*Supporting Information*

# STRUCTURE OF OXIDIZED HYDROLYSIS LIGNIN

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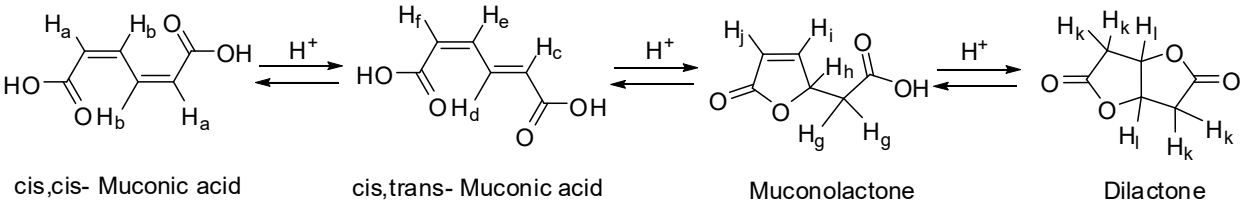
**Contents**

**1. $^1$H NMR spectra of *cis*-,*cis*-muconic acid 1 in the acid $H_2SO_4$ and TfOH showing the formation of *cis*-,*trans*-muconic acid 1, muconolactone 2 and dilactone 3**



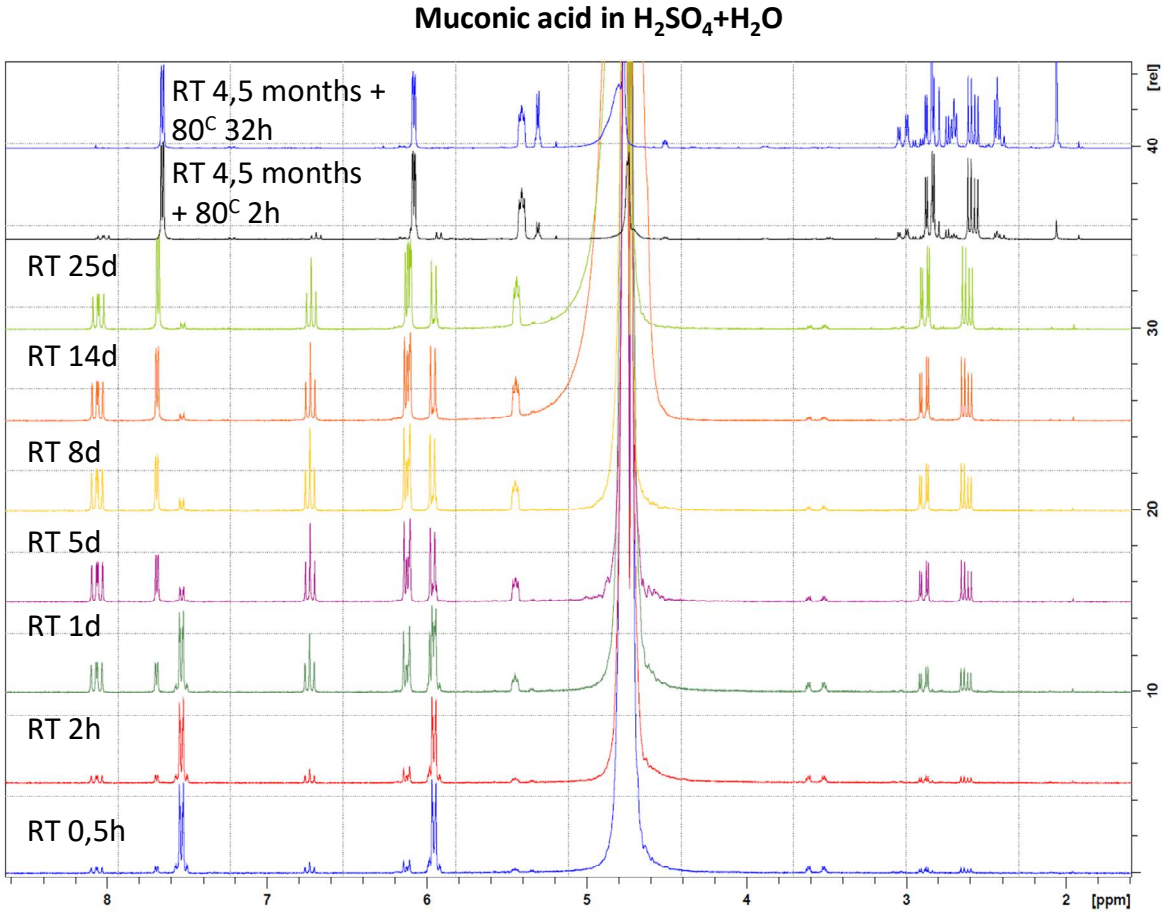




Fig. S1. Monitoring of $^1$H NMR spectra of *cis*-,*cis*-muconic acid **1** in $H_2SO_4$-$H_2O$ (400 MHz).

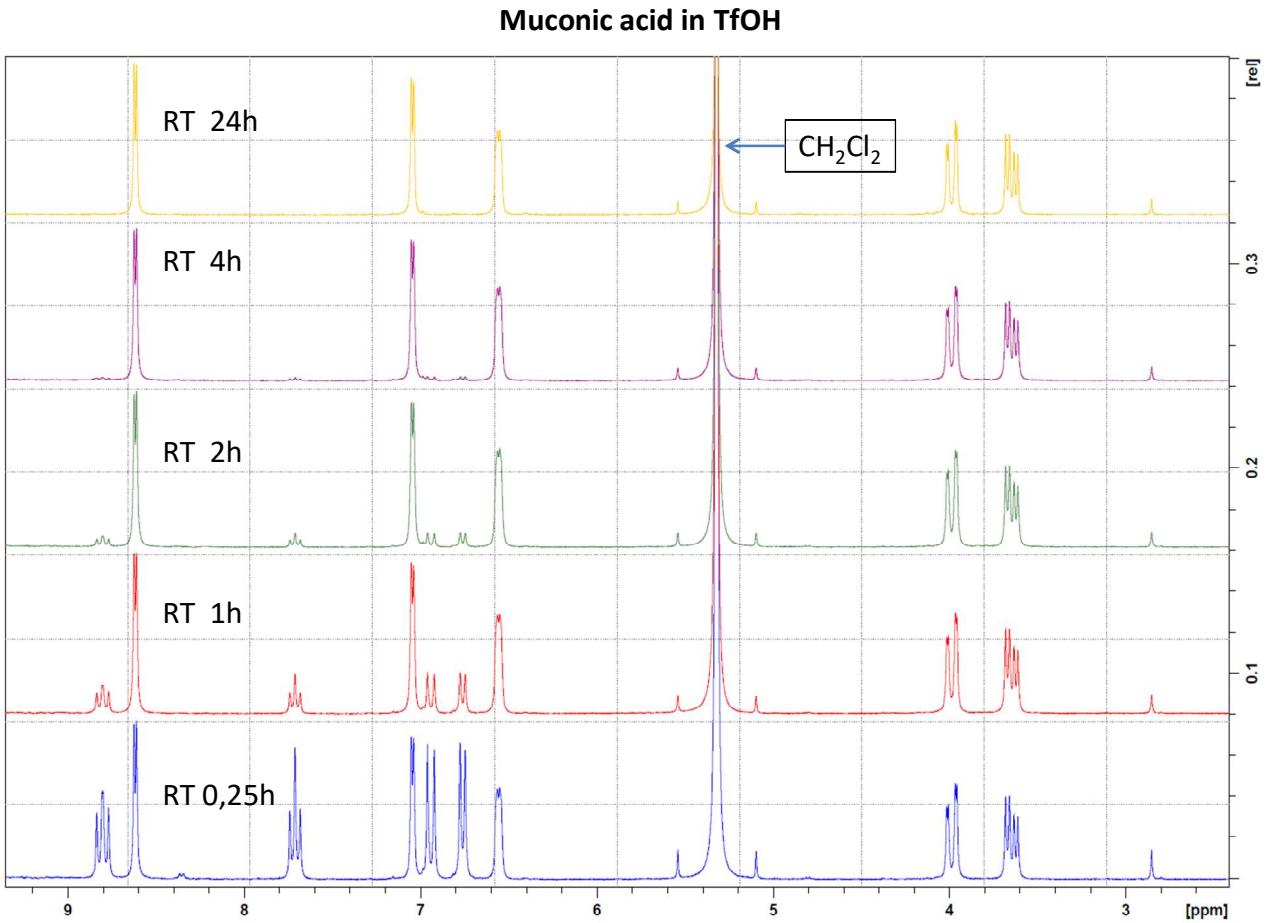



Fig. S2. Monitoring of $^1$H NMR spectra of *cis*-,*cis*-muconic acid **1** in TfOH (400 MHz).

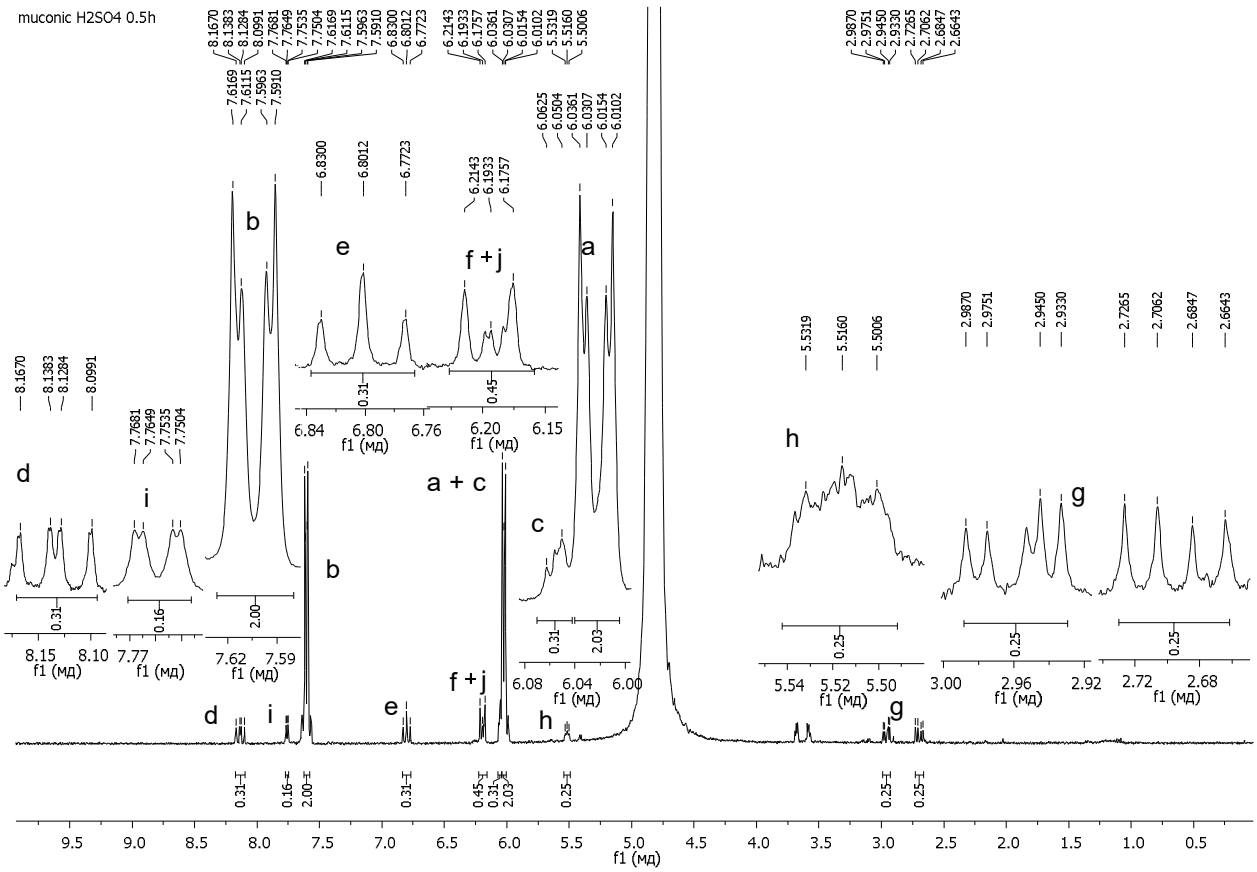



Fig. S3. $^1$H NMR spectrum of muconic acid in $H_2SO_4$-$H_2O$ (400 MHz), (r.t., after 0.25 h).

