectrum of 4-butyl-1,3-dioxolan-2-one **[10a]** in $CDCl_3$ (300 MHz) at RT.

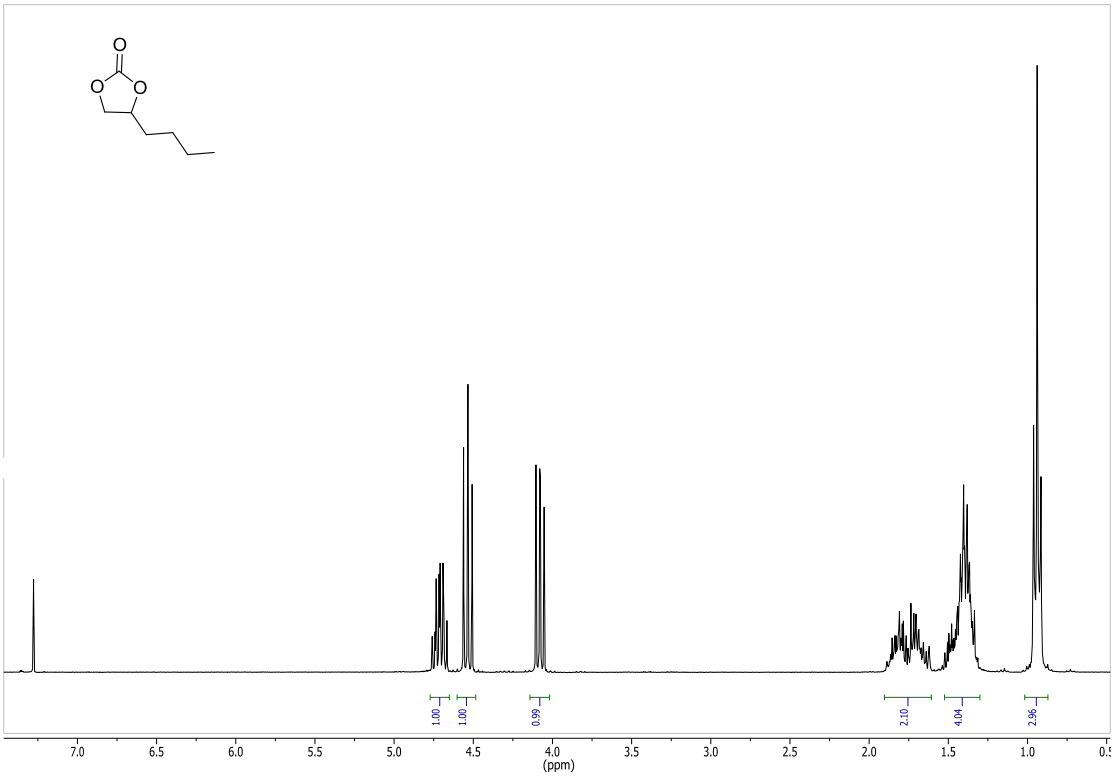


Figure 17. IR spectrum of 4-butyl-1,3-dioxolan-2-one **[10a]**.

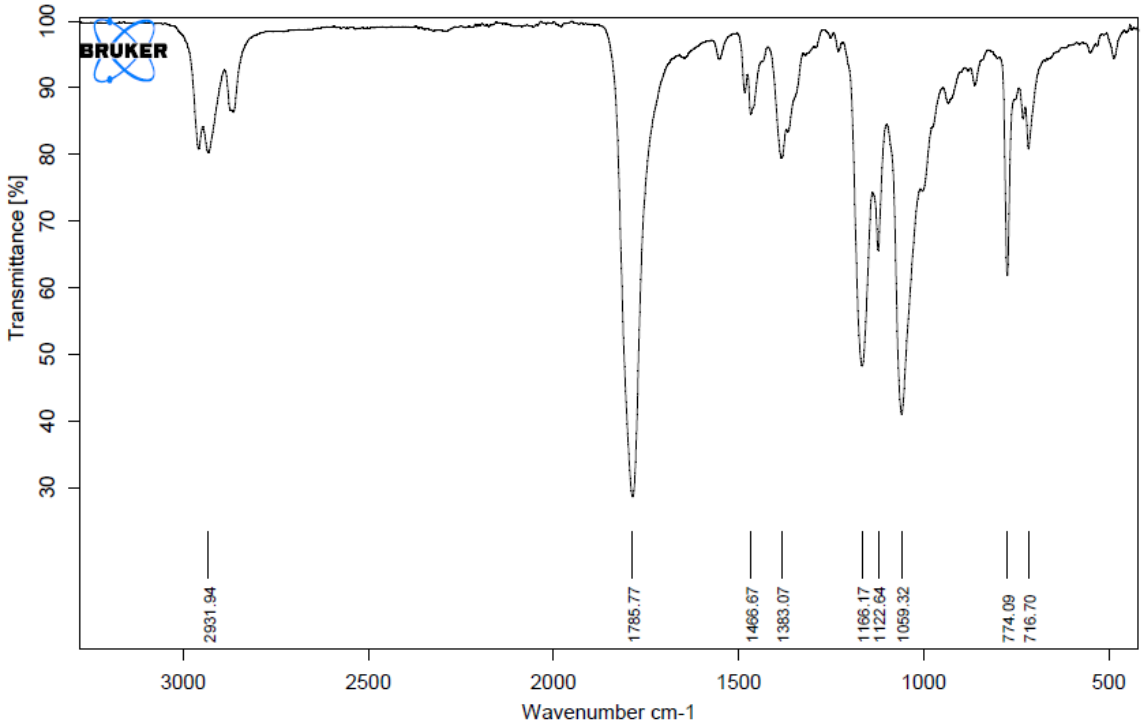


Figure 18. ^{1}H NMR spectrum of 4-(but-3-en-1-yl)-1,3-dioxolan-2-one **[10b]** in $CDCl_3$ (300 MHz) at RT.

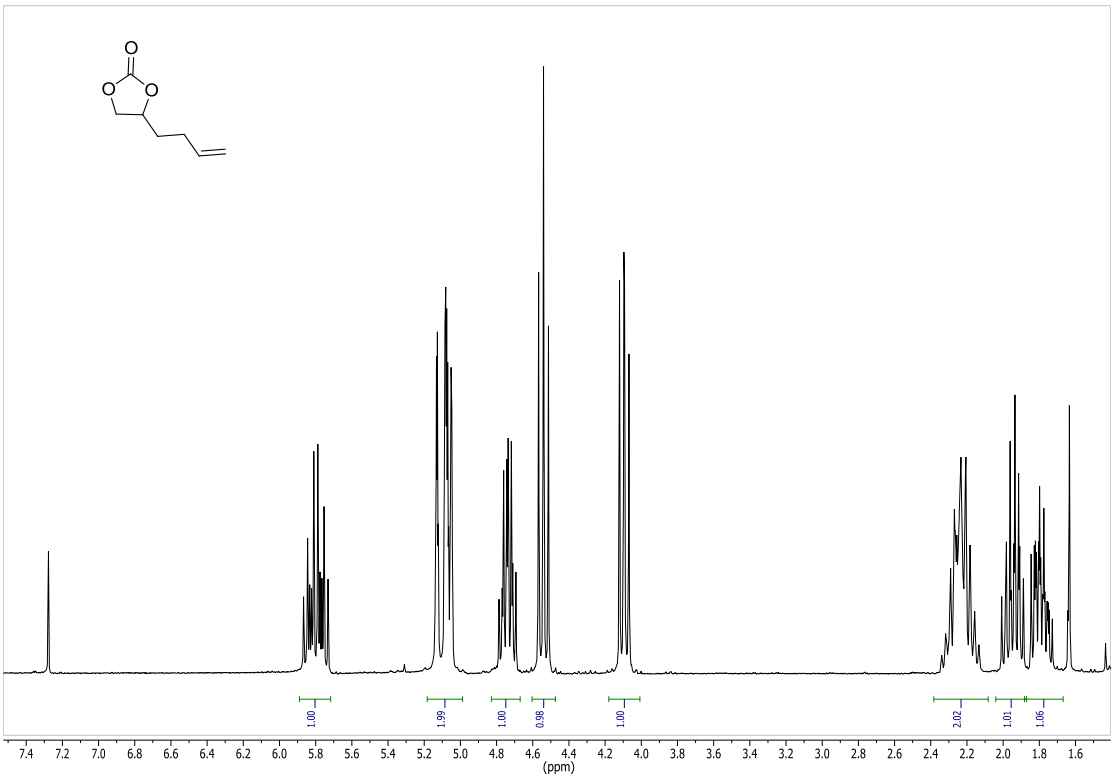


Figure 19. IR spectrum of 4-(but-3-en-1-yl)-1,3-dioxolan-2-one **[10b]**.

