

**The selection of the best derivatization reagents  
for the determination of polyamines in homemade wine samples**

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**Faculty of Chemistry**

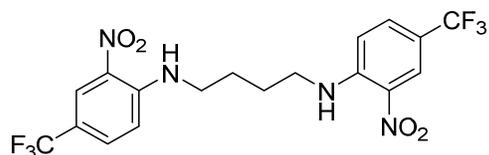
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## PA<sub>s</sub>-FNBT

### *N',N'*-Bis(2-nitro-4-(trifluoromethyl)phenyl)butane-1,4-diamine (Put-FNBT)



**Yields:** 0.4290 g, 92%

**Melting point** 138-140 °C

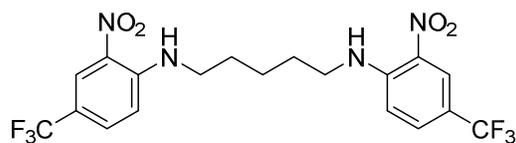
**<sup>1</sup>H NMR** (700 MHz, CDCl<sub>3</sub>) δ ppm 1.91 – 1.97 (m, 4 H), 3.46 (m, 4 H), 6.93 (d, *J*=9.03 Hz, 2 H), 7.63 (dd, *J*=9.03, 2.15 Hz, 2 H), 8.29 (br. s., 2 H), 8.47 (d, *J*=1.29 Hz, 2 H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm 26.32 (2xCH<sub>2</sub>), 42.70 (2xCH<sub>2</sub>), 114.23 (2xCH), 117.72 (q, *J*=34.7 Hz, 2xC-CF<sub>3</sub>), 123.53 (q, *J*=270.9 Hz, 2xCF<sub>3</sub>), 125.02 (q, *J*=4.24 Hz, 2xCH), 131.07 (2xC-NO<sub>2</sub>), 132.26 (q, *J*=3.08 Hz, 2xCH), 146.64 (2xC-NH-).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ ppm -62.93 (s, 2xCF<sub>3</sub>).

**FTIR** (ATR) (cm<sup>-1</sup>): 3361.29, 3094.13, 2956.20, 2922.73, 2872.34, 1631.67, 1572.37, 1529.28, 1472.68, 1430.08, 1411.09, 1363.11, 1316.72, 1250.23, 1218.49, 1182.98, 1115.74, 1076.29, 1061.05, 968.74, 939.92, 915.52, 899.19, 818.21, 765.66, 749.95, 694.56, 642.40, 613.84, 559.19, 516.19, 485.75, 432.26.

### *N',N'*-Bis(2-nitro-4-(trifluoromethyl)phenyl)pentane-1,5-diamine (Cad-FNBT)



**Yields:** 0.4704 g, 98%

**Melting point** 92-94 °C

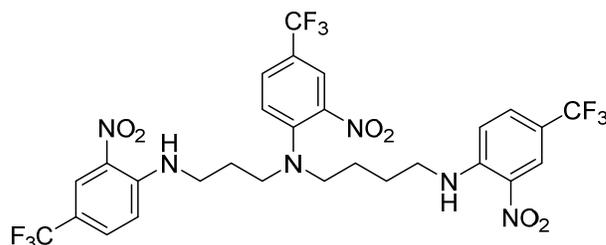
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 1.58 – 1.69 (m, 2 H), 1.85 (quin, *J*=7.34 Hz, 4 H), 3.35 – 3.44 (m, 4 H), 6.94 (d, *J*=9.10 Hz, 2 H), 7.63 (dd, *J*=9.10, 2.05 Hz, 2 H), 8.28 (br. s., 2 H), 8.47 (d, *J*=1.17 Hz, 2 H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm 24.44 (CH<sub>2</sub>), 28.47 (2xCH<sub>2</sub>), 42.90 (2xCH<sub>2</sub>), 114.34 (2xCH), 117.38 (q, *J*=34.5 Hz, 2xC-CF<sub>3</sub>), 123.56 (q, *J*=270.5 Hz, 2xCF<sub>3</sub>), 124.93 (q, *J*=4.24 Hz, 2xCH), 130.85 (2xC-NO<sub>2</sub>), 132.15 (q, *J*=3.08 Hz, 2xCH), 146.77 (2xC-NH-).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ ppm -62.89 (s, 2xCF<sub>3</sub>).

