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Supporting Information

# Synthetic Lignin Oligomers: Analytical Techniques, Challenges, and Opportunities

Myriam Rojas,* Frederico G. Fonseca, Ursel Hornung, Axel Funke, and Nicolaus Dahmen

Supporting information I

# Synthetic Lignin Oligomers: Analytical Techniques, Challenges, and Opportunities

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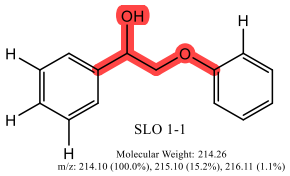
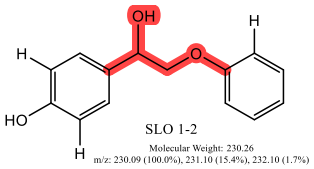
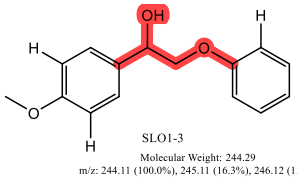
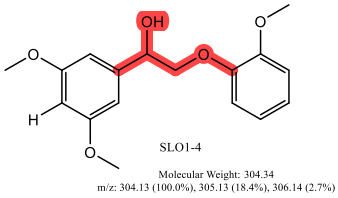
*Chemical structures of SLO, Molecular weight and m/z values.*

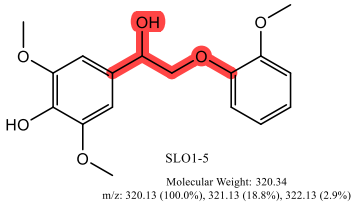
## Dimers

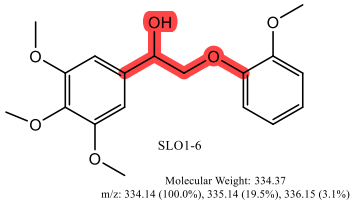


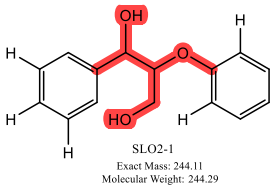



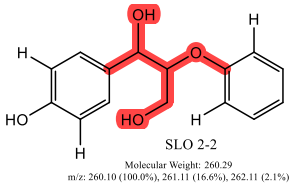



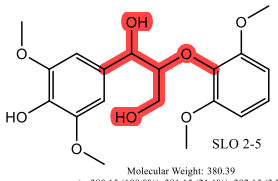



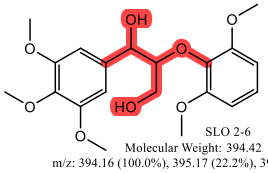





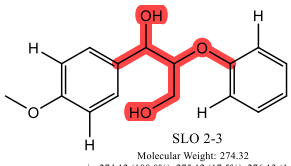
SLO 2-5

Molecular Weight: 380.39
m/z: 380.15 (100.0%), 381.15 (21.1%), 382.15 (3.7%)



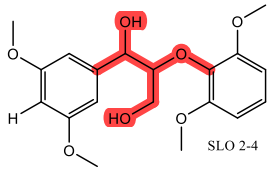
SLO 2-6

Molecular Weight: 394.42
m/z: 394.16 (100.0%), 395.17 (22.2%), 396.17 (4.0%)



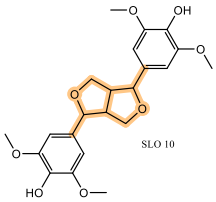
SLO 2-3

Molecular Weight: 274.32
m/z: 274.12 (100.0%), 275.12 (17.5%), 276.13 (1.5%)



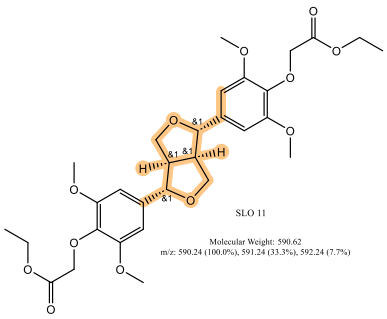
SLO 2-4

Molecular Weight: 364.39
m/z: 364.15 (100.0%), 365.16 (21.1%), 366.16 (3.6%)