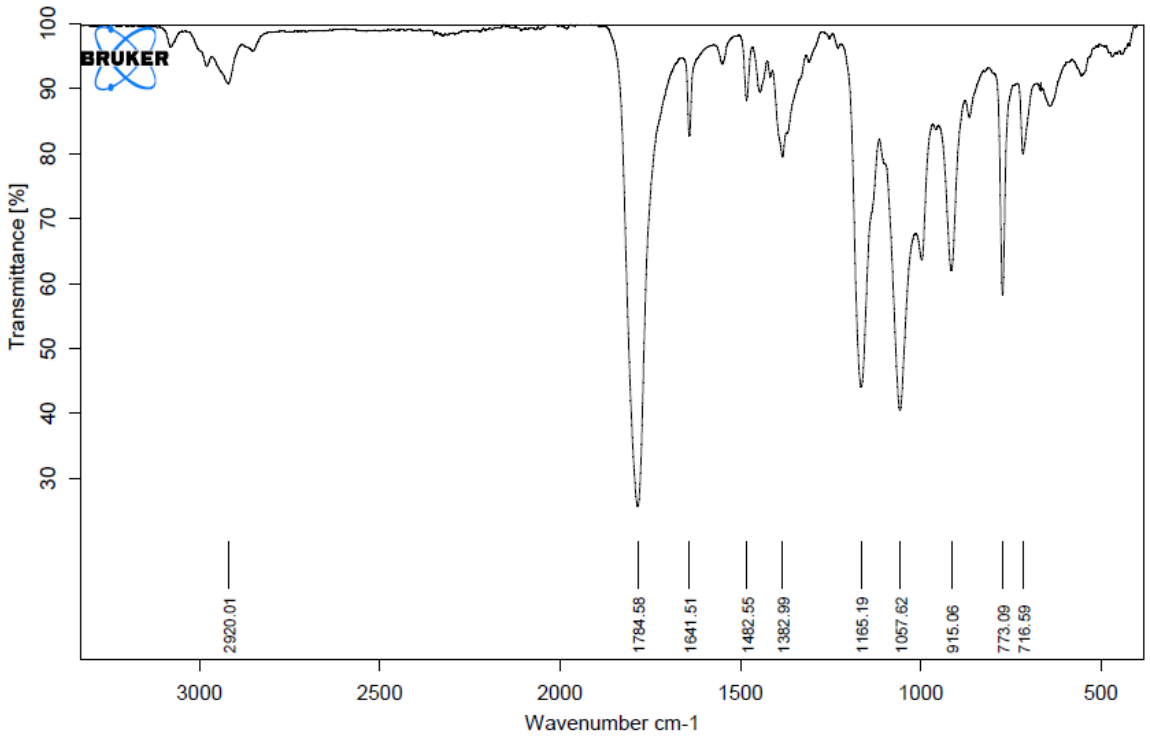


Figure 20. ^{1}H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one **[10c]** in $CDCl_3$ (300 MHz) at RT.

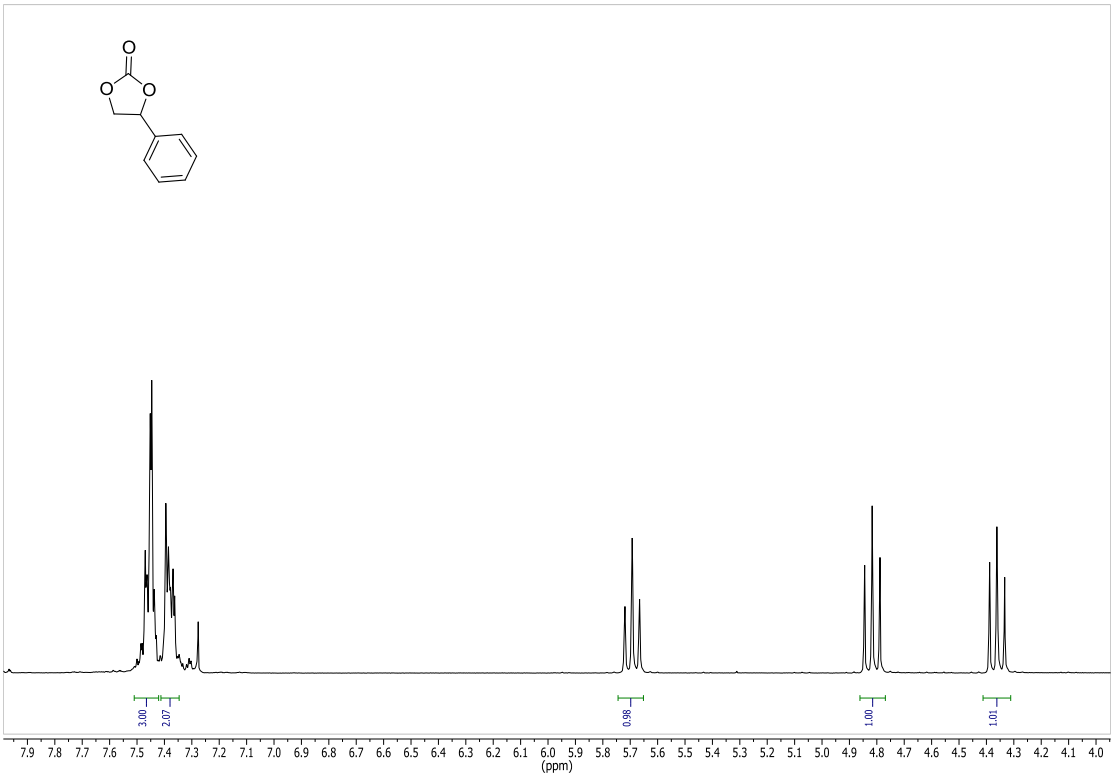


Figure 21. IR spectrum of of 4-phenyl-1,3-dioxolan-2-one **[10c]**.

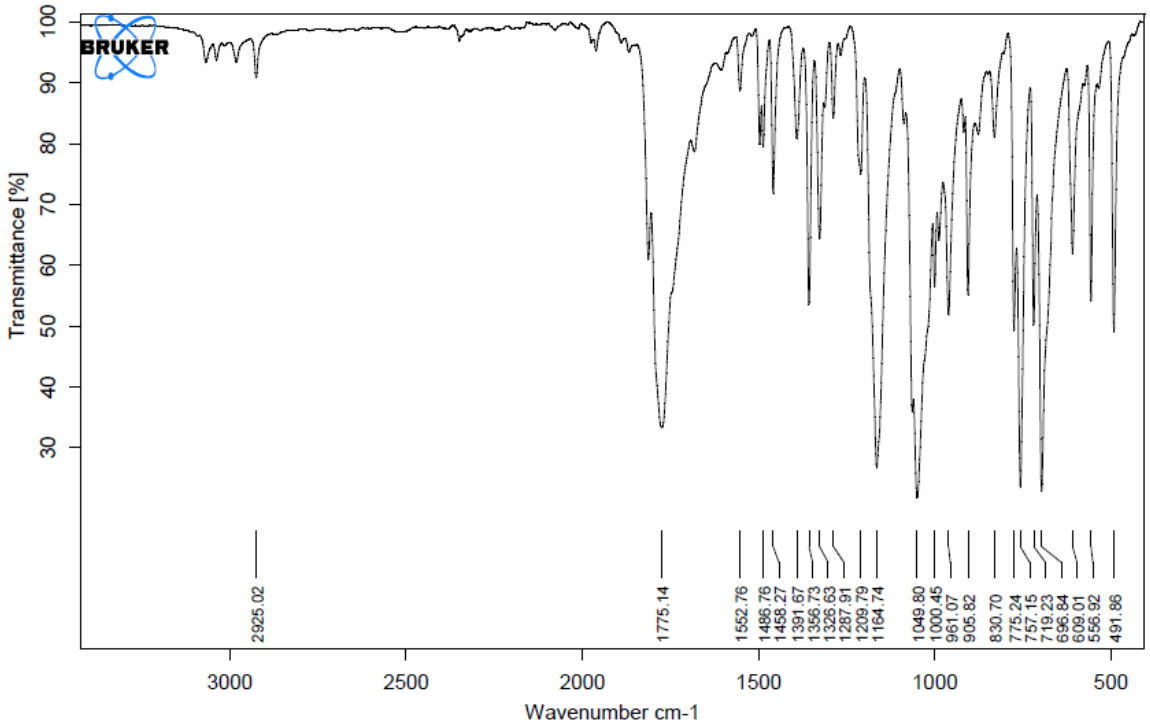


Figure 22. ^{1}H NMR spectrum of 4-chloromethyl-1,3-dioxolan-2-one [10d] in $CDCl_3$ (300 MHz) at RT.

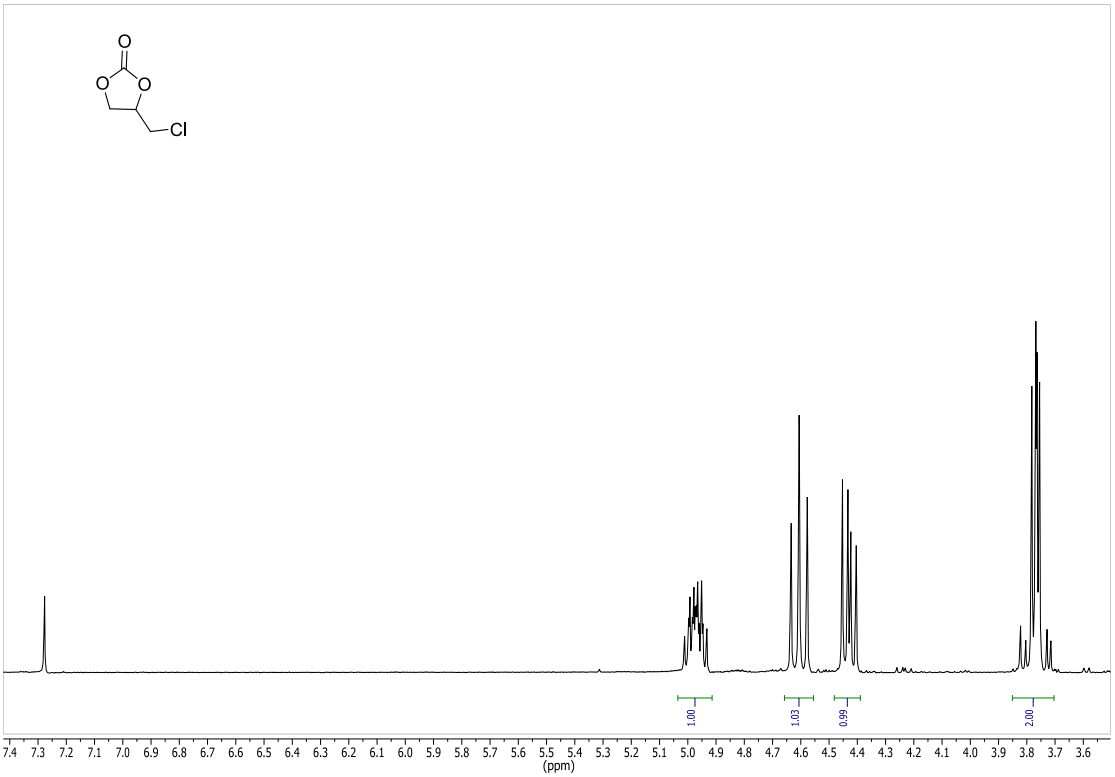


Figure 23. IR spectrum of 4-chloromethyl-1,3-dioxolan-2-one **[10d]**.