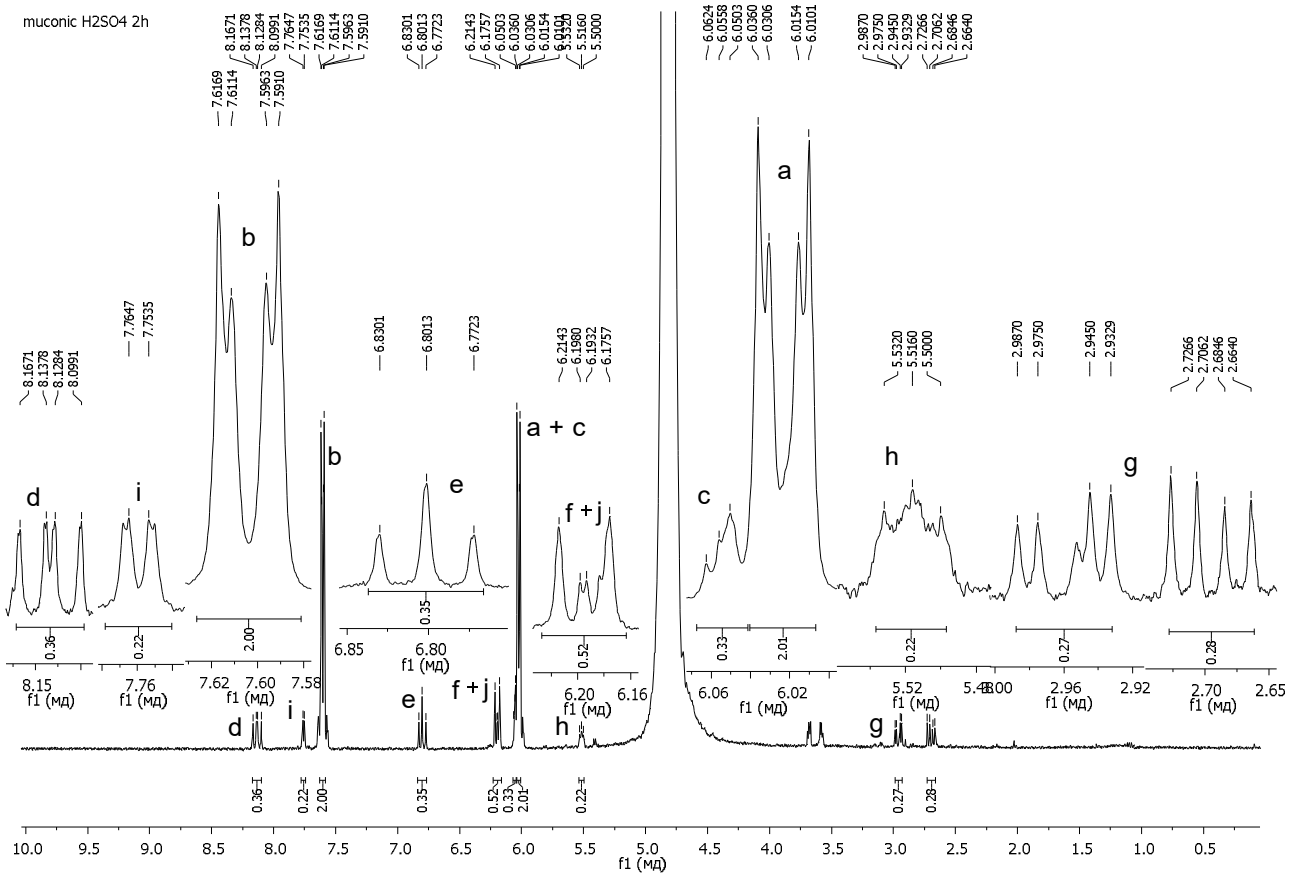



Fig. S4. $^{1}$H NMR spectrum of muconic acid in $H_2SO_4$-$H_2O$ (400 MHz), (r.t., after 2 h).

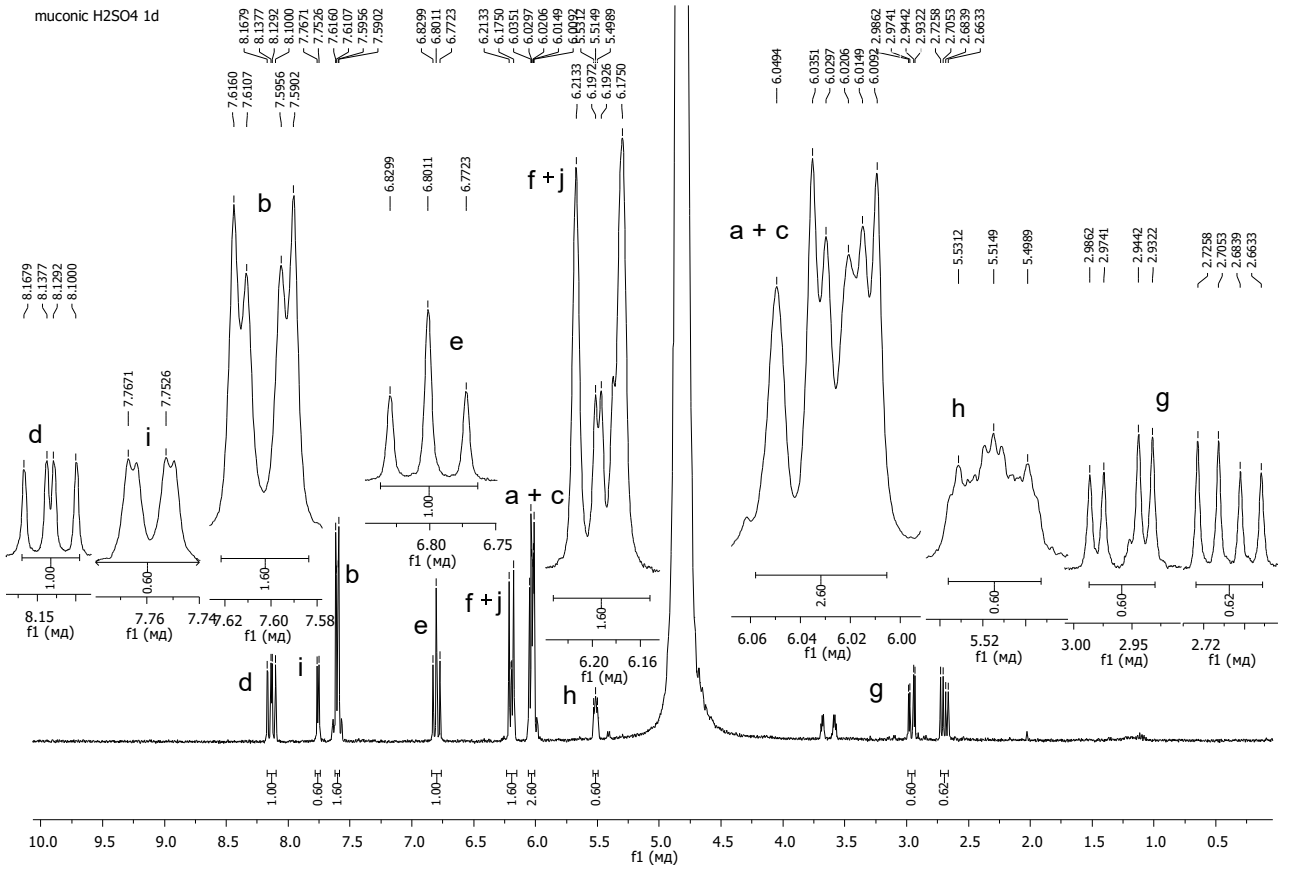



Fig. S5. $^{1}$H NMR spectrum of muconic acid in $H_2SO_4$-$H_2O$ (400 MHz), (r.t., after 1 d).

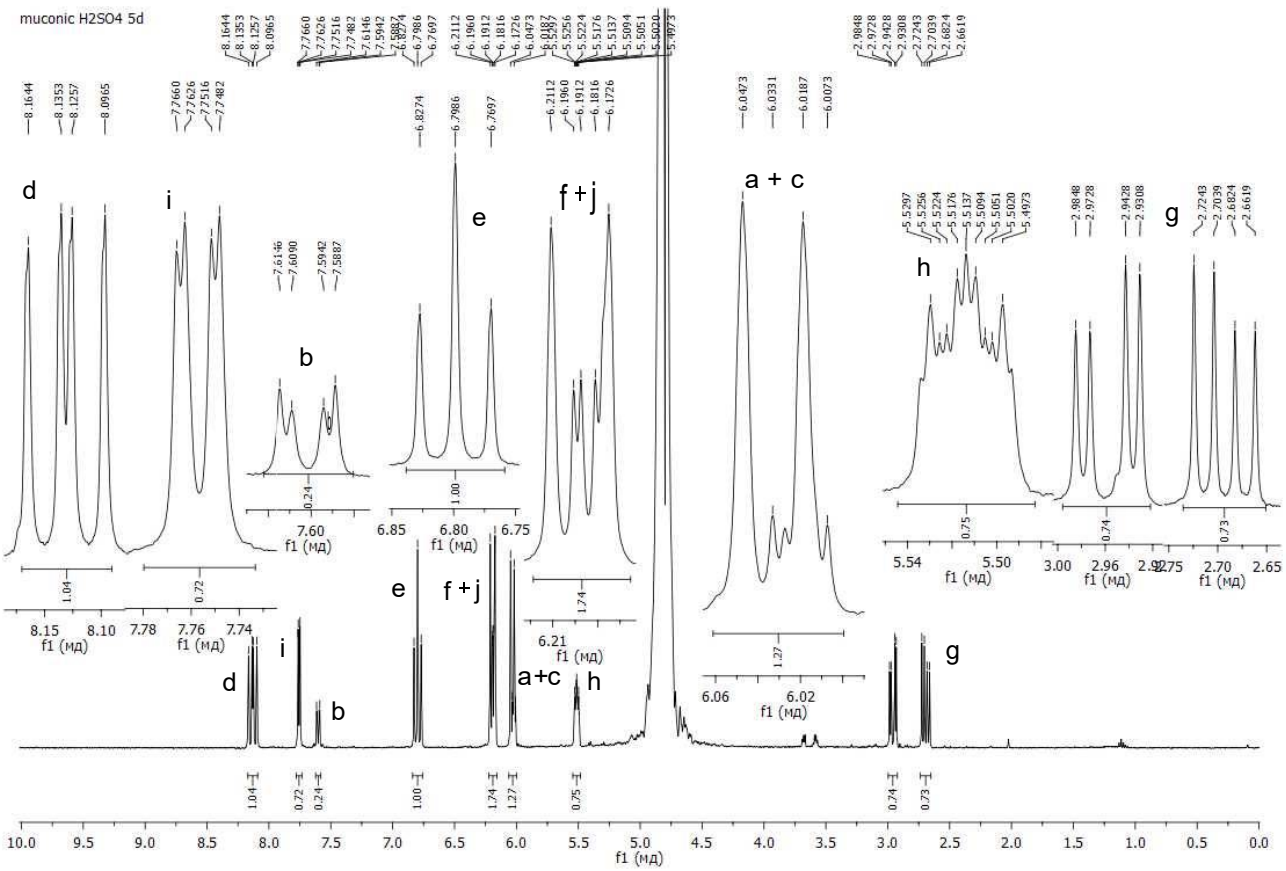



Fig. S6. $^{1}$H NMR spectrum of muconic acid in $H_2SO_4$-$H_2O$ (400 MHz), (r.t., after 5 d).