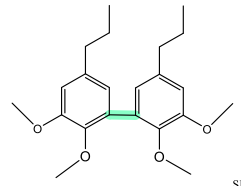
SLO 10

Molecular Weight: 418.44
m/z: 418.16 (100.0%), 419.17 (24.4%), 420.17 (4.5%)



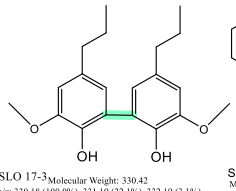
SLO 11

Molecular Weight: 590.62
m/z: 590.24 (100.0%), 591.24 (33.3%), 592.24 (7.7%)



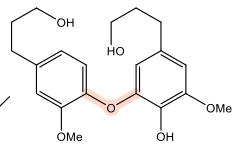
SLO 17-1

Molecular Weight: 358.48
m/z: 358.21 (100.0%), 359.22 (24.3%), 360.22 (3.6%)



SLO 17-3

Molecular Weight: 330.42
m/z: 330.18 (100.0%), 331.19 (22.1%), 332.19 (3.1%)



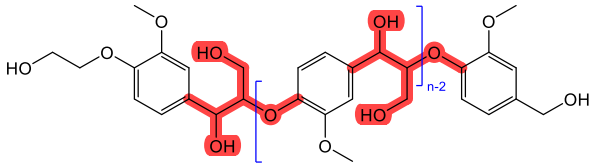
SLO 18

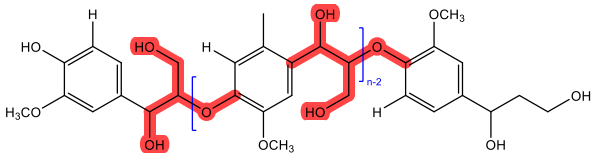
Molecular Weight: 362.42
m/z: 362.17 (100.0%), 363.18 (22.2%), 364.18 (3.6%)

## Trimers

**SLO 3**

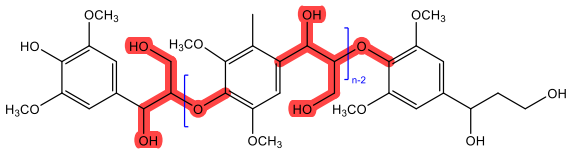
Molecular Weight: 590.62
m/z: 590.24 (100.0%), 591.24 (33.3%), 592.24 (7.7%)





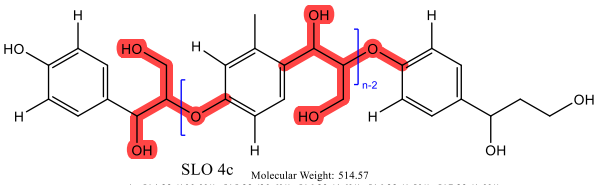
SLO 4a

Molecular Weight: 604.65
m/z: 604.25 (100.0%), 605.26 (34.4%), 606.26 (8.2%), 607.26 (1.5%)



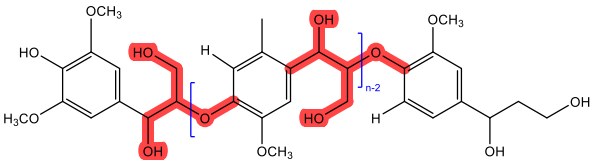
SLO 4b

Molecular Weight: 694.73
m/z: 694.28 (100.0%), 695.29 (37.9%), 696.29 (10.1%), 697.29 (2.0%)



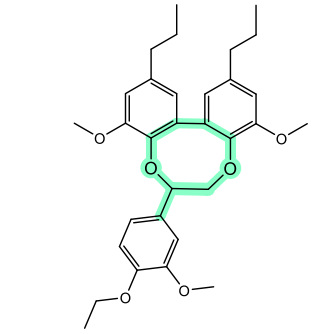

SLO 4c Molecular Weight: 514.57

m/z: 514.22 (100.0%), 515.22 (30.6%), 516.23 (4.6%), 516.22 (1.8%), 517.23 (1.0%)