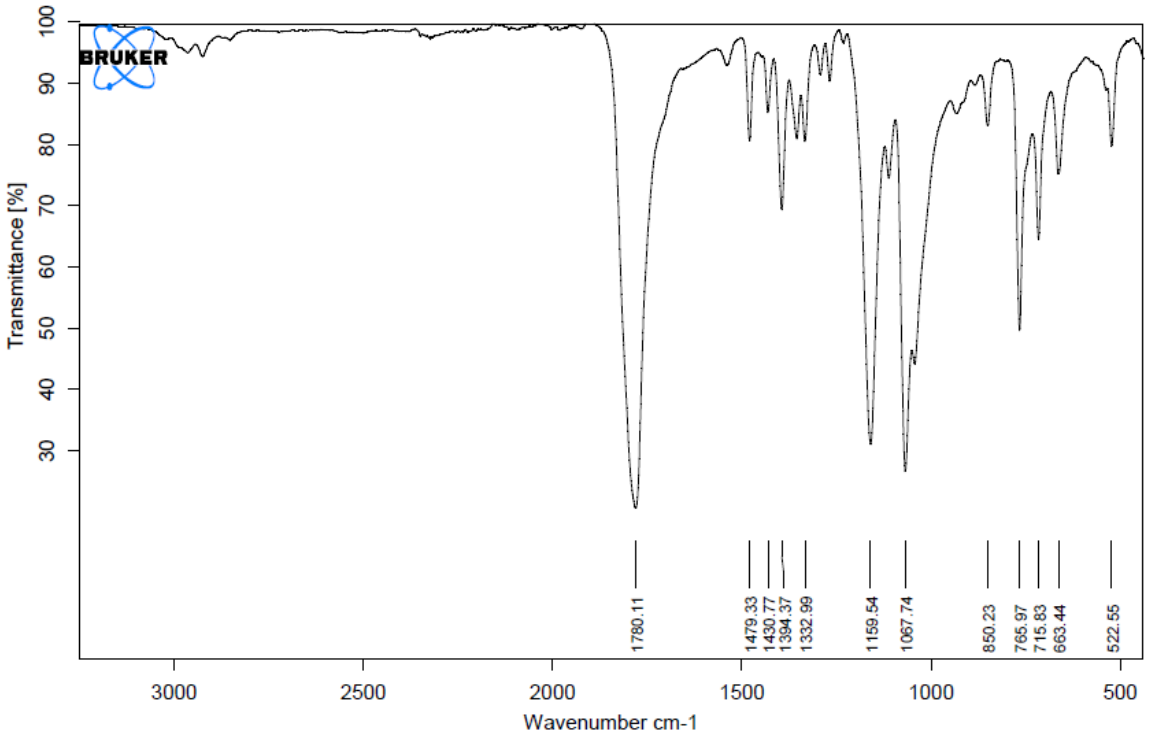


Figure 24. ^{1}H NMR spectrum of 4-butoxymethyl-1,3-dioxolan-2-one **[10e]** in $CDCl_3$ (300 MHz) at RT.

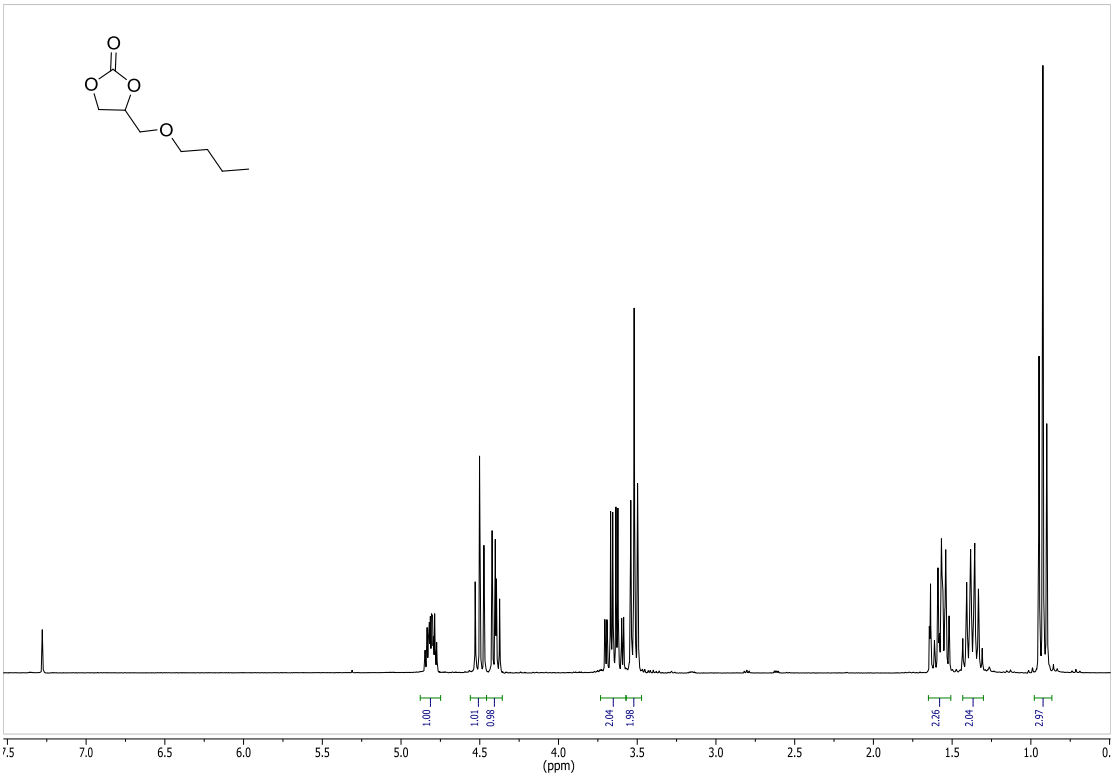


Figure 25. IR spectrum of 4-butoxymethyl-1,3-dioxolan-2-one **[10e]**.

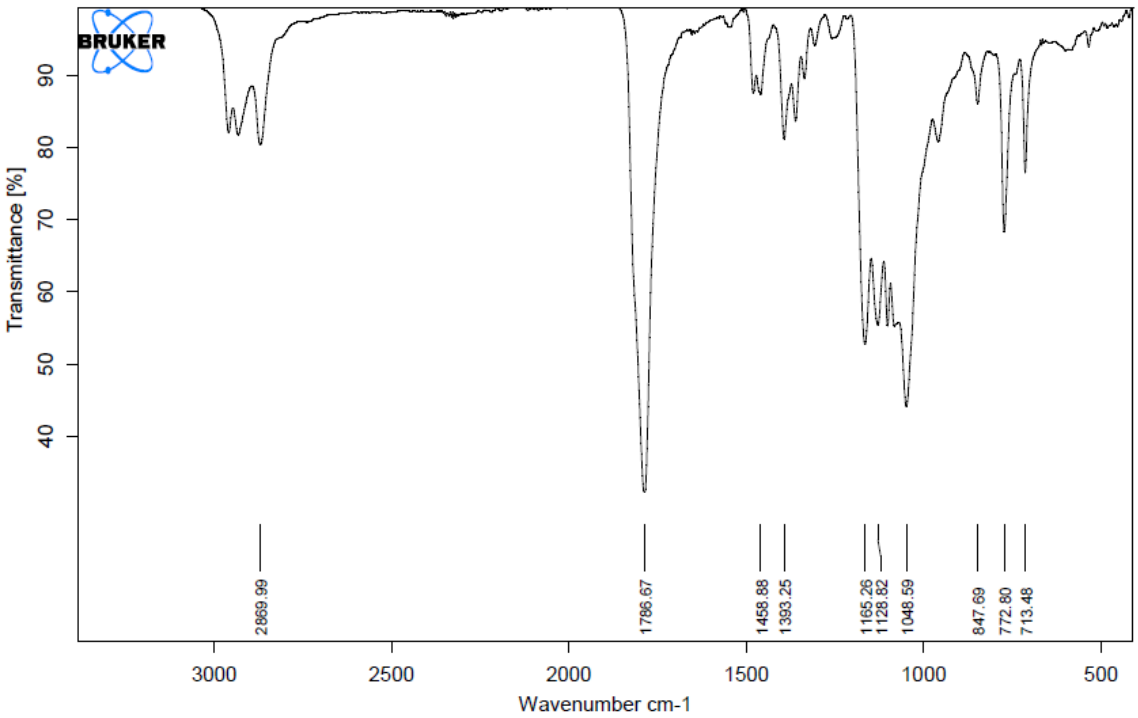


Figure 26. ^{1}H NMR spectrum of 4-(hydroxymethyl)-1,3-dioxolan-2-one **[10g]** in DMSO (300 MHz) at RT.