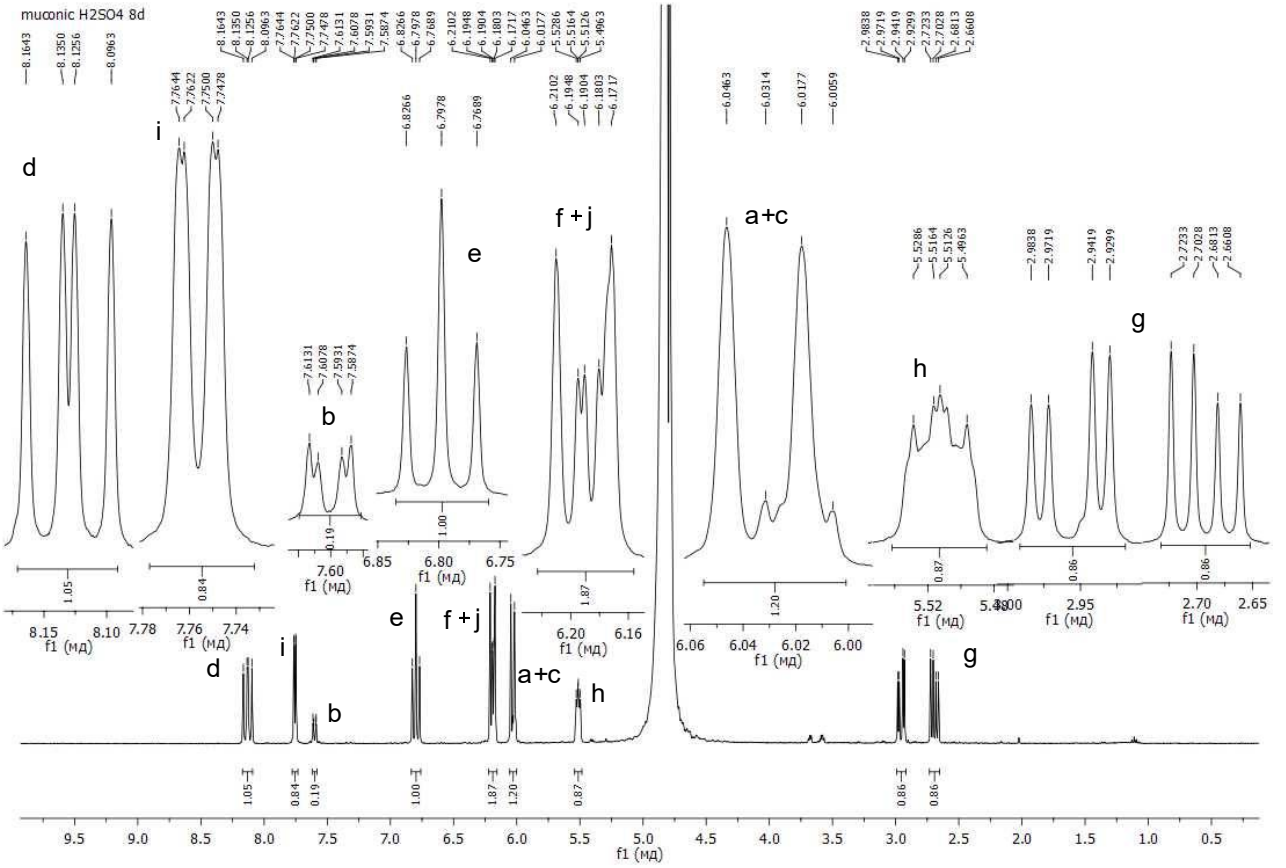



Fig. S7. $^{1}$H NMR spectrum of muconic acid in $H_2SO_4$-$H_2O$ (400 MHz), (r.t., after 8 d).

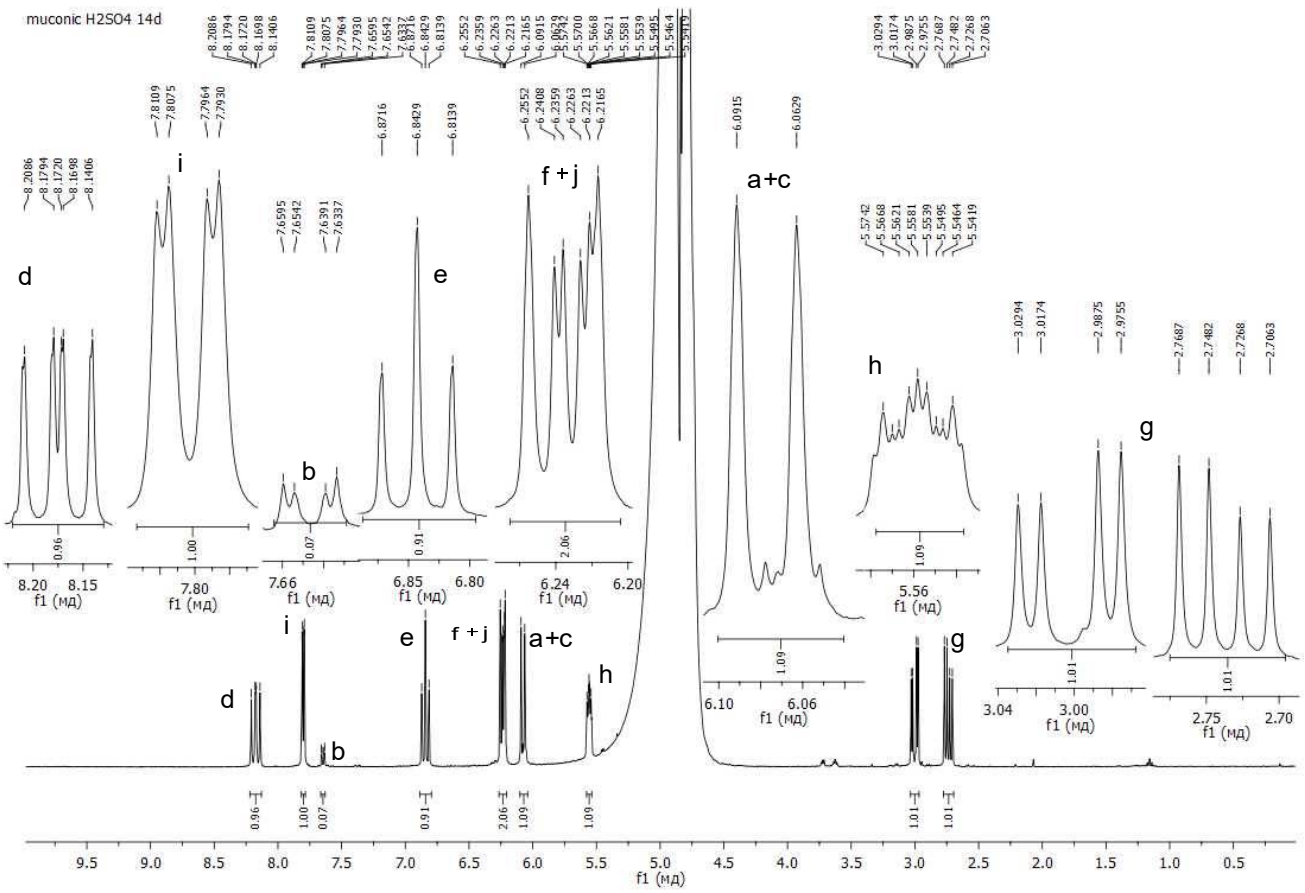



Fig. S8. $^{1}$H NMR spectrum of muconic acid in $H_2SO_4$-$H_2O$ (400 MHz), (r.t., after 14d).

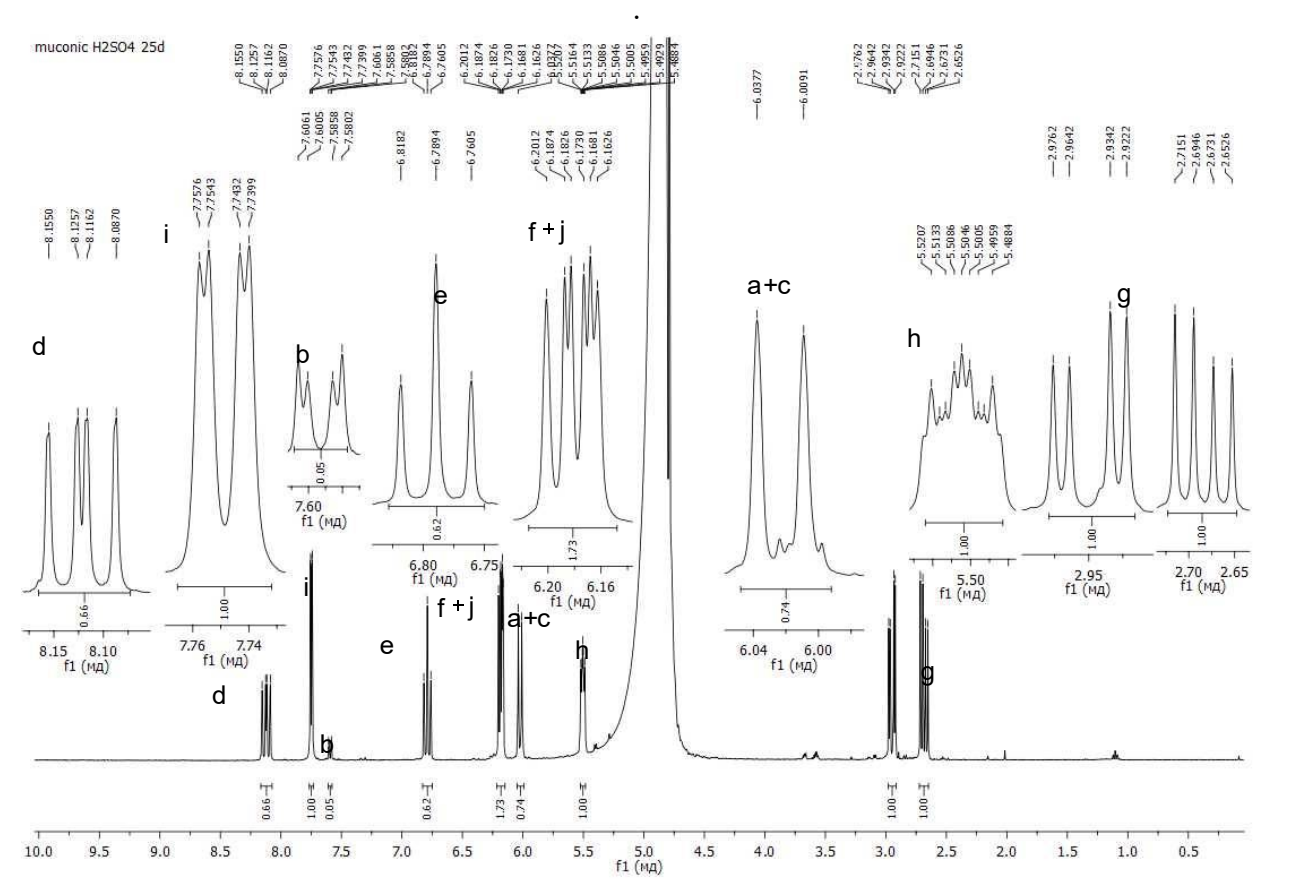



Fig. S9. $^{1}$H NMR spectrum of muconic acid in $H_2SO_4$-$H_2O$ (400 MHz), (r.t., after 25 d).

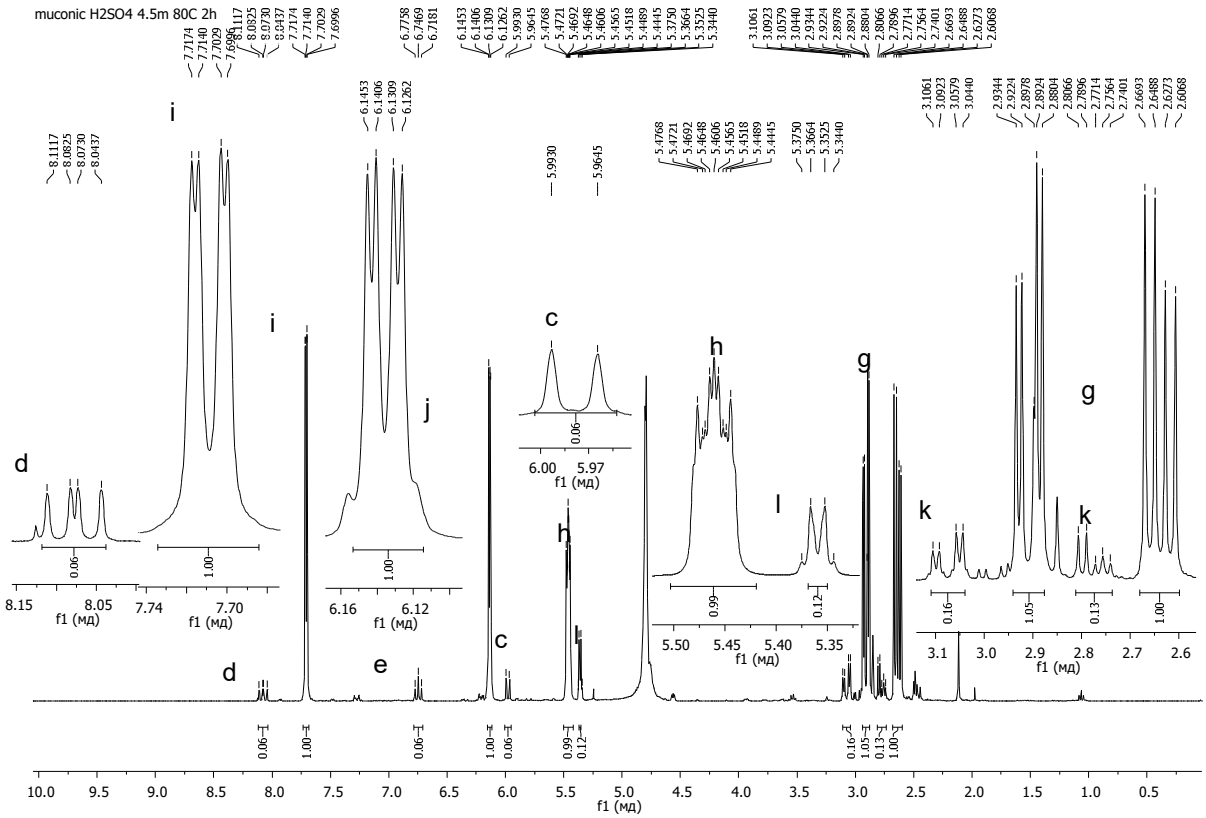



Fig. S10. $^{1}$H NMR spectrum of muconic acid in $H_2SO_4$-$H_2O$ (400 MHz), (r.t., after 4.5 months and heating at 80°C, 2h).