SLO 4d Exact Mass: 634.26

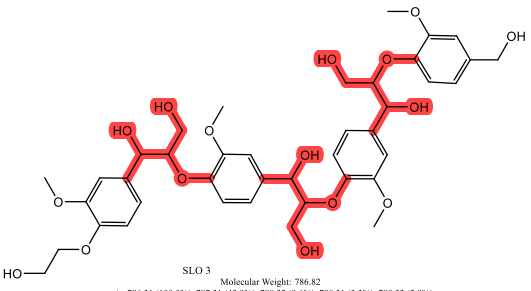
m/z: 634.26 (100.0%), 635.27 (35.6%), 636.27 (8.8%), 637.27 (1.6%)




SLO 15 Molecular Weight: 506.64

m/z: 506.27 (100.0%), 507.27 (34.2%), 508.27 (6.7%)

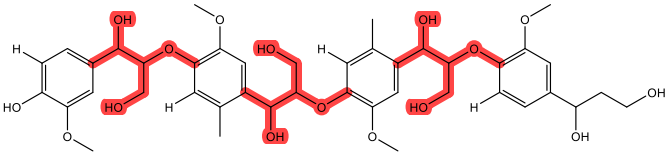
## Tetramers




SLO 3

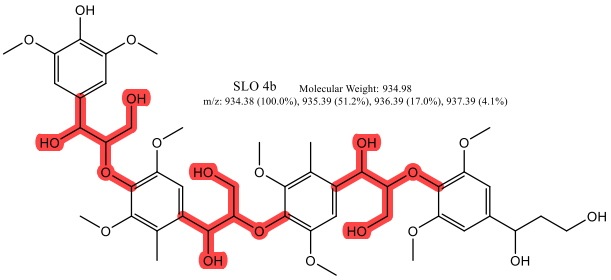
Molecular Weight: 786.82

m/z: 786.31 (100.0%), 787.31 (43.9%), 788.32 (9.6%), 788.31 (3.3%), 789.32 (2.8%)



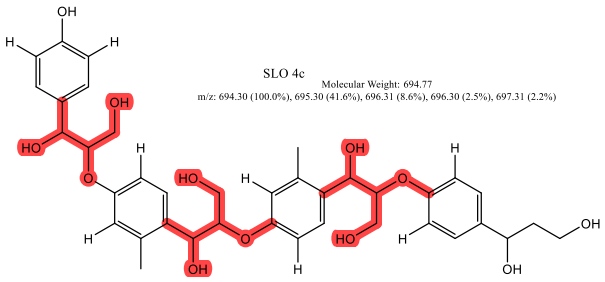

SLO 4a Molecular Weight: 814.88

m/z: 814.34 (100.0%), 815.34 (45.4%), 816.35 (13.9%), 817.35 (3.1%), 815.35 (1.2%)

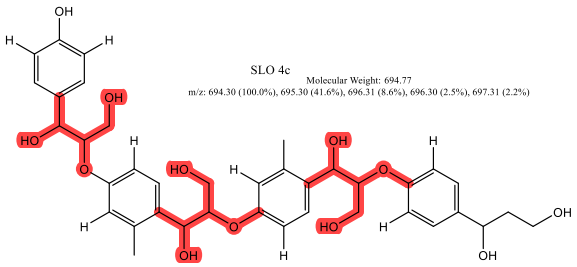



SLO 4b Molecular Weight: 934.98

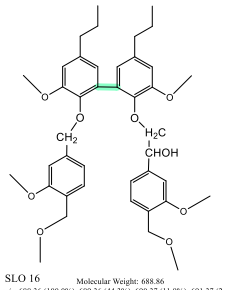
m/z: 934.38 (100.0%), 935.39 (51.2%), 936.39 (17.0%), 937.39 (4.1%)



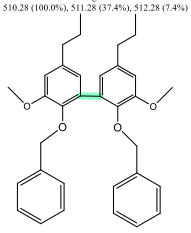
SLO 4c
Molecular Weight: 694.77
m/z: 694.30 (100.0%), 695.30 (41.6%), 696.31 (8.6%), 696.30 (2.5%), 697.31 (2.2%)