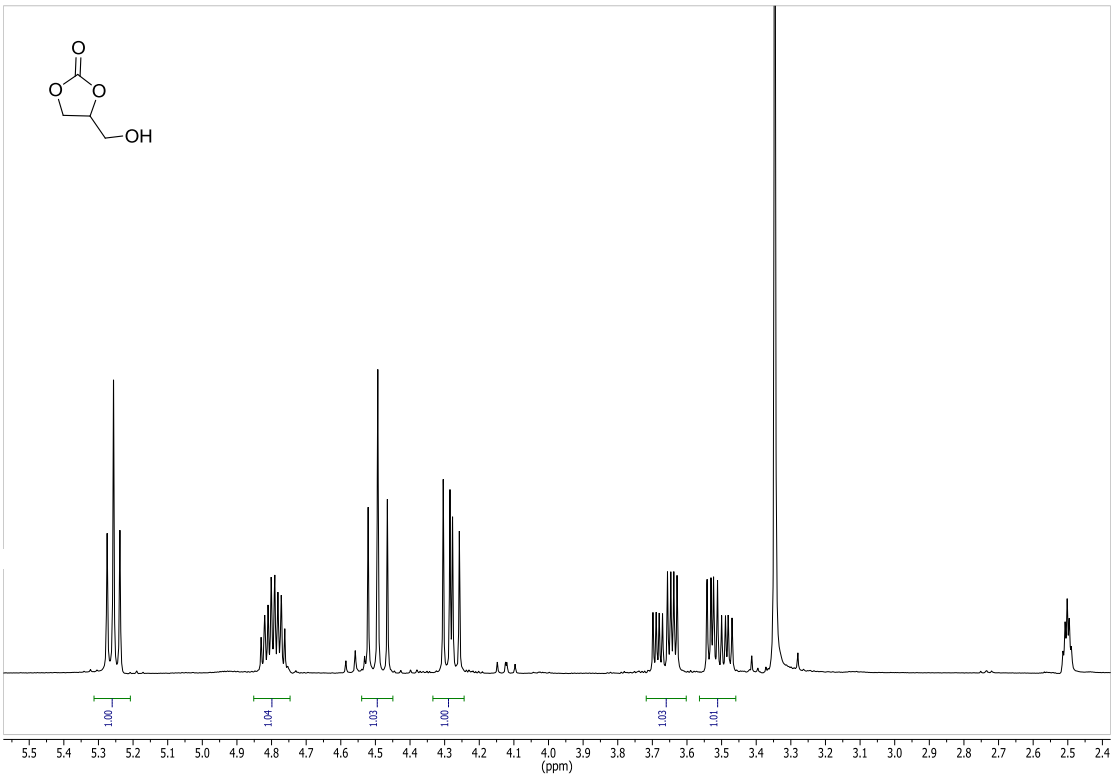


Figure 27. IR spectrum of 4-(hydroxymethyl)-1,3-dioxolan-2-one **[10g]**.

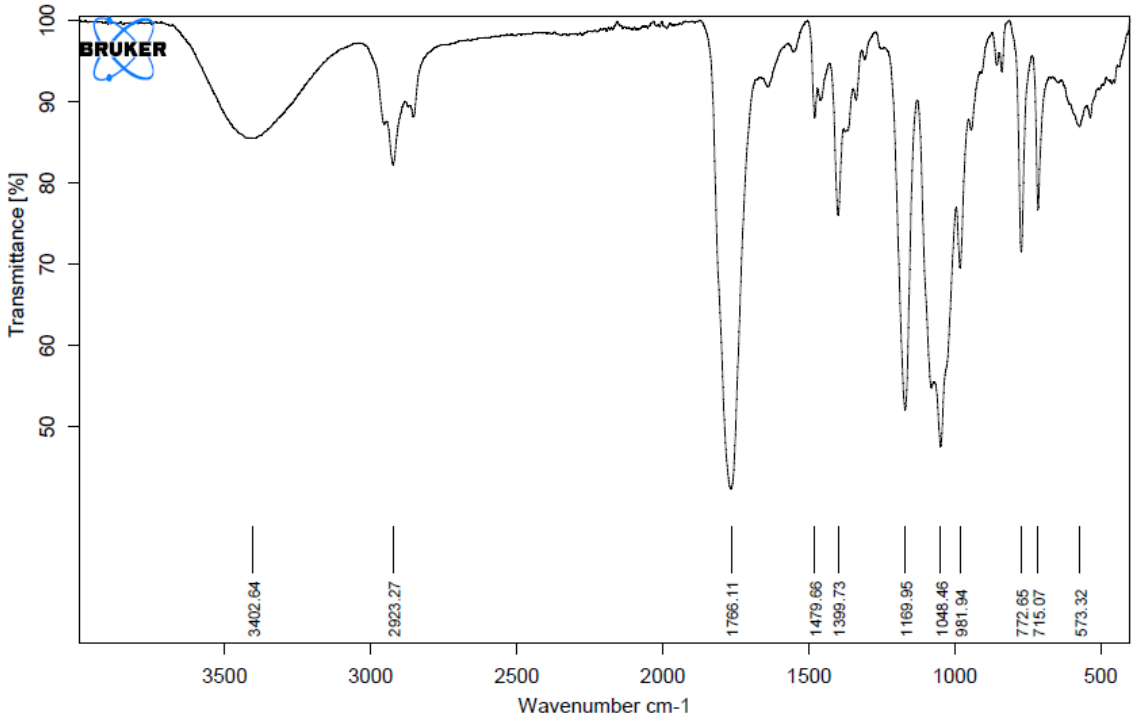


Figure 28. ^{1}H NMR spectrum of 4-((prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one **[10i]** in $CDCl_3$ (300 MHz) at RT.

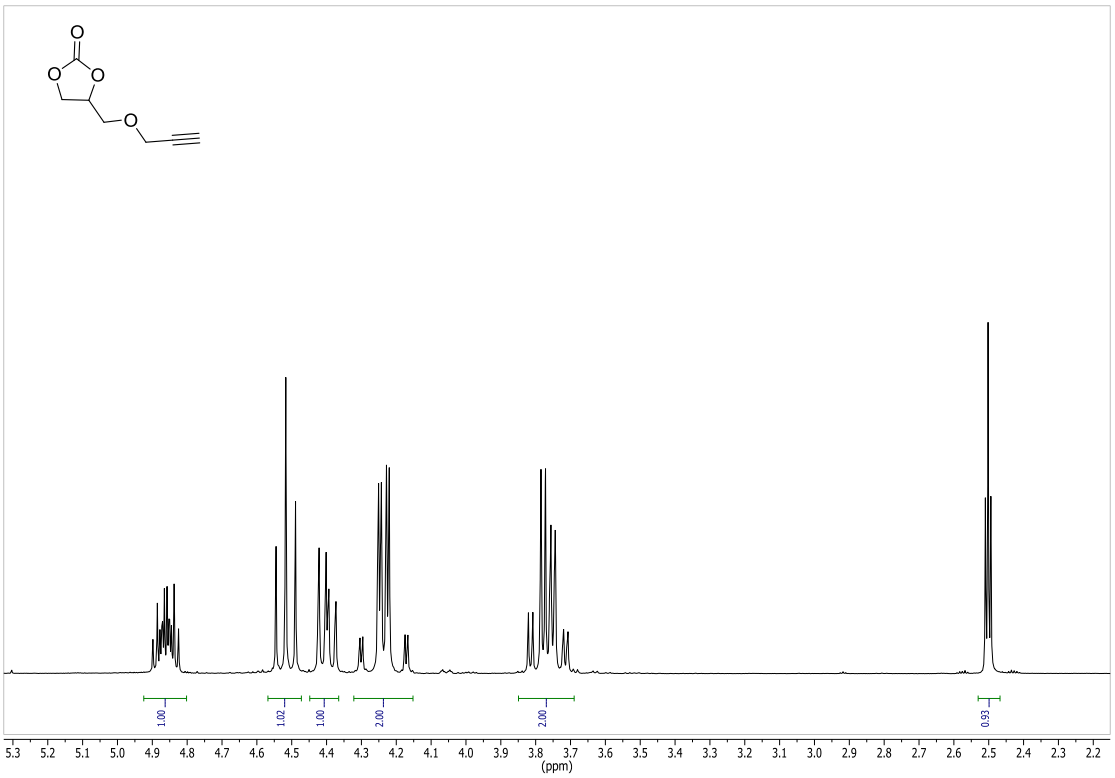


Figure 29. IR spectrum of 4-((prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one **[10i]**.