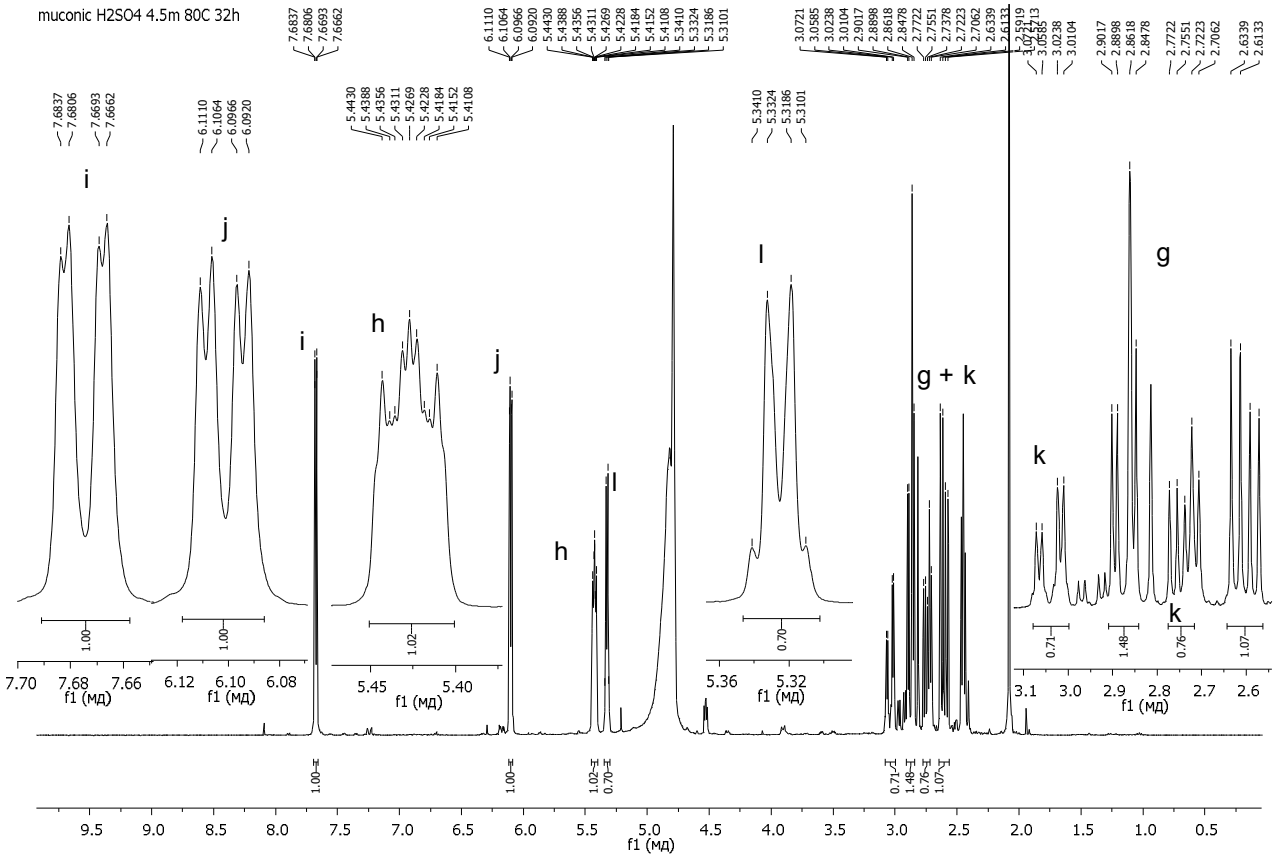



Fig. S11. $^{1}$H NMR spectrum of muconic acid in $H_2SO_4$-$H_2O$ (400 MHz), (r.t., after 4.5 months and heating at 80°C, 32 h).

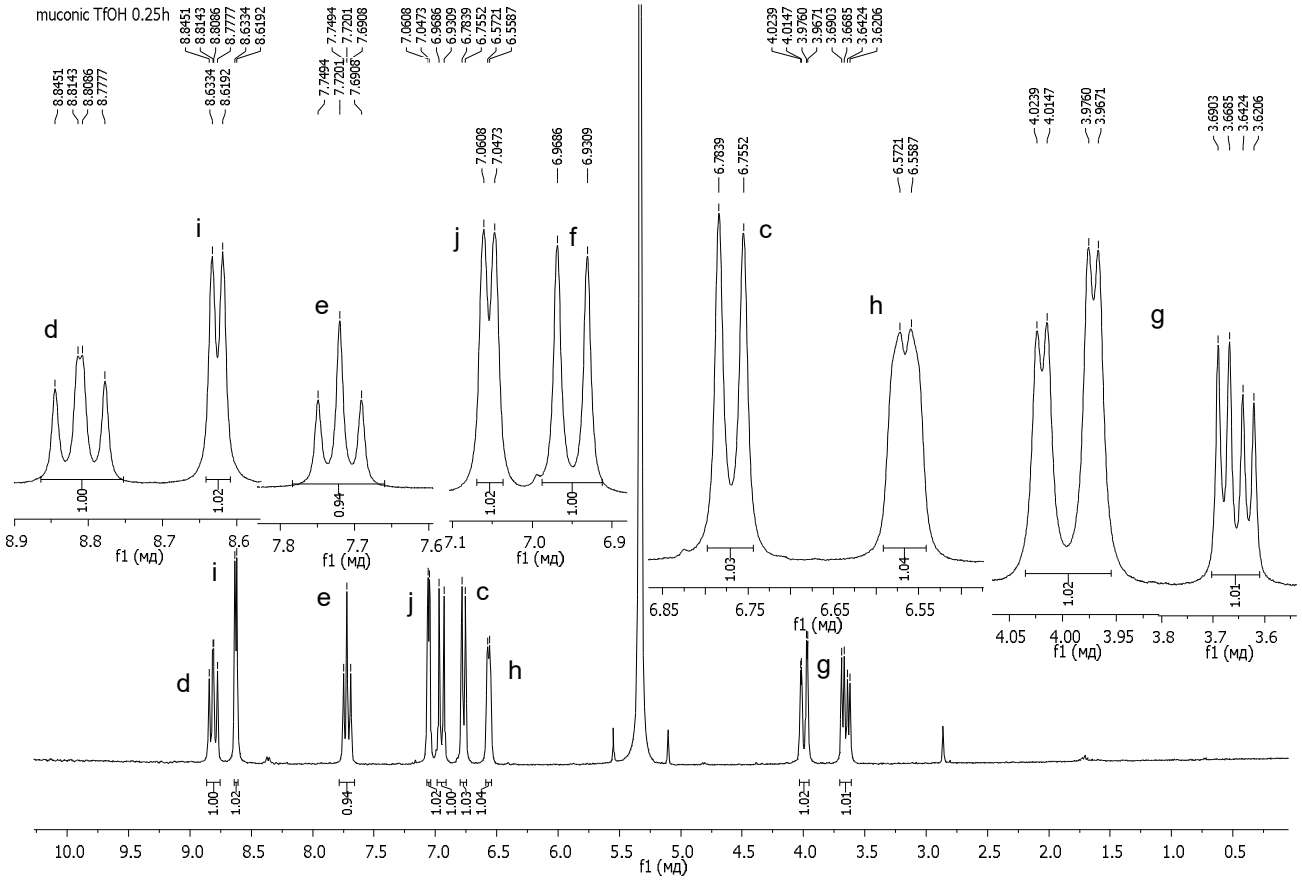



Fig. S12. $^{1}$H NMR spectrum of muconic acid in TfOH (400 MHz), (r.t., after 0.25 h).

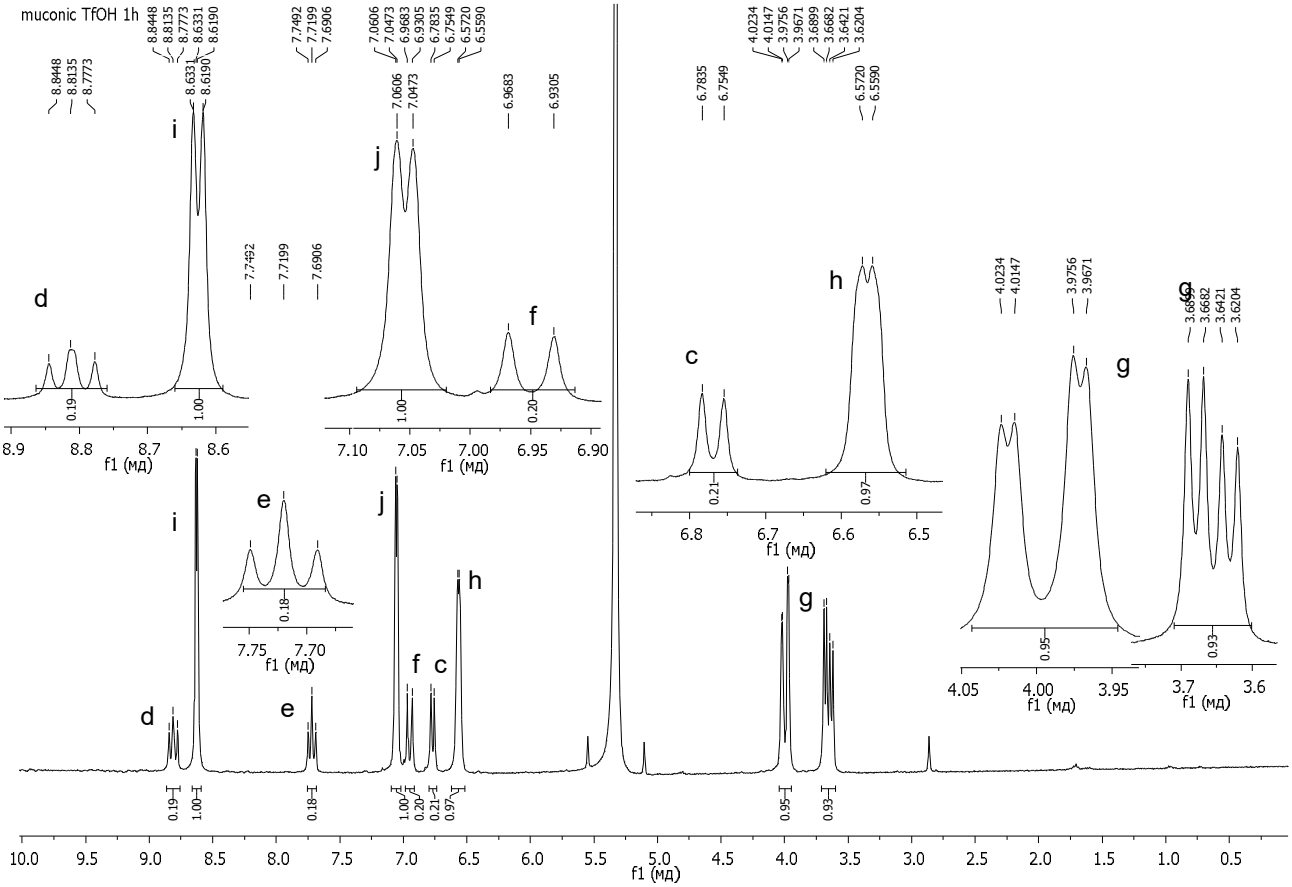



Fig. S13. $^{1}$H NMR spectrum of muconic acid in TfOH (400 MHz), (r.t., after 0.25 h).