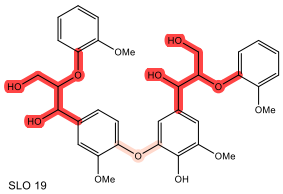
SLO 4c
Molecular Weight: 694.77
m/z: 694.30 (100.0%), 695.30 (41.6%), 696.31 (8.6%), 696.30 (2.5%), 697.31 (2.2%)



SLO 16
Molecular Weight: 688.86
m/z: 688.36 (100.0%), 689.36 (44.3%), 690.37 (11.9%), 691.37 (2.3%)



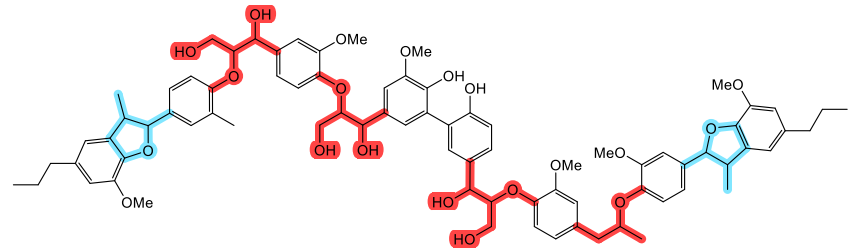
SLO 17-2
Molecular Weight: 510.67
m/z: 510.28 (100.0%), 511.28 (37.4%), 512.28 (7.4%)



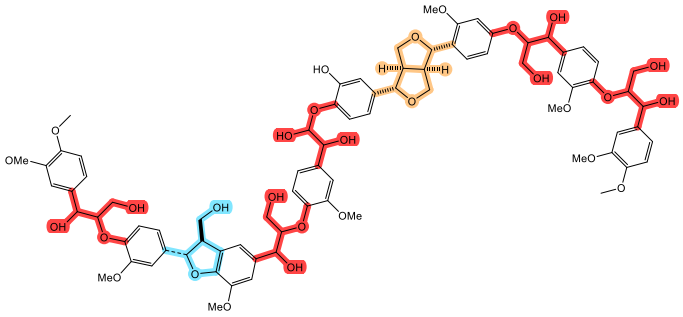
SLO 19
m/z: 638.24 (100.0%), 639.24 (37.7%), 640.24 (9.2%)

## Bigger structures

**SLO 9**
Molecular Weight: 1393.58
m/z: 1392.61 (100.0%), 1393.61 (87.3%), 1394.61 (40.6%), 1395.62 (14.6%), 1396.62 (4.0%), 1394.62 (1.6%)



**SLO 13**
Molecular Weight: 1517.59
m/z: 1516.57 (100.0%), 1517.58 (88.7%), 1518.58 (44.8%), 1519.58 (16.1%), 1520.59 (2.4%), 1520.58 (2.4%), 1521.59 (1.1%)



**SLO 14**

Molecular Weight: 1443.51

m/z: 1442.54 (100.0%), 1443.54 (85.3%), 1444.54 (40.6%), 1445.55 (10.0%), 1445.54 (4.7%), 1446.55 (4.0%), 1447.55 (1.0%)

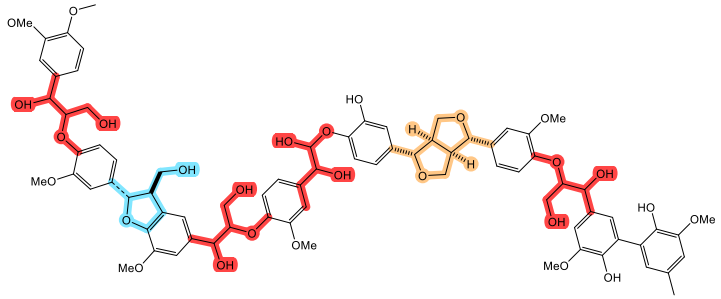


*Table 1: Thermophysical parameter values estimated for the different SLOs. Methods chosen based on the work of Fonseca and Funke (2024)[1], for the case when reasonable values could be found for all structures. Formulas and parameters for the estimation of the temperature-dependent properties are provided in a separate Excel file.*