FTIR (ATR) (cm<sup>-1</sup>): 3380.38, 3361.94, 3101.57, 2933.92, 2870.89, 1634.29, 1574.73, 1525.96, 1473.49, 1434.88, 1413.71, 1362.20, 1321.19, 1296.30, 1266.65, 1250.88, 1225.76, 1188.70, 1150.48, 1129.40, 1101.52, 1079.07, 972.77, 918.73, 910.21, 897.82, 819.49, 764.36, 732.74, 690.58, 642.87, 617.41, 580.19, 516.51, 486.46, 453.85, 430.09.

***N,N'*-Bis(2-nitro-4-(trifluoromethyl)phenyl)-*N'*-(3-((2-nitro-4-(trifluoromethyl)phenyl)-amino)propyl)butane-1,4-diamine (Spd-FNBT)**



**Yields:** 0.6835 g, 96%

**Melting point** 210-215 °C

<sup>1</sup>H NMR (400 MHz, Acetonitrile-*d*<sub>3</sub>) δ ppm 1.59 - 1.70 (m, 4 H), 1.89 - 1.98 (m, 2 H), 3.23 - 3.41 (m, 8 H), 6.94 (d, *J*=9.10 Hz, 1 H), 7.01 (d, *J*=9.10 Hz, 1 H), 7.29 (d, *J*=8.80 Hz, 1 H), 7.53 - 7.63 (m, 3 H), 7.90 (dd, *J*=2.20, 0.73 Hz, 1 H), 8.13 (t, *J*=5.43 Hz, 1 H), 8.20 (t, *J*=5.28 Hz, 1 H), 8.31 (dt, *J*=1.98, 0.92 Hz, 2 H).

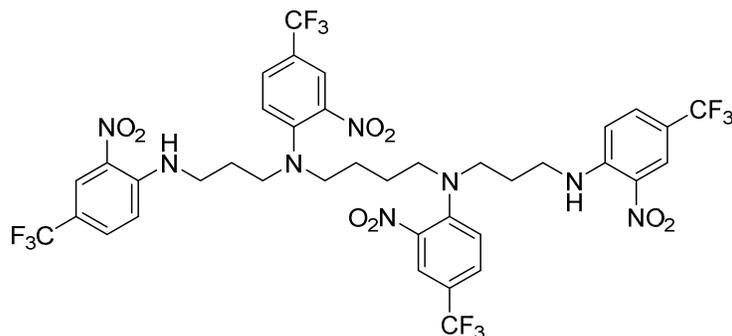
<sup>13</sup>C NMR (101 MHz, Acetonitrile-*d*<sub>3</sub>) δ ppm 25.65 (CH<sub>2</sub>), 26.71 (CH<sub>2</sub>), 27.34 (CH<sub>2</sub>), 41.20 (CH<sub>2</sub>), 43.66 (CH<sub>2</sub>), 50.02 (CH<sub>2</sub>), 52.49 (CH<sub>2</sub>), 116.55 (CH), 116.77 (CH), 117.25 (q, *J*=34.3 Hz, C-CF<sub>3</sub>), 117.40 (q, *J*=33.9 Hz, C-CF<sub>3</sub>), 121.03 (q, *J*=33.9 Hz, C-CF<sub>3</sub>), 123.39 (CH), 125.09 (q, *J*=270.5 Hz, CF<sub>3</sub>), 125.28 (q, *J*=3.85 Hz, CH), 125.36 (q, *J*=269.7 Hz, CF<sub>3</sub>), 125.40 (q, *J*=269.7 Hz, CF<sub>3</sub>), 125.78 (q, *J*=4.24 Hz, CH), 125.80 (q, *J*=4.24 Hz, CH), 130.67 (q, *J*=3.47 Hz, CH), 132.06 (C-NO<sub>2</sub>), 132.21 (C-NO<sub>2</sub>), 133.06 (q, *J*=3.08 Hz, 2xCH), 141.66 (C-NO<sub>2</sub>), 148.23 (C-N), 148.31 (C-NH-), 148.42 (C-NH-).

<sup>19</sup>F NMR (376 MHz, Acetonitrile-*d*<sub>3</sub>) δ ppm -63.35 (s, 2xCF<sub>3</sub>), -63.32 (s, CF<sub>3</sub>).

<sup>19</sup>F NMR (376 MHz, THF-*d*<sub>8</sub>) δ ppm -63.64 (s, CF<sub>3</sub>), -63.60 (s, CF<sub>3</sub>), -63.57 (s, CF<sub>3</sub>).

FTIR (ATR) (cm<sup>-1</sup>): 3372.04, 3327.38, 3112.24, 2942.34, 2858.91, 1639.20, 1572.56, 1536.29, 1466.59, 1434.49, 1414.60, 1385.34, 1364.13, 1322.24, 1260.51, 1231.31, 1185.06, 1155.11, 1107.27, 1079.47, 901.71, 872.74, 819.99, 762.10, 714.97, 692.98, 645.25, 615.92, 541.15, 515.27, 432.98, 417.90.