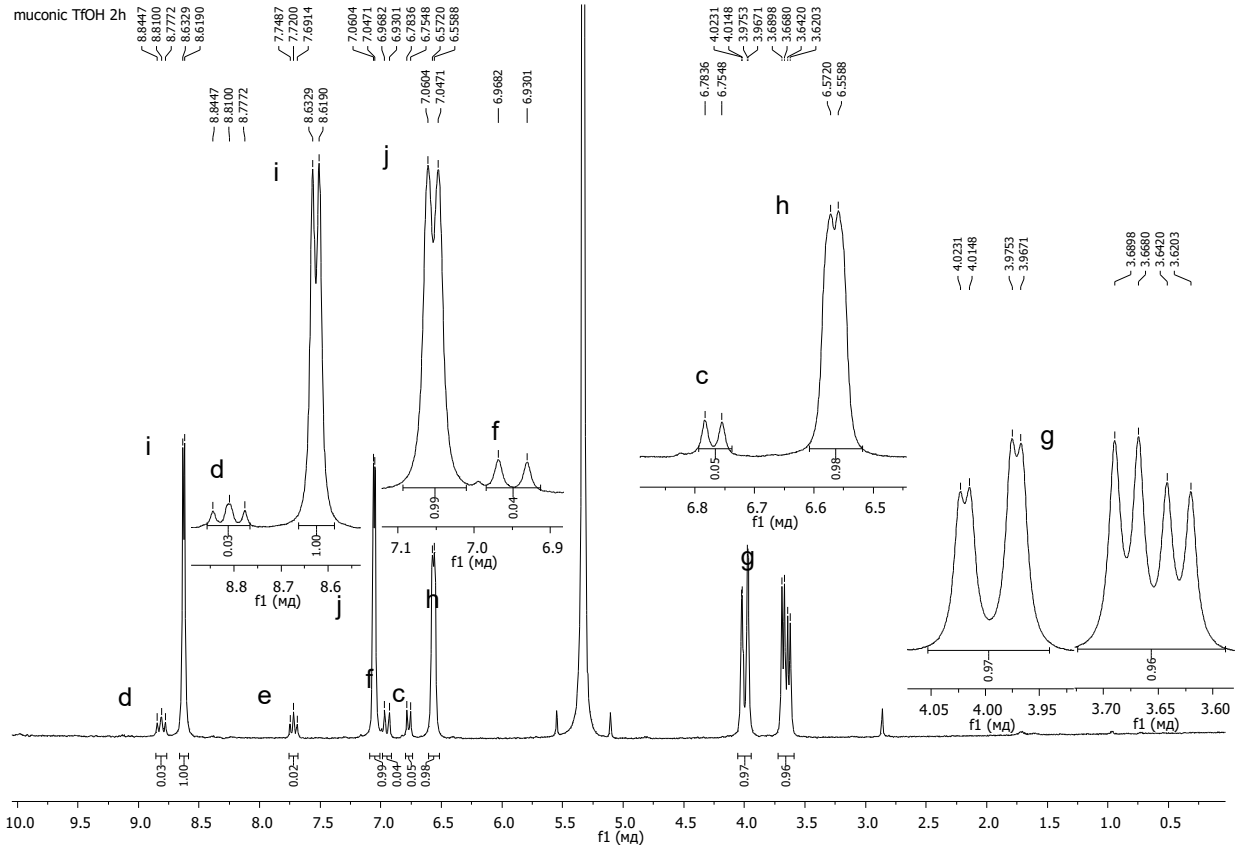



Fig. S14. $^{1}$H NMR spectrum of muconic acid in TfOH (400 MHz), (r.t., after 2 h).

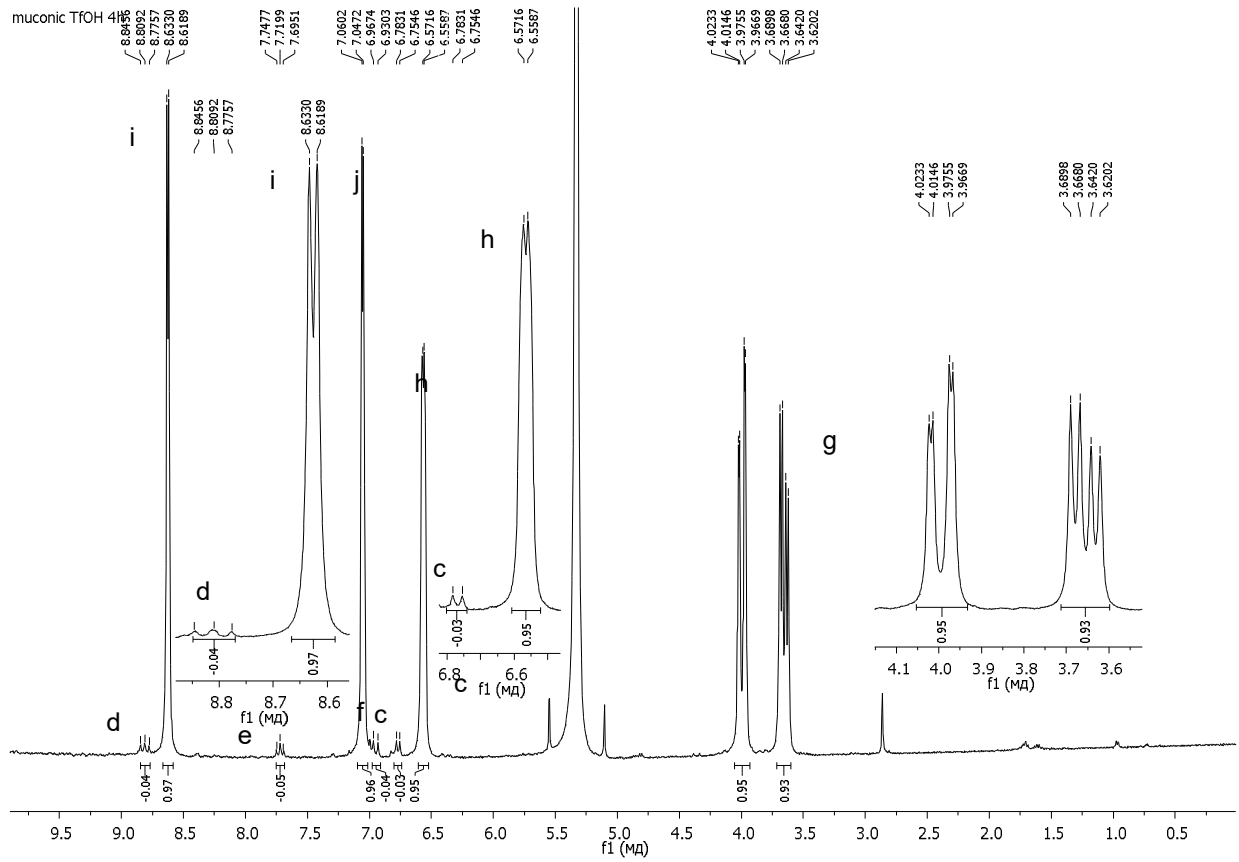



Fig. S15. $^{1}$H NMR spectrum of muconic acid in TfOH (400 MHz), (r.t., after 4 h).

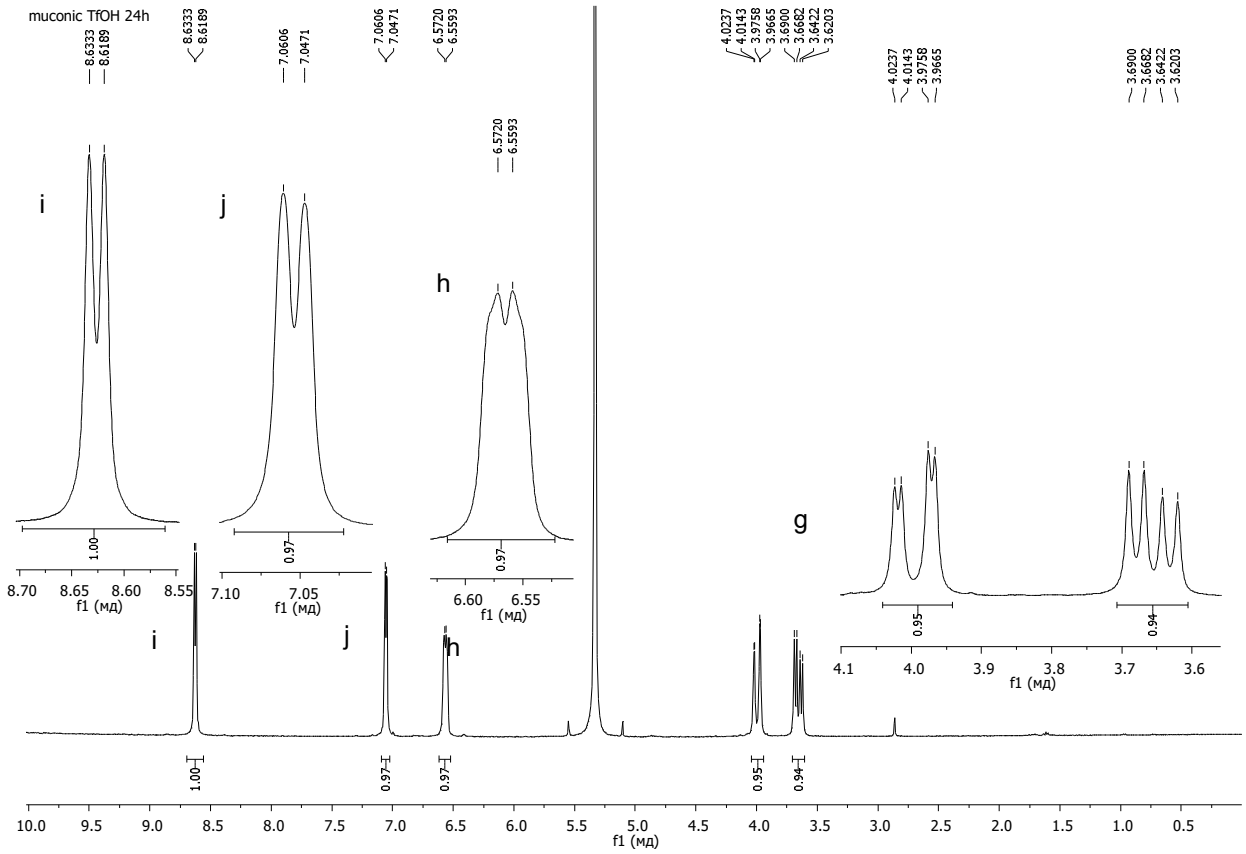



Fig. S16. $^{1}$H NMR spectrum of muconic acid in TfOH (400 MHz), (r.t., after 24 h).

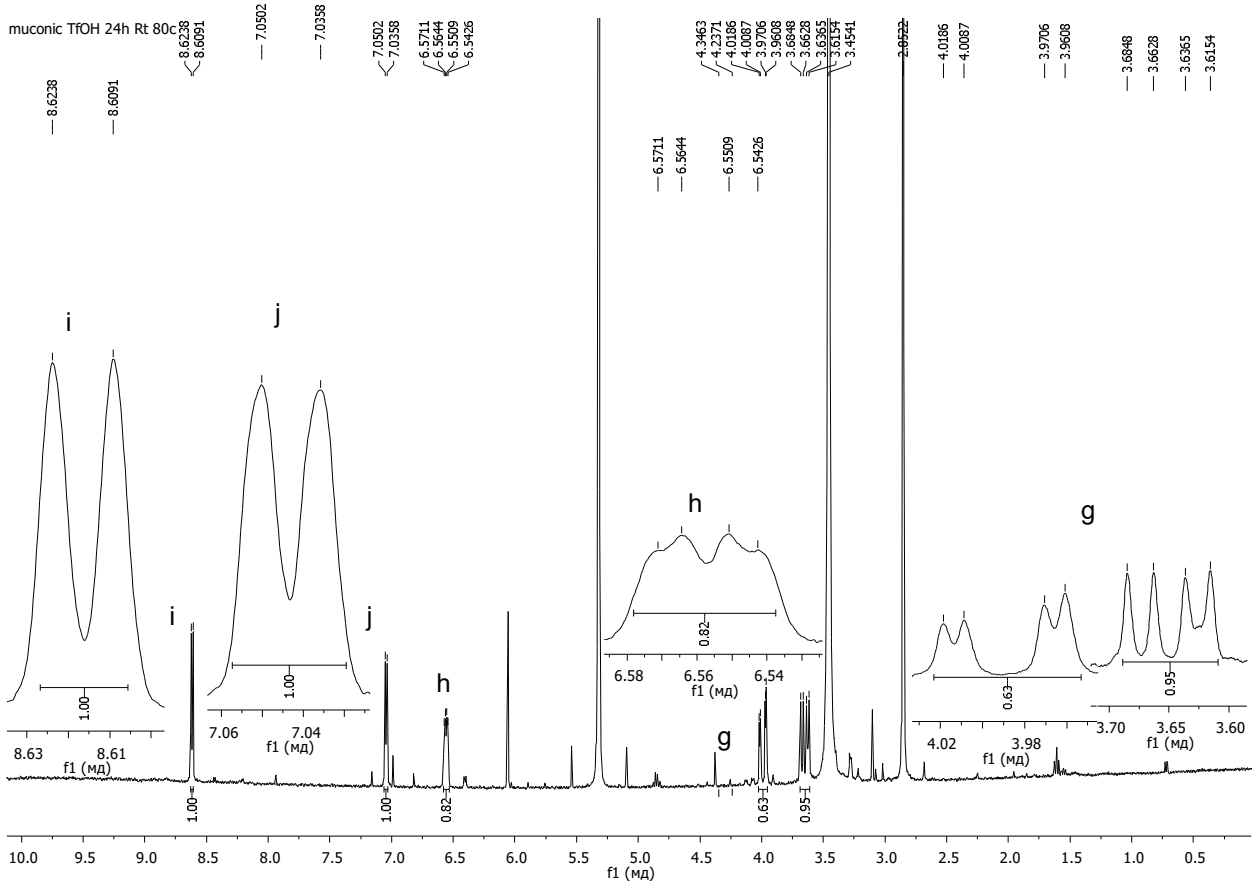



Fig. S17. $^{1}$H NMR spectrum of muconic acid in TfOH (400 MHz), (r.t., after 24 h and heating at 80ºC, 24 h).