| ID | Formula | Molecular Weight | Normal Boiling Point | Critical Temperature | Critical Pressure | Critical Volume | Ideal Gas Heat Capacity* | Standard Enthalpy of Formation* | Vapor pressure* | Enthalpy of Vaporization* | Standard Liquid Volume* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Unit | | $g \cdot mol^{-1}$ | °C | °C | bar | $cm^3 \cdot mol^{-1}$ | $J \cdot mol^{-1} \cdot K^{-1}$ | $kJ \cdot mol^{-1}$ | kPa | $kJ \cdot mol^{-1}$ | $cm^3 \cdot mol^{-1}$ |
| Method | | | Joback[2] | Gani[3] | Nanoollal-Rarey[4] | Joback[2] | Benson[5] | Benson[5] | Nanoollal-Rarey[6] | Ducros[7–9] | ACD/Labs** |
| SLO1-1 | $C_{14}H_{14}O_2$ | 214.26 | 414.1 | 496.7 | 30.75 | 634.5 | 235.1 | -159.9 | $1.34\times10^{-2}$ | 128.2 | 188.8 |
| SLO 1-2 | $C_{14}H_{14}O_3$ | 230.26 | 494.7 | 546.4 | 39.34 | 600.5 | 255.9 | -336.1 | $8.97\times10^{-4}$ | 120.7 | 184.3 |
| SLO1-3 | $C_{15}H_{16}O_3$ | 244.29 | 464.4 | 525.4 | 28.57 | 708.5 | 272.6 | -314.4 | $1.39\times10^{-3}$ | 98.7 | 212.9 |
| SLO 1-4 | $C_{17}H_{20}O_5$ | 304.34 | 564.9 | 572.0 | 24.58 | 856.5 | 368.8 | -621.0 | $1.70\times10^{-5}$ | 117.3 | 260.9 |
| SLO1-5 | $C_{17}H_{20}O_6$ | 320.34 | 645.6 | 625.9 | 30.56 | 822.5 | 389.6 | -797.2 | $5.35\times10^{-7}$ | 130.4 | 259.3 |
| SLO 1-6 | $C_{18}H_{22}O_6$ | 334.37 | 615.2 | 591.4 | 22.89 | 930.5 | 411.8 | -775.5 | $1.81\times10^{-6}$ | 119.7 | 284.9 |
| SLO2-1 | $C_{15}H_{16}O_3$ | 244.29 | 528.7 | 534.4 | 32.34 | 703.5 | 273.1 | -348.7 | $2.59\times10^{-4}$ | 127.4 | 203.2 |
| SLO 2-2 | $C_{15}H_{16}O_4$ | 260.29 | 578.3 | 575.8 | 41.96 | 637.5 | 293.9 | -524.9 | $1.69\times10^{-5}$ | 162.4 | 201.7 |
| SLO2-3 | $C_{15}H_{18}O_4$ | 274.32 | 548.0 | 528.9 | 30.12 | 745.5 | 316.1 | -503.2 | $6.49\times10^{-5}$ | 125.6 | 227.2 |
| SLO 2-4 | $C_{19}H_{24}O_7$ | 364.39 | 729.8 | 614.7 | 24.05 | 999.5 | 445.1 | -966.7 | $2.36\times10^{-8}$ | 155.4 | 299.2 |
| SLO2-5 | $C_{19}H_{24}O_8$ | 380.39 | 810.5 | 642.4 | 28.24 | 965.5 | 407.9 | -764.5 | $1.19\times10^{-9}$ | 144.6 | 297.7 |
| SLO 2-6 | $C_{20}H_{26}O_8$ | 394.42 | 780.1 | 613.5 | 22.44 | 1073.5 | 488.1 | -1121.2 | $2.08\times10^{-8}$ | 162.4 | 323.2 |
| SLO3 | $C_{40}H_{50}O_{16}$ | 786.82 | 1902.2 | 761.2 | 16.13 | 2103.5 | 937.6 | -2351.9 | $6.39\times10^{-27}$ | 409.7 | 578.8 |