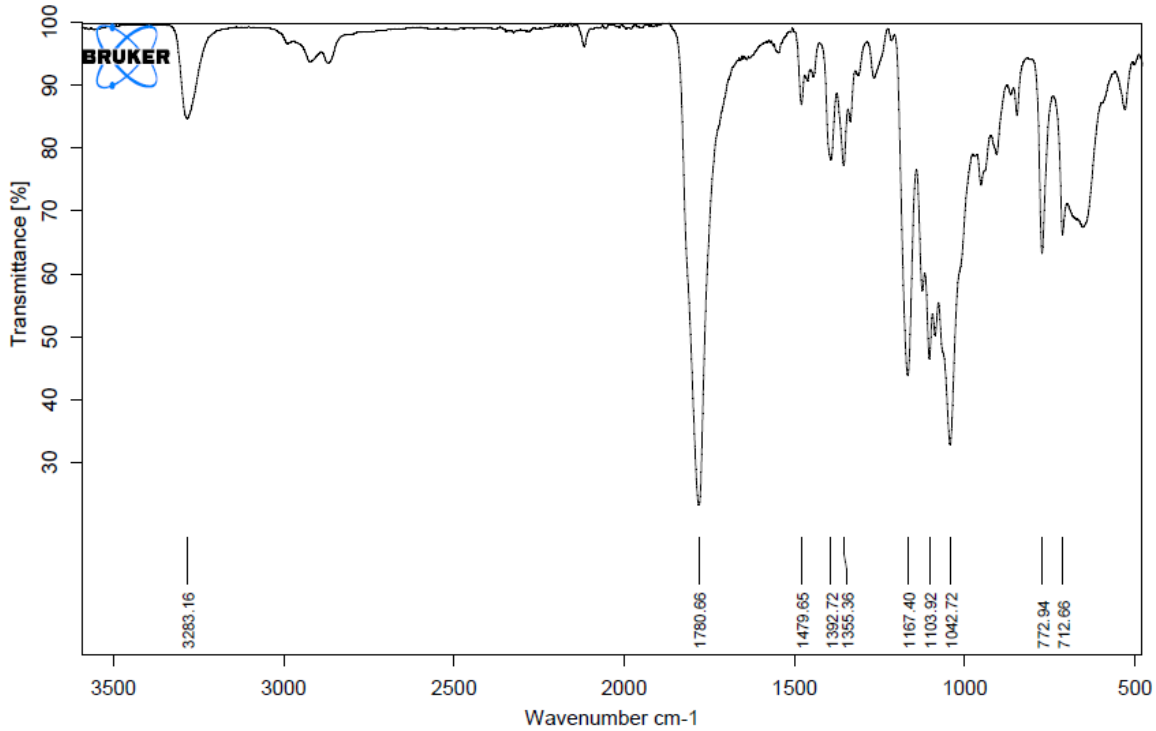


Figure 30. ^{1}H NMR spectrum of 8,8a-dihydro-3aH-indeno[1,2-d][1,3]dioxol-2-one **[10j]** in $CDCl_3$ (300 MHz) at RT.

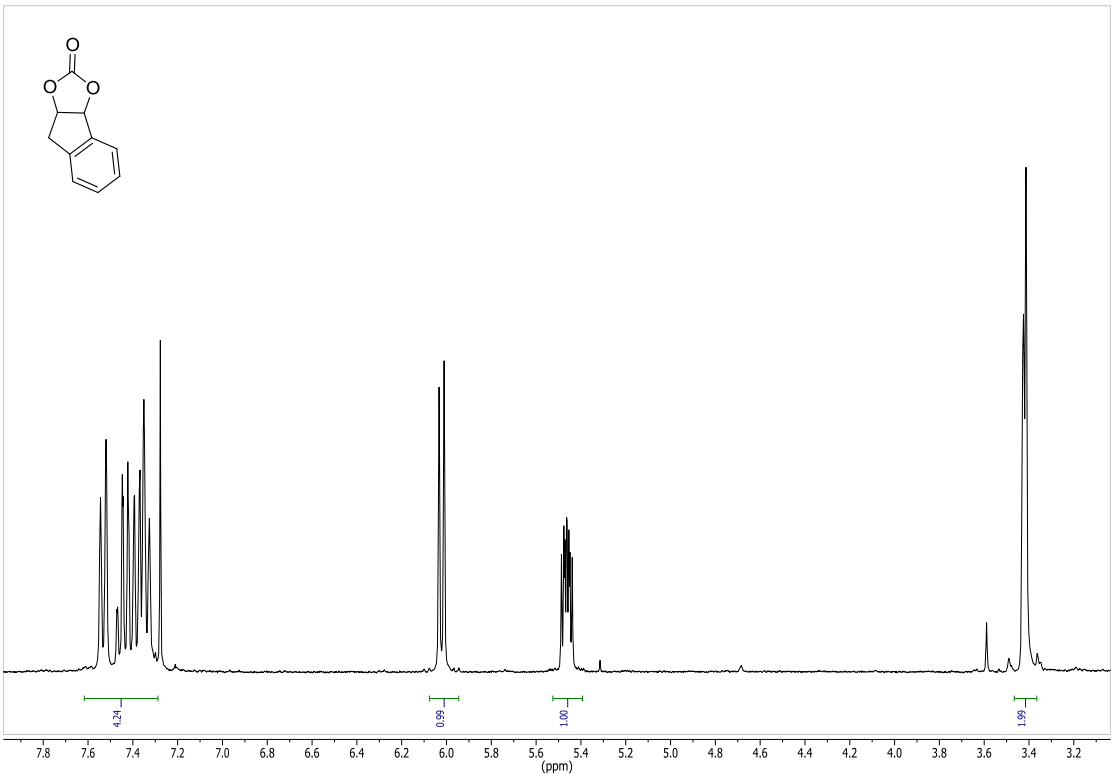


Figure 31. IR spectrum of 8,8a-dihydro-3aH-indeno[1,2-d][1,3]dioxol-2-one **[10j]**.

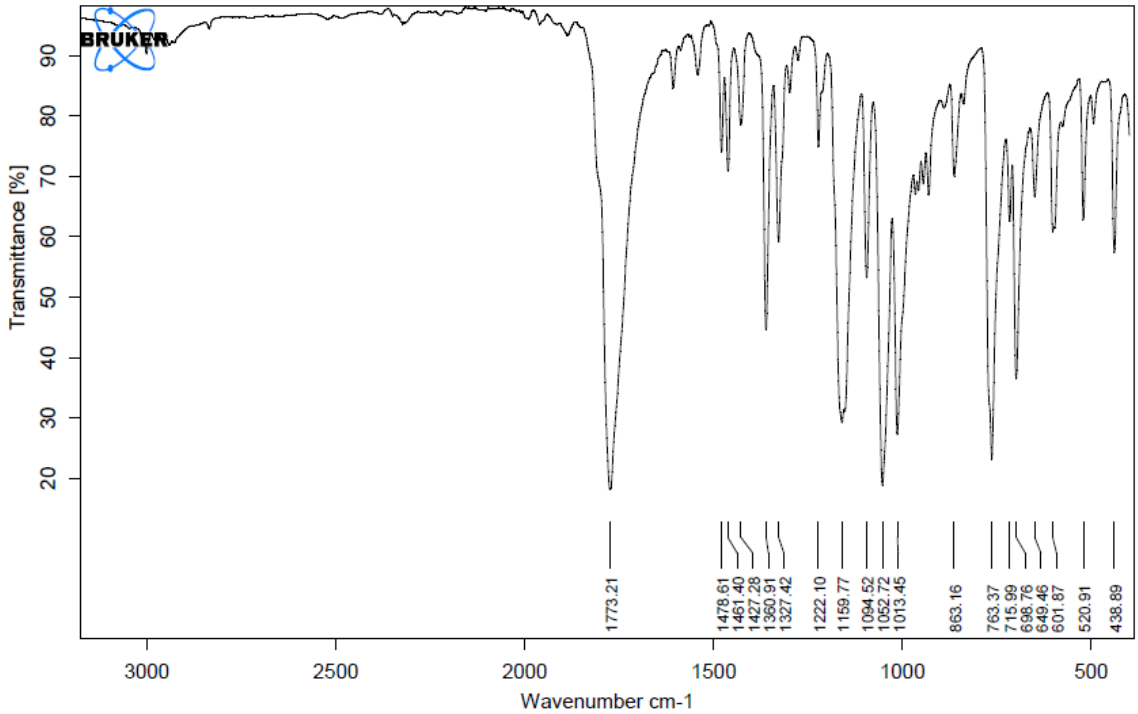


Figure 32. ^{1}H NMR spectrum of 4-(morpholinomethyl)-1,3-dioxolan-2-one **[10k]** in $CDCl_3$ (300 MHz) at RT.