## 2. NMR and IR spectra of derivatives of oxidized hydrolysis lignin

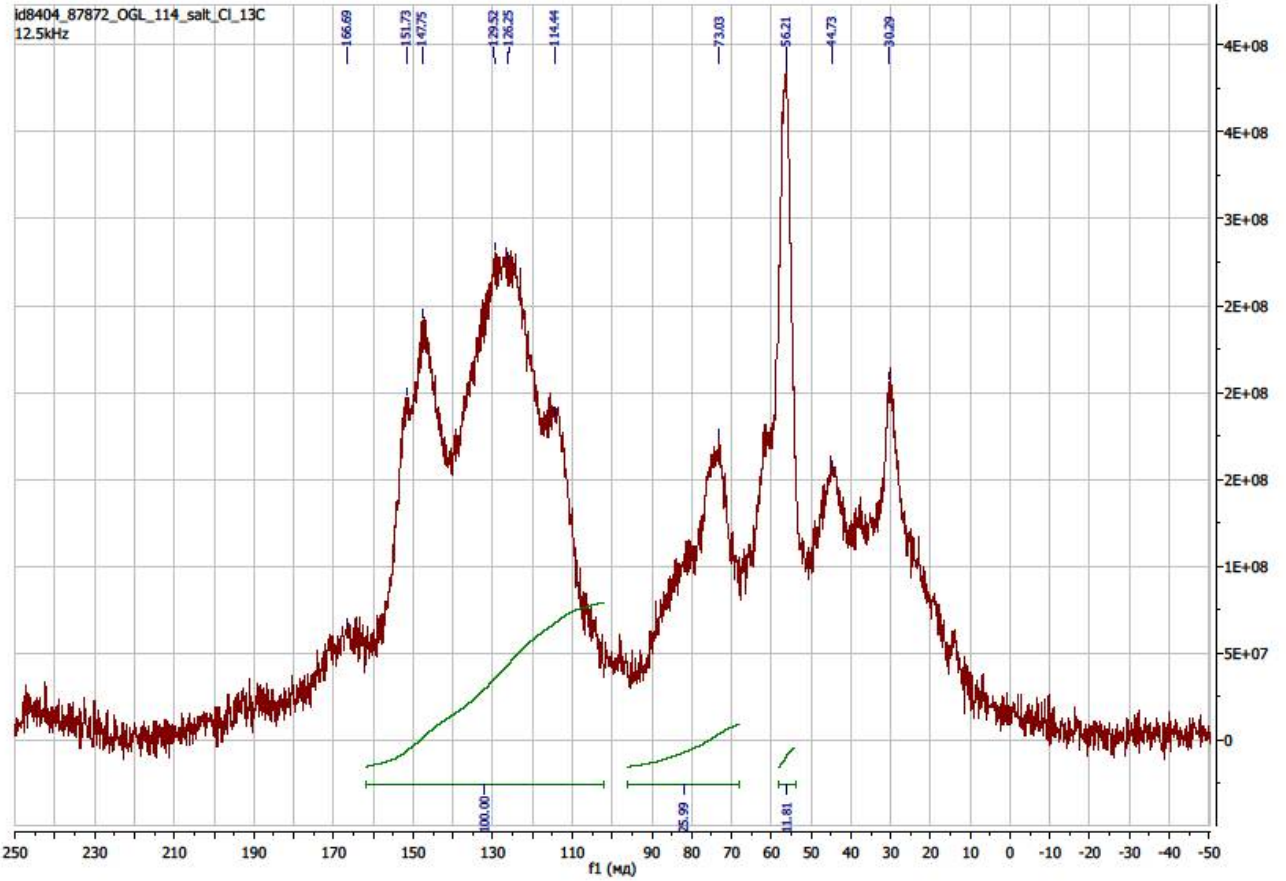



Fig. S18. Solid state $^{13}$C NMR spectrum of **Cl-OHL** (100 MHz).

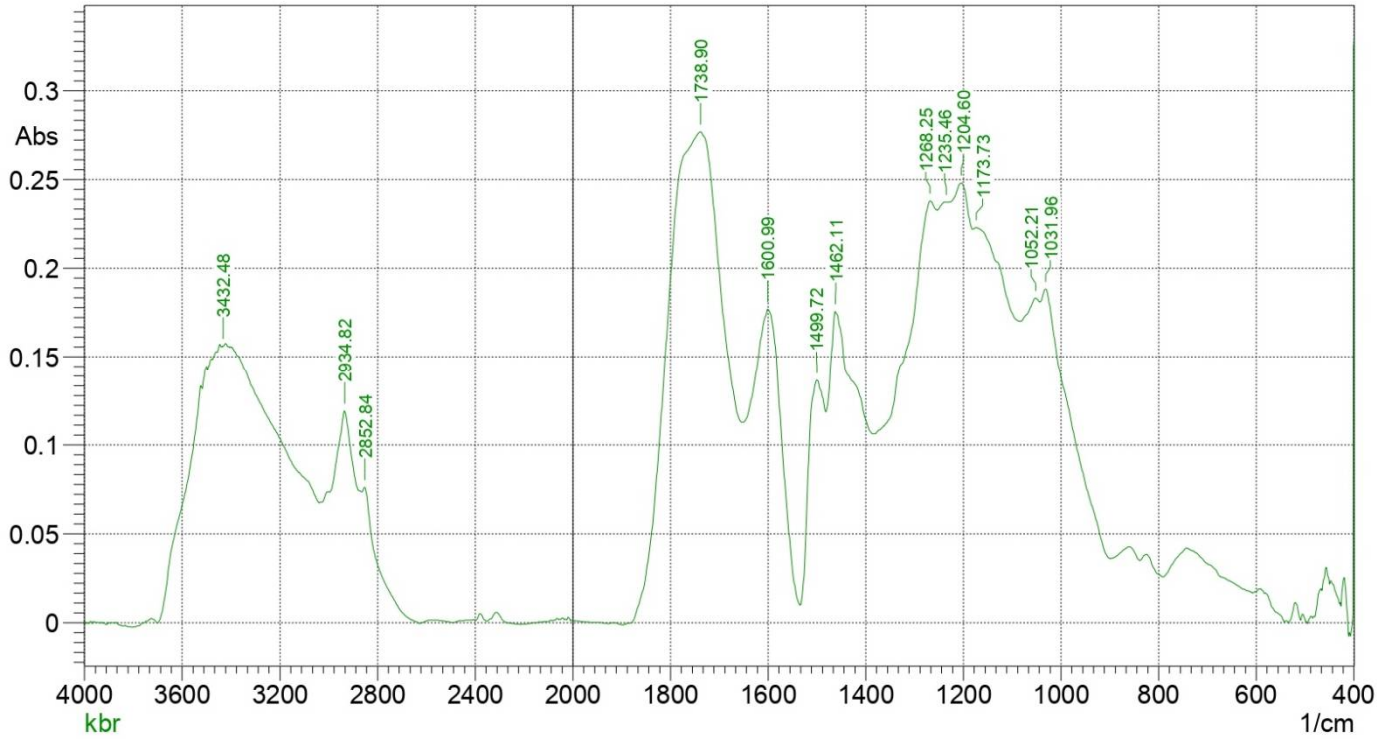



Fig. S19. IR spectrum of **Cl-OHL** (KBr).

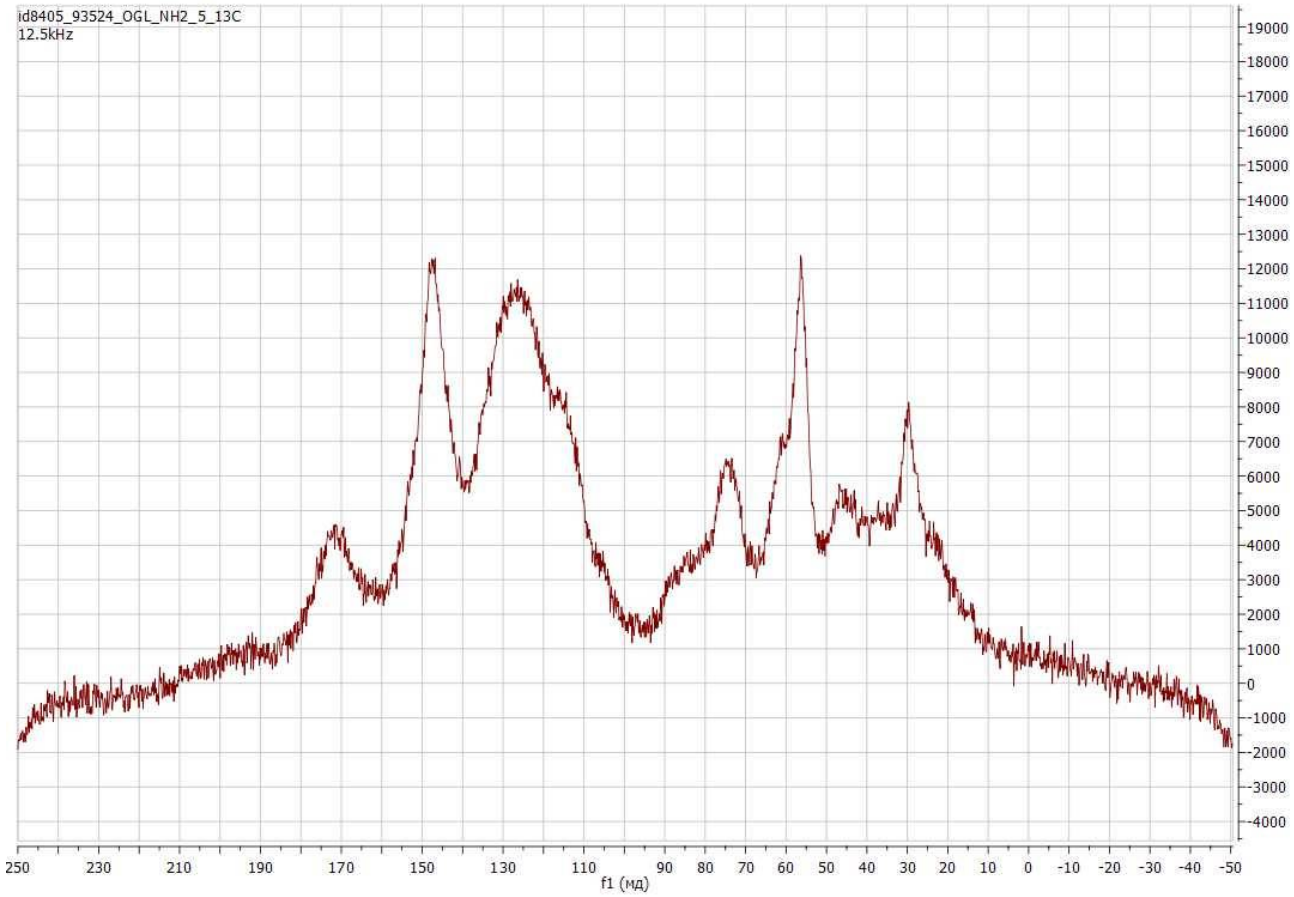



Fig. S20. Solid state $^{13}C$ NMR spectrum of **$NH_2$-OHL** (100 MHz).