| SLO 4-1(a) | $C_{42}H_{54}O_{16}$ | 814.88 | 2010.7 | 755.7 | 14.60 | 2157.5 | 950.8 | -2180.3 | $2.24\times10^{-27}$ | 410.0 | 603.0 |
| SLO4-2 (b) | $C_{46}H_{62}O_{20}$ | 934.98 | 2235.4 | 790.9 | 11.89 | 2518.5 | 1243.4 | -3209.0 | $6.61\times10^{-33}$ | 481.3 | 699.0 |
| SLO 4-3(c) | $C_{38}H_{46}O_{12}$ | 694.77 | 1809.6 | 740.8 | 18.71 | 1861.5 | 785.3 | -1808.4 | $5.00\times10^{-23}$ | 405.6 | 507.0 |
| SLO9 | $C_{79}H_{92}O_{22}$ | 1393.58 | 3205.0 | 838.3 | 4.45 | 3774.5 | 1659.4 | -3113.0 | $5.40\times10^{-41}$ | 635.9 | 1074.5 |
| SLO 10 | $C_{22}H_{26}O_8$ | 418.44 | 820.4 | 656.8 | 26.47 | 501.5 | 467.2 | -1075.1 | $1.06\times10^{-8}$ | 183.6 | 326.2 |
| SLO11 | $C_{30}H_{38}O_{12}$ | 590.62 | 1166.1 | 708.7 | 12.97 | 1547.5 | 688.9 | -1695.4 | $1.49\times10^{-11}$ | 212.9 | 483.4 |
| SLO 13 | $C_{77}H_{86}O_{30}$ | 1491.51 | 3694.2 | 897.4 | 7.94 | 3750.5 | 1653.9 | -4024.7 | $2.72\times10^{-58}$ | 777.8 | 1052.3 |
| SLO14 | $C_{75}H_{82}O_{27}$ | 1415.45 | 3407.4 | 898.8 | 8.56 | 3476.5 | 1545.8 | -3513.9 | $4.75\times10^{-51}$ | 681.5 | 1002.2 |
| SLO 15 | $C_{31}H_{38}O_6$ | 506.64 | 910.0 | 684.9 | 10.21 | 1510.5 | 648.9 | -788.0 | $8.61\times10^{-9}$ | 161.2 | 458.9 |
| SLO16 | $C_{41}H_{52}O_9$ | 688.86 | 1269.1 | 738.9 | 7.09 | 2000.5 | 882.6 | -1292.0 | $8.26\times10^{-15}$ | 253.1 | 614.5 |
| SLO 17-1 | $C_{22}H_{30}O_4$ | 358.48 | 602.5 | 619.8 | 14.34 | 1123.5 | 496.7 | -538.6 | $6.56\times10^{-6}$ | 123.2 | 349.2 |
| SLO17-2 | $C_{34}H_{38}O_4$ | 510.67 | 930.5 | 690.2 | 9.60 | 1579.5 | 596.8 | 87.1 | $2.15\times10^{-8}$ | 158.8 | 470.7 |
| SLO 17-3 | $C_{20}H_{26}O_4$ | 330.42 | 663.2 | 644.5 | 22.76 | 907.5 | 401.1 | -439.0 | $5.26\times10^{-7}$ | 140.3 | 298.2 |
| SLO18 | $C_{20}H_{26}O_6$ | 362.42 | 789.4 | 652.3 | 17.95 | 997.5 | 411.5 | -687.6 | $2.85\times10^{-9}$ | 168.1 | 300.1 |
| SLO 9 | $C_{34}H_{38}O_{12}$ | 638.67 | 1399.5 | 731.7 | 16.80 | 1539.5 | 761.0 | -1605.5 | $9.71\times10^{-17}$ | 301.1 | 482.1 |

*: At standard (NTP) conditions.

**: Estimated using the ACD/Labs Percepta Platform, available on the ChemSketch software package (free version).

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