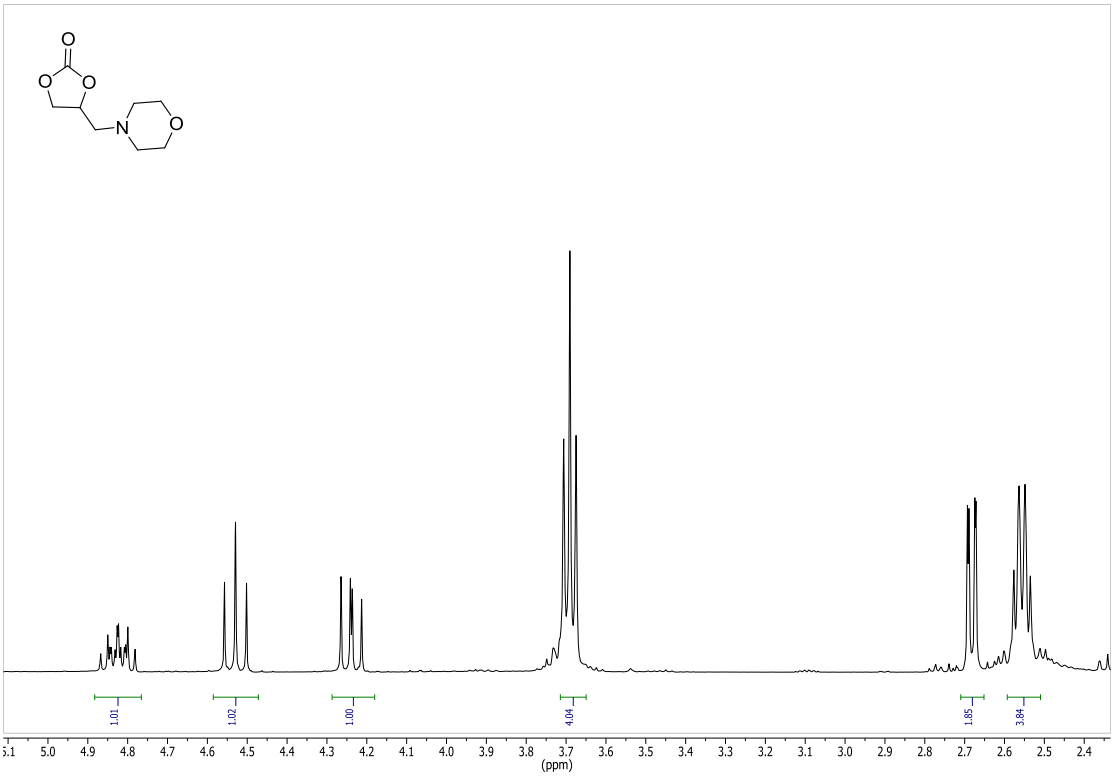


Figure 33. IR spectrum of 4-(morpholinomethyl)-1,3-dioxolan-2-one **[10k]**.

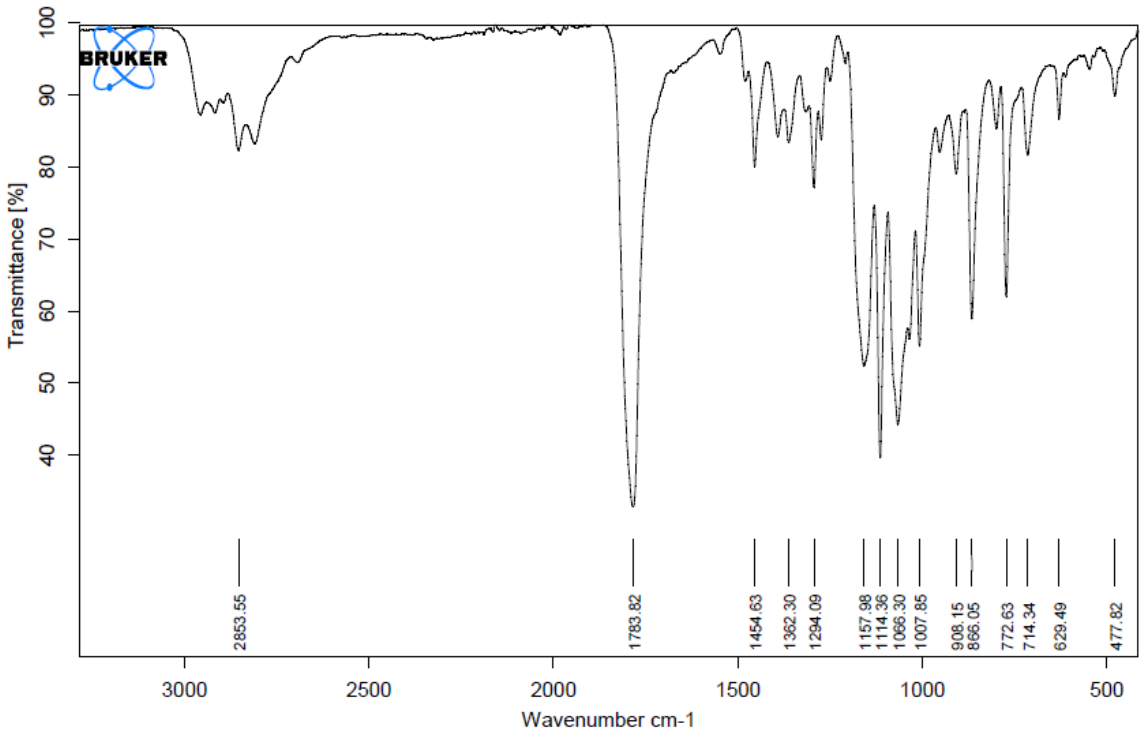


Figure 34. ^{1}H NMR spectrum of 1,4-di(oxiran-2-yl)butane **[10l]** in $CDCl_3$ (300 MHz) at RT.

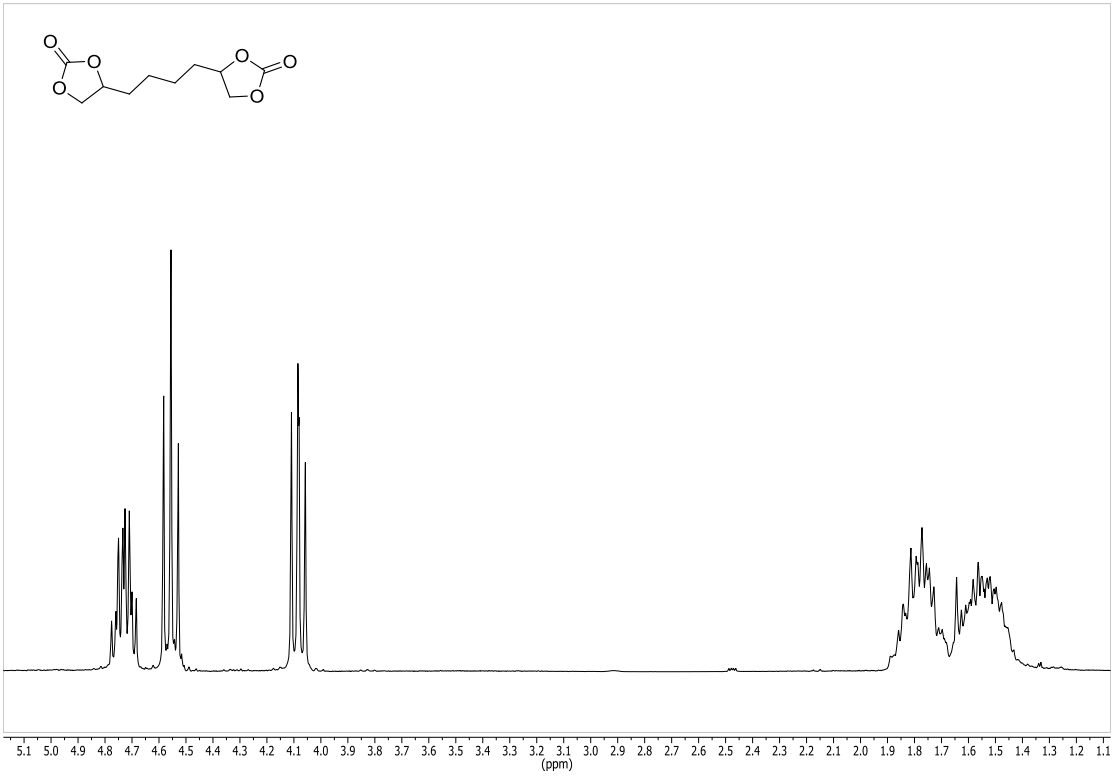
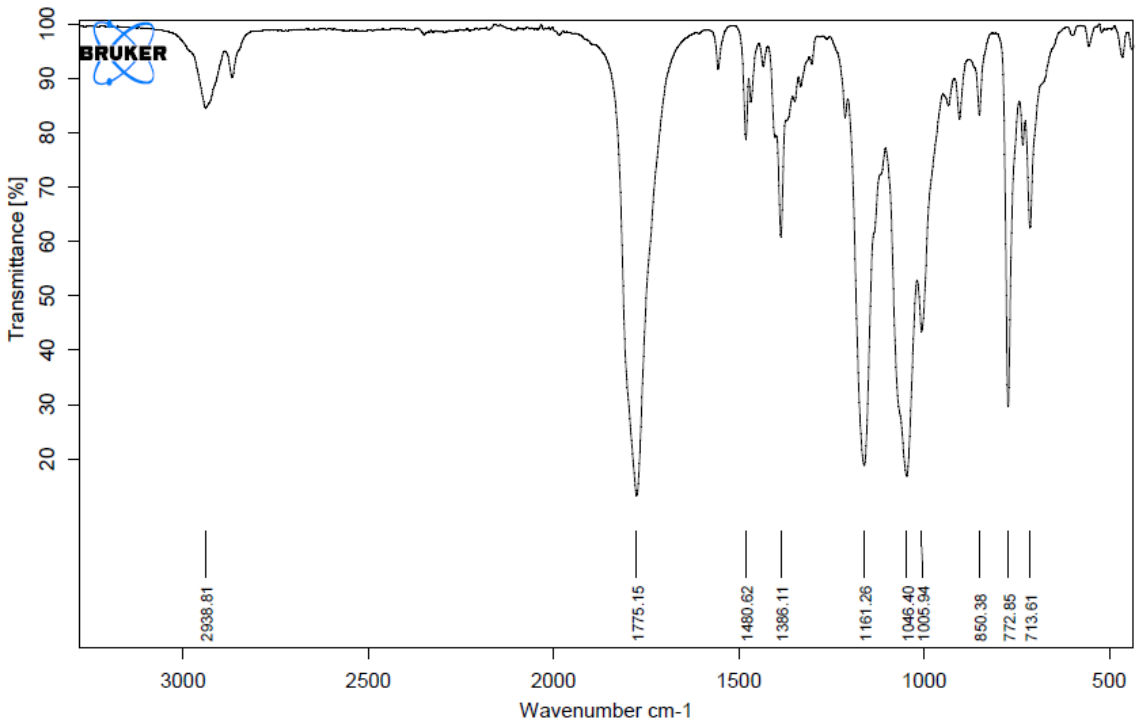


Figure 35. IR spectrum of 1,4-di(oxiran-2-yl)butane **[10l]**.