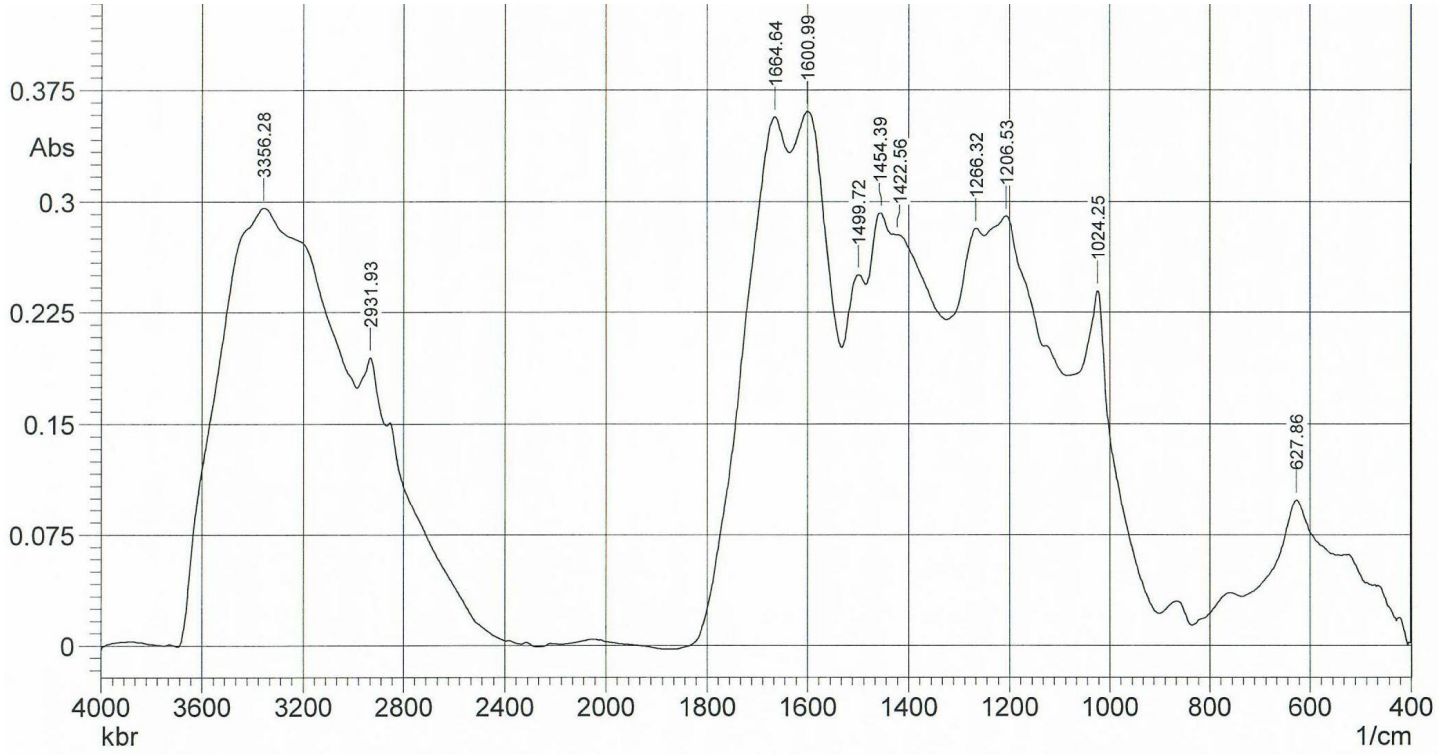



Fig. S21. IR spectrum of **$NH_2$-OHL** (KBr).

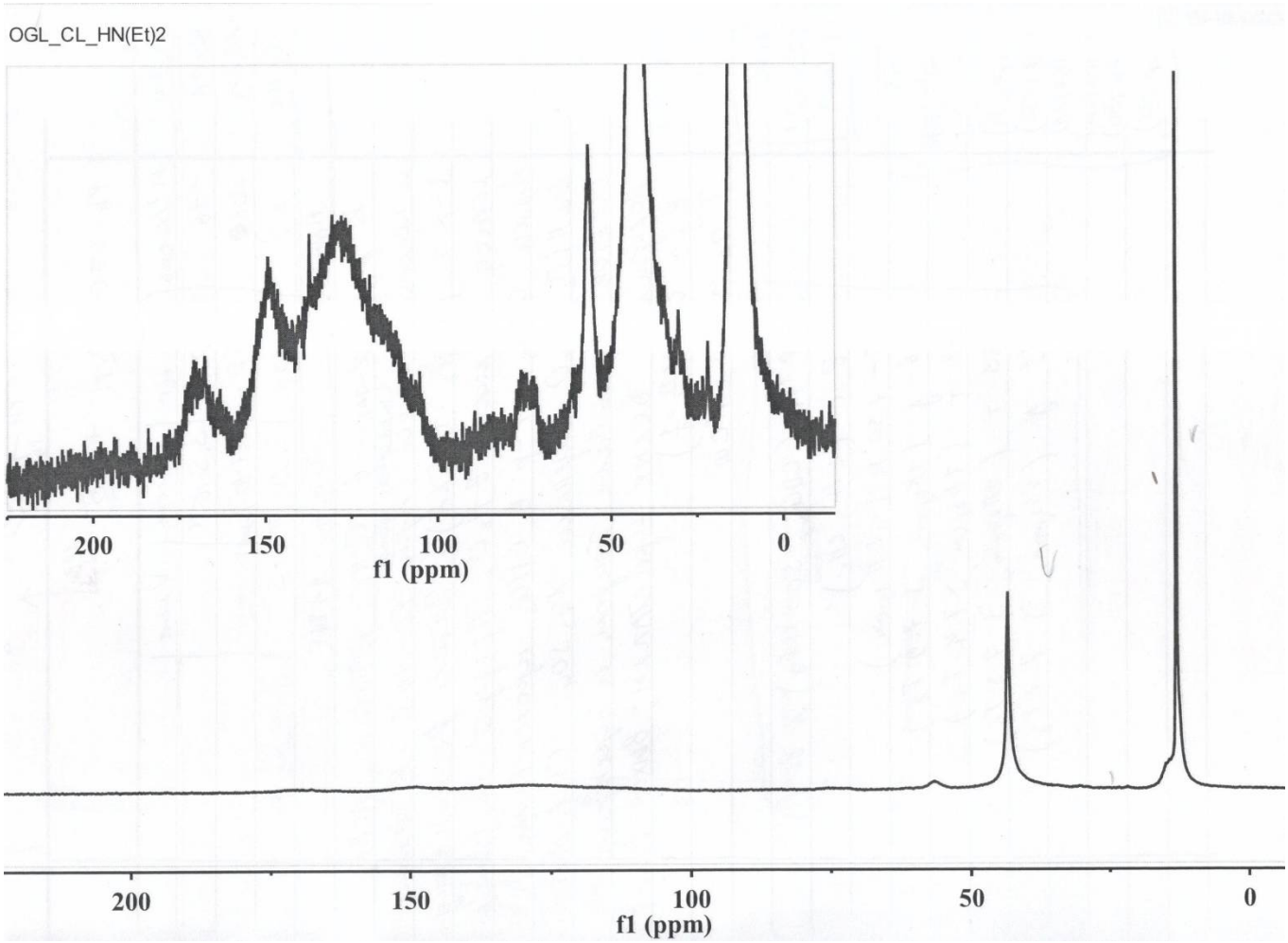



Fig. S22. Solid state $^{13}C$ NMR spectrum of **NEt$_2$-OHL** (100 MHz).

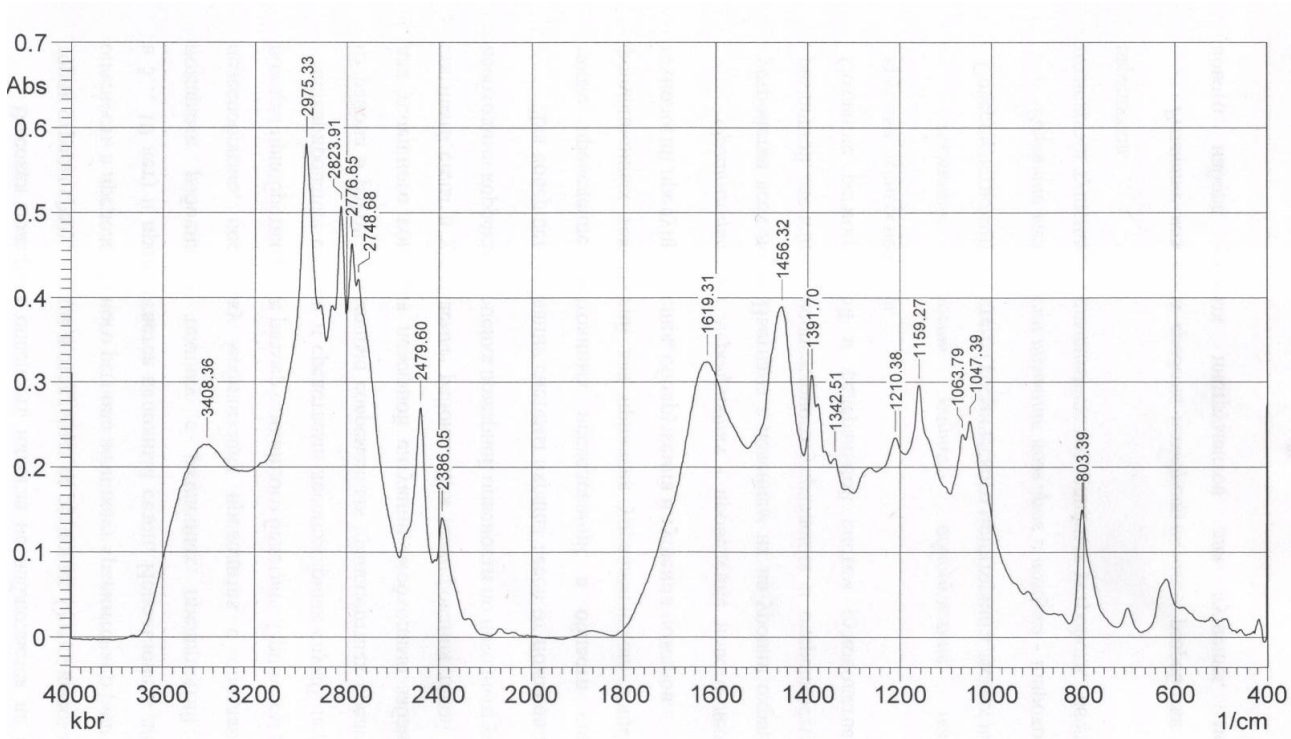



Fig. S23. IR spectrum of **NEt$_2$-OHL** (KBr).

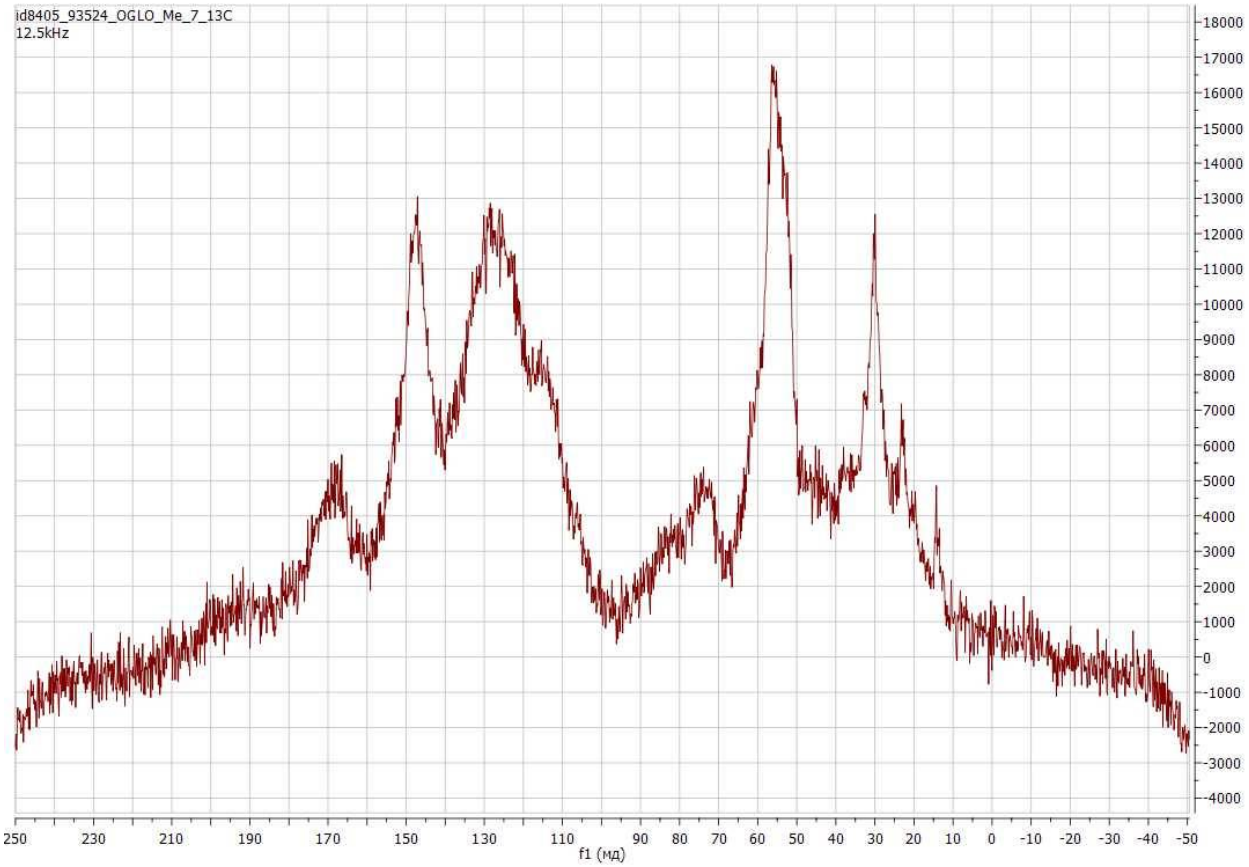



Fig. S24. Solid state $^{13}$C NMR spectrum of **MeO-OHL** (100 MHz).