ADDITIONAL IR, ^{1}H AND ^{13}C NMR SPECTRA OF PRODUCTS FROM FIGURE 4:

Figure 36. ^{1}H NMR spectrum of 4-*tert*butoxymethyl-1,3-dioxolan-2-one **[10f]** in $CDCl_3$ (500 MHz) at RT.

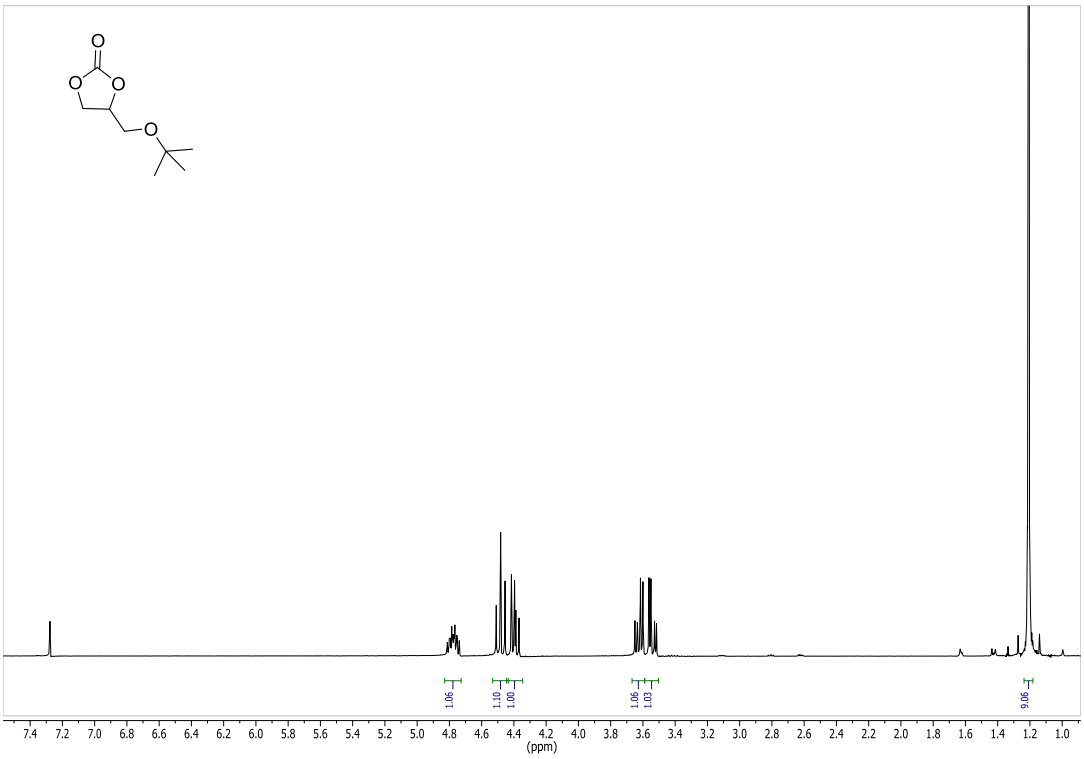


Figure 37. ^{13}C NMR spectrum of 4-*tert*butoxymethyl-1,3-dioxolan-2-one **[10f]** in $CDCl_3$ (126 MHz) at RT.

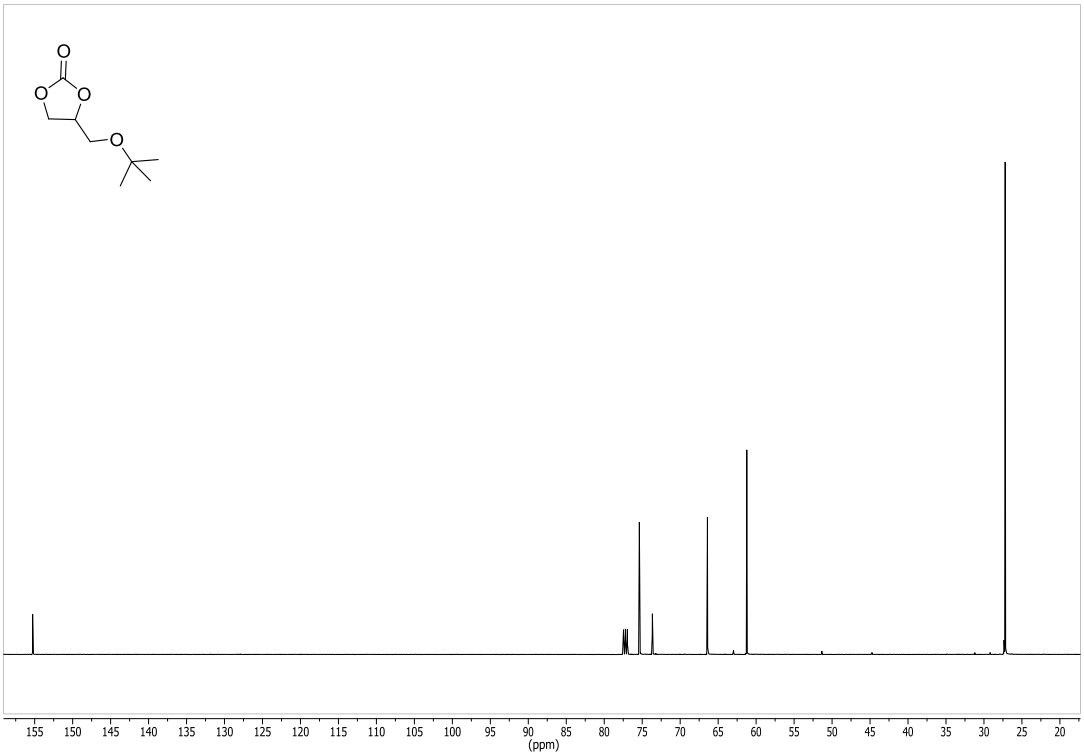


Figure 38. IR spectrum of 4-*tert*butoxymethyl-1,3-dioxolan-2-one **[10f]**.

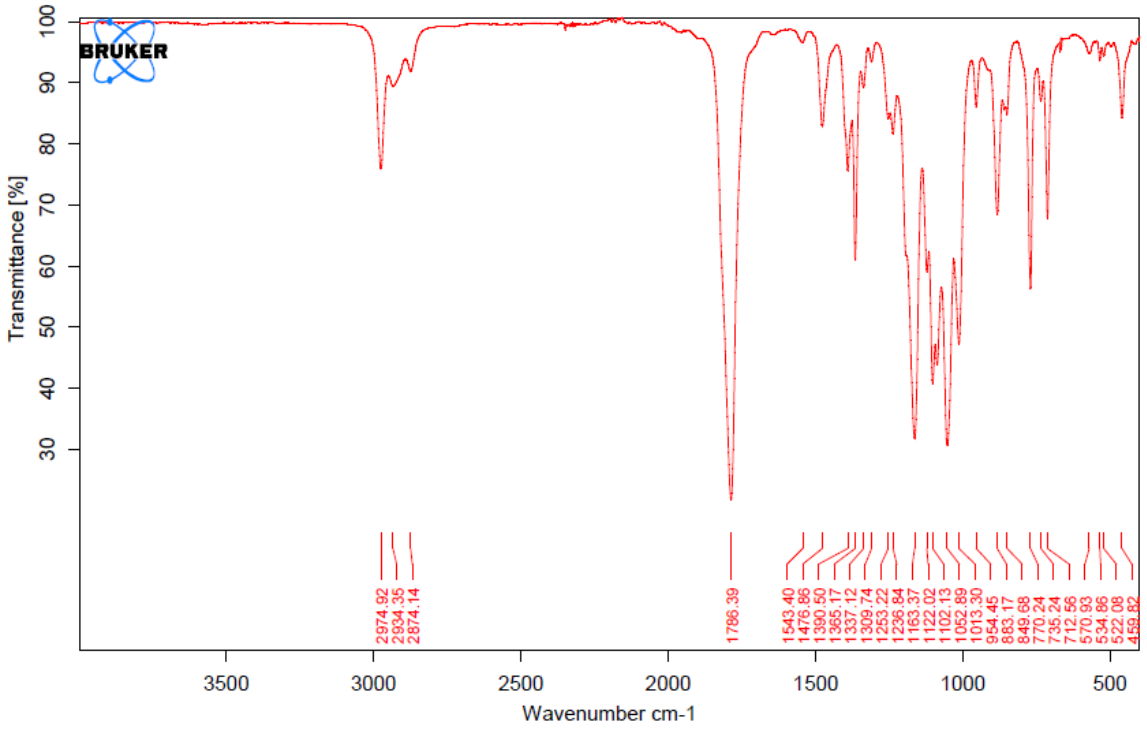
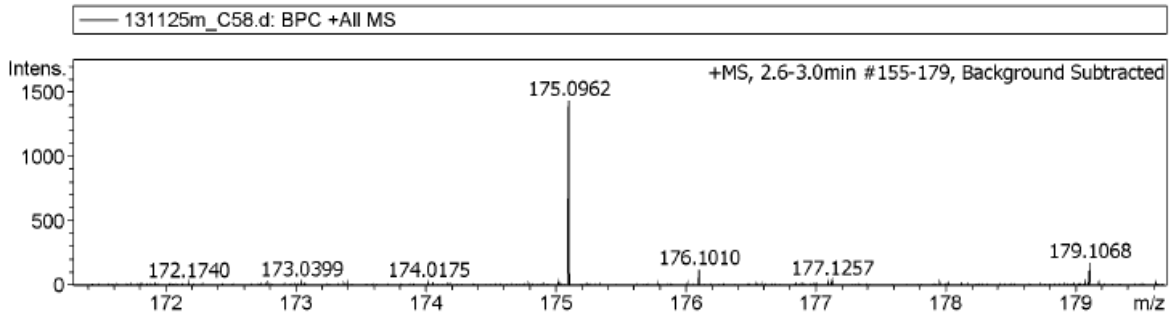


Figure 39. Mass spectrum (HR-MS) of 4-*tert*butoxymethyl-1,3-dioxolan-2-one **[10f]**.



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
175.0962	1	C8H15O4	175.0965	1.5	7.8	1	100.00	1.5	even	ok

FURTHER X-RAY CRYSTALLOGRAPHIC IMAGES OF COMPLEXES 4 AND 6:

Figure 40. Part of the coordination polymer formed by complex **4** in the solid state through Zn-N(pyr) coordinative patterns. Color codes: Zn = green, O = red, N = blue.

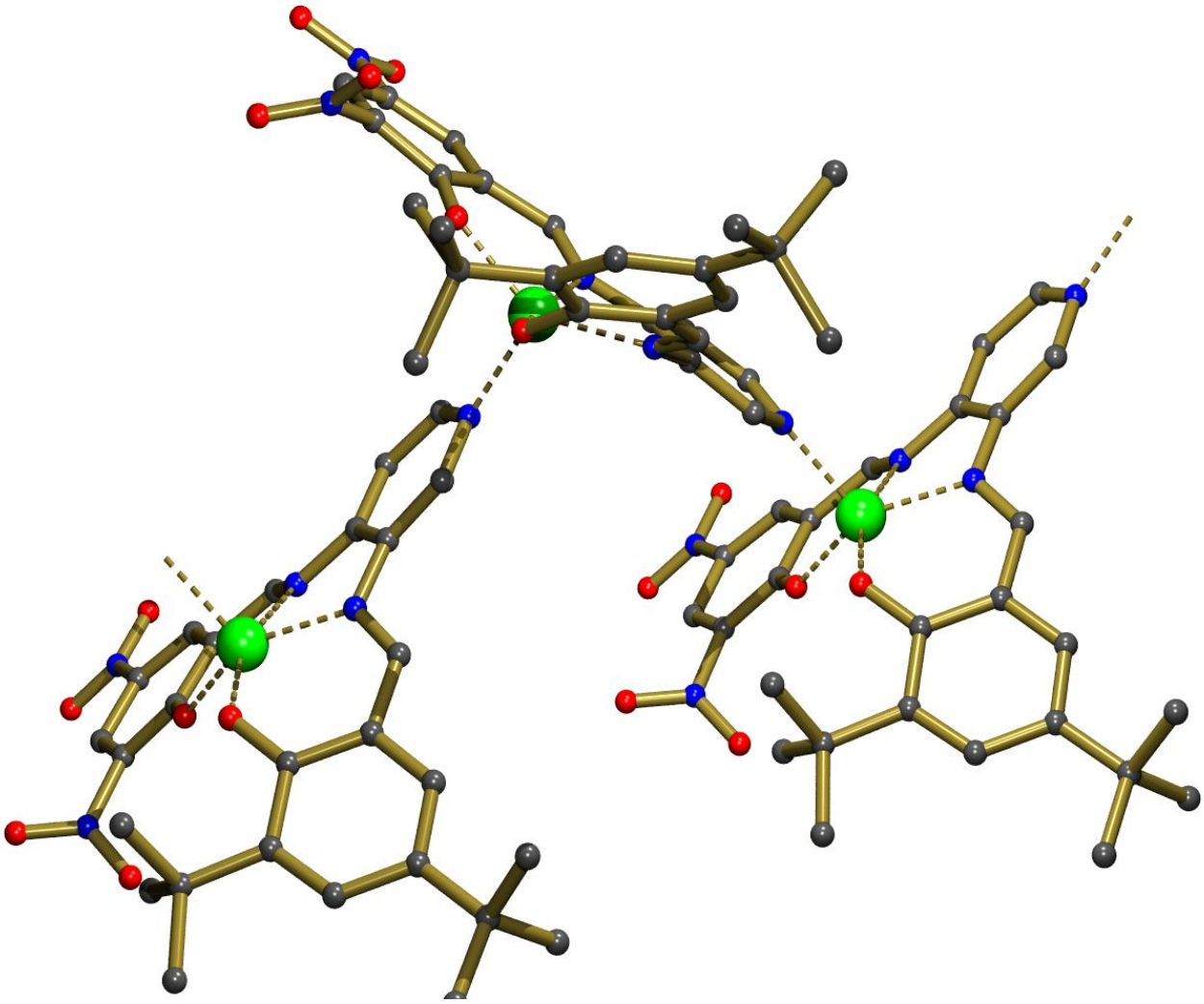
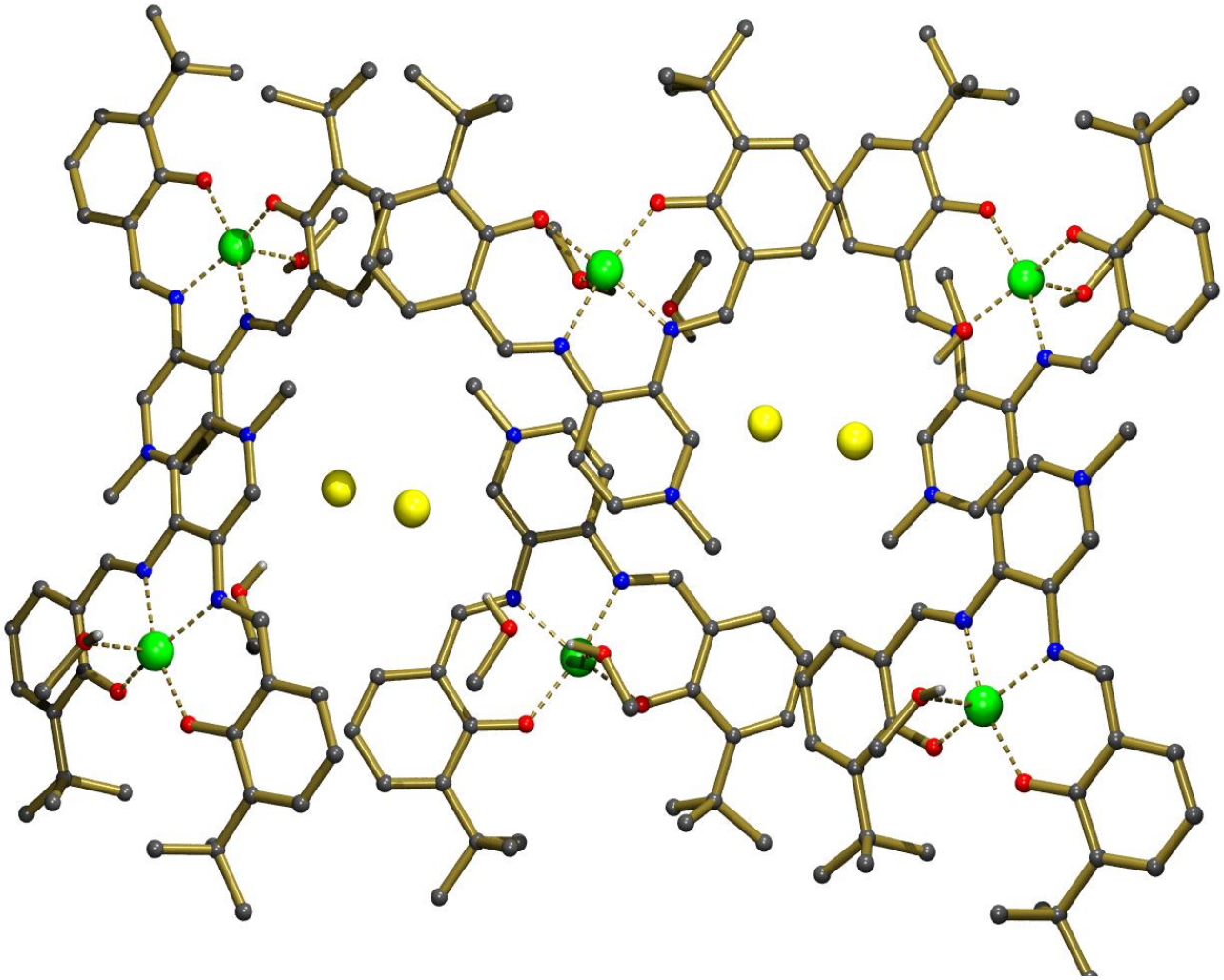


Figure 41. Part of the packing diagram for complex **6**. Color codes: Zn = green, O = red, N = blue, I = yellow.



^{1}H NMR COMPARISON BETWEEN Zn(SALPYR) 1 AND ITS N-METHYLATED FORM 6:

Figure 42: Aromatic region of the ^{1}H NMR spectrum displayed for both **1** and **6** (acetone-d_6):