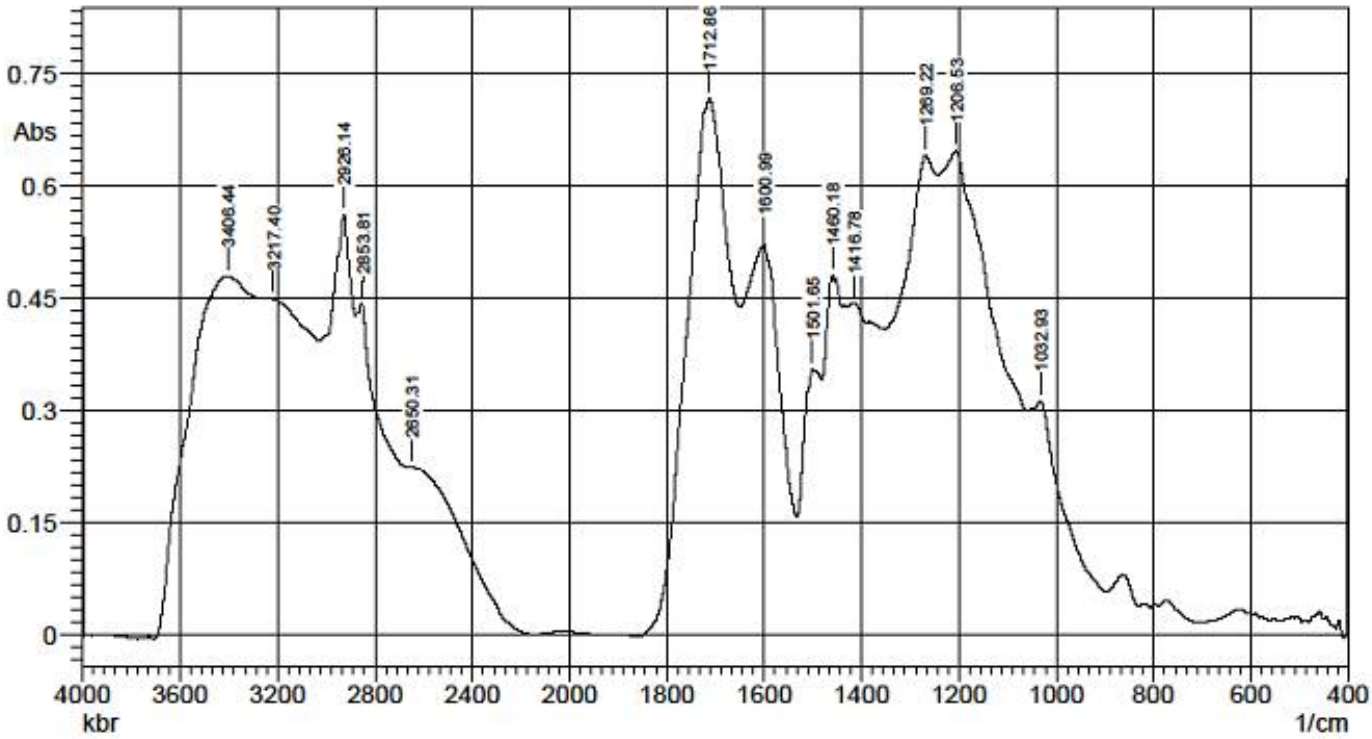



Fig. S25. IR spectrum of **MeO-OHL** (KBr).

## 3. X-ray data for compound 3

**Compound 3**

**Table S1. Crystal data and structure refinement for 3.**

| | |
|---|---|
| Identificationcode | zak3 |
| Empiricalformula | $C_6H_6O_4$ |
| Formulaweight | 142.11 |
| Temperature/K | 100(2) |
| Crystalsystem | monoclinic |
| Spacegroup | $P2_1/n$ |
| a/Å | 9.9244(15) |
| b/Å | 6.1496(6) |
| c/Å | 10.3688(19) |
| α/° | 90 |
| β/° | 113.69(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 579.52(17) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.629 |
| μ/mm$^{-1}$ | 0.140 |
| F(000) | 296.0 |
| Crystalsize/mm$^3$ | 0.26 × 0.16 × 0.10 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 7.348 to 54.972 |
| Indexranges | -10 ≤ h ≤ 12, -7 ≤ k ≤ 7, -13 ≤ l ≤ 13 |
| Reflectionscollected | 3012 |
| Independentreflections | 1322 [$R_{int}$ = 0.0230, $R_{sigma}$ = 0.0329] |
| Data/restraints/parameters | 1322/0/91 |
| Goodness-of-fit on $F^2$ | 1.044 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0365, $wR_2$ = 0.0855 |
| Final R indexes [all data] | $R_1$ = 0.0459, $wR_2$ = 0.0922 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.34/-0.23 |

**Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| O7 | 4760.6(11) | 1567.6(16) | 3662.2(10) | 14.7(2) |
| O3 | 6201.6(11) | 39.5(15) | 1733.7(10) | 14.0(3) |
| O10 | 3534.5(11) | 4550.6(17) | 2605.1(12) | 19.0(3) |
| O6 | 8542.2(11) | 6.5(16) | 3257.0(12) | 19.1(3) |
| C8 | 3976.8(15) | 2762(2) | 2506.0(15) | 13.7(3) |
| C4 | 7278.0(16) | -340(2) | 3026.4(15) | 13.6(3) |
| C5 | 6614.4(15) | -1195(2) | 4004.3(15) | 14.2(3) |
| C9 | 3773.2(15) | 1517(2) | 1185.6(15) | 14.4(3) |
| C1 | 5013.6(15) | -626(2) | 3268.7(15) | 13.3(3) |
| C2 | 4757.2(15) | -440(2) | 1713.4(15) | 13.1(3) |

**Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O7 | 17.4(5) | 13.8(5) | 13.4(5) | -1.1(4) | 6.6(4) | 2.4(4) |
| O3 | 14.3(5) | 14.6(5) | 14.7(5) | 1.4(4) | 7.5(4) | 0.7(4) |
| O10 | 18.6(5) | 15.4(5) | 24.0(6) | -1.7(5) | 9.5(5) | 2.9(4) |
| O6 | 13.6(5) | 16.6(5) | 27.8(6) | 1.8(5) | 9.0(5) | -0.1(4) |
| C8 | 10.1(6) | 15.0(7) | 17.1(7) | 0.1(6) | 6.7(6) | -0.4(5) |
| C4 | 16.3(7) | 8.4(6) | 16.5(7) | -0.9(6) | 6.9(6) | 1.5(5) |
| C5 | 15.2(7) | 12.5(6) | 14.1(7) | 0.5(6) | 5.2(6) | 0.4(5) |
| C9 | 12.2(6) | 16.0(7) | 14.5(7) | 0.2(6) | 4.9(6) | 0.8(5) |
| C1 | 15.4(7) | 10.7(6) | 14.6(7) | -0.6(6) | 6.9(6) | -0.5(5) |
| C2 | 12.0(6) | 12.5(6) | 14.1(7) | -2.3(6) | 4.7(5) | -2.0(5) |

**Table S4. Bond Lengths for 3.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O7 | C8 | 1.3539(17) | C8 | C9 | 1.510(2) |
| O7 | C1 | 1.4599(16) | C4 | C5 | 1.5084(19) |
| O3 | C4 | 1.3571(18) | C5 | C1 | 1.5016(19) |
| O3 | C2 | 1.4555(16) | C9 | C2 | 1.507(2) |
| O10 | C8 | 1.2036(17) | C1 | C2 | 1.533(2) |
| O6 | C4 | 1.1982(17) | | | |

**Table S5. Bond Angles for 3.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C8 | O7 | C1 | 110.86(11) | C1 | C5 | C4 | 103.64(11) |
| C4 | O3 | C2 | 111.06(10) | C2 | C9 | C8 | 104.16(11) |
| O7 | C8 | C9 | 110.34(11) | O7 | C1 | C5 | 109.83(11) |
| O10 | C8 | O7 | 121.32(13) | O7 | C1 | C2 | 104.52(11) |
| O10 | C8 | C9 | 128.34(14) | C5 | C1 | C2 | 104.26(11) |
| O3 | C4 | C5 | 109.93(11) | O3 | C2 | C9 | 109.51(11) |
| O6 | C4 | O3 | 120.81(13) | O3 | C2 | C1 | 104.70(11) |
| O6 | C4 | C5 | 129.26(14) | C9 | C2 | C1 | 104.54(11) |

**Table S6 Torsion Angles for 3.**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O7 | C8 | C9 | C2 | -9.05(14) | C4 | O3 | C2 | C9 | 125.75(12) |
| O7 | C1 | C2 | O3 | 91.47(11) | C4 | O3 | C2 | C1 | 14.15(14) |
| O7 | C1 | C2 | C9 | -23.66(13) | C4 | C5 | C1 | O7 | -87.25(13) |
| O3 | C4 | C5 | C1 | -16.81(14) | C4 | C5 | C1 | C2 | 24.26(14) |
| O10 | C8 | C9 | C2 | 171.42(14) | C5 | C1 | C2 | O3 | -23.83(14) |
| O6 | C4 | C5 | C1 | 163.11(14) | C5 | C1 | C2 | C9 | -138.97(11) |
| C8 | O7 | C1 | C5 | 130.41(12) | C1 | O7 | C8 | O10 | 173.07(12) |
| C8 | O7 | C1 | C2 | 19.07(14) | C1 | O7 | C8 | C9 | -6.50(14) |
| C8 | C9 | C2 | O3 | -91.89(13) | C2 | O3 | C4 | O6 | -178.40(12) |
| C8 | C9 | C2 | C1 | 19.82(14) | C2 | O3 | C4 | C5 | 1.54(14) |

**Table S7. Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for 3.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H5A | 6749 | -2756 | 4127 | 17 |
| H5B | 7051 | -498 | 4919 | 17 |
| H9A | 2755 | 1081 | 684 | 17 |
| H9B | 4069 | 2387 | 563 | 17 |
| H1 | 4371 | -1707 | 3428 | 16 |
| H2 | 4323 | -1761 | 1179 | 16 |

**Crystal structure determination of 3**

**Crystal Data** for $C_6H_6O_4$ ($M$ =142.11 g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a$ = 9.9244(15) Å, $b$ = 6.1496(6) Å, $c$ = 10.3688(19) Å, $\beta$ = 113.69(2)°, $V$ = 579.52(17) Å$^3$, $Z$ = 4, $T$ = 100(2) K, μ(MoKα) = 0.140 mm$^{-1}$, *Dcalc* = 1.629 g/cm$^3$, 3012 reflections measured (7.348° ≤ 2Θ ≤ 54.972°), 1322 unique ($R_{int}$ = 0.0230, $R_{sigma}$ = 0.0329) which were used in all calculations. The final $R_1$ was 0.0365 (I >2σ(I)) and $wR_2$ was 0.0922 (all data).

**Refinement model description**

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

2.a Ternary CH refined with riding coordinates:

C1(H1), C2(H2)

2.b Secondary CH2 refined with riding coordinates:

C5(H5A,H5B), C9(H9A,H9B)