***N,N'*-(Butane-1,4-diyl)bis(*N,N'*-bis(2-nitro-4-(trifluoromethyl)phenyl)propane-1,3-diamine) (Spm-FNBT)**



**Yields:** 0.9101 g, 95%

**Melting point** 135-138 °C

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 1.50 (m, 4 H), 1.95 (quin, *J*=6.75 Hz, 4 H), 3.11 (m, 4 H), 3.31 (t, *J*=6.60 Hz, 4 H), 3.34 – 3.42 (m, 4 H), 6.87 (d, *J*=8.80 Hz, 2 H), 7.17 (d, *J*=8.51 Hz, 2 H), 7.55 – 7.63 (m, 4 H), 7.92 (d, *J*=1.76 Hz, 2 H), 8.18 (br. s., 2 H), 8.43 (d, *J*=1.17 Hz, 2 H).

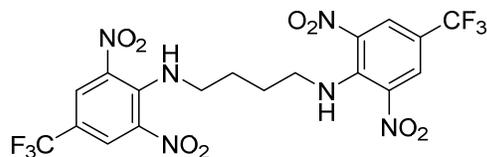
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm 24.47 (2xCH<sub>2</sub>), 26.44 (2xCH<sub>2</sub>), 40.04 (2xCH<sub>2</sub>), 48.65 (2xCH<sub>2</sub>), 52.57 (2xCH<sub>2</sub>), 114.25 (2xCH), 117.75 (q, *J*=34.3 Hz, 2xC-CF<sub>3</sub>), 121.86 (2xCH), 122.39 (q, *J*=34.7 Hz, 2xC-CF<sub>3</sub>), 123.09 (q, *J*=271.7 Hz, 2xCF<sub>3</sub>), 123.50 (q, *J*=270.9 Hz, 2xCF<sub>3</sub>), 123.89 (q, *J*=3.85 Hz, 2xCH), 124.96 (q, *J*=4.24 Hz, 2xCH), 129.55 (q, *J*=3.08 Hz, 2xCH), 130.85 (2xC-NO<sub>2</sub>), 132.25 (q, *J*=3.08 Hz, 2xCH), 141.67 (2xC-NO<sub>2</sub>), 146.18 (2xC-N), 146.60 (2xC-NH-).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ ppm -62.97 (s, 2xCF<sub>3</sub>), -63.11 (s, 2xCF<sub>3</sub>).

**FTIR** (ATR) (cm<sup>-1</sup>): 3378.55, 3112.64, 2940.92, 2879.32, 1737.77, 1637.83, 1624.32, 1578.28, 1561.10, 1528.88, 1504.03, 1434.93, 1398.70, 1374.89, 1359.85, 1320.33, 1281.02, 1263.55, 1235.35, 1205.34, 1194.68, 1155.46, 1126.91, 1079.87, 1044.47, 974.57, 920.86, 905.13, 866.33, 828.08, 818.06, 773.97, 763.14, 753.93, 714.96, 689.30, 670.46, 637.59, 607.08, 569.50, 518.77, 474.95.

## **PAs-CNBF**

***N,N'*-Bis(2,6-dinitro-4-(trifluoromethyl)phenyl)butane-1,4-diamine (Put-CNBF)**



**Yields:** 0.5230 g, 94%

**Melting point** 190-194 °C

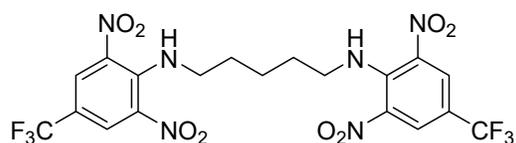
**<sup>1</sup>H NMR** (400 MHz, Acetone-*d*<sub>6</sub>) δ ppm 1.89 (dt, *J*=6.09, 3.26 Hz, 4 H), 3.12 – 3.20 (m, 4 H), 8.52 (s, 4 H), 8.58 (br. s., 2 H).

**<sup>13</sup>C NMR** (101 MHz, Acetone-*d*<sub>6</sub>) δ ppm 27.73 (2xCH<sub>2</sub>), 46.98 (2xCH<sub>2</sub>), 116.06 (q, *J*=35.8 Hz, 2xC-CF<sub>3</sub>), 123.96 (q, *J*=270.9 Hz, 2xCF<sub>3</sub>), 129.76 (q, *J*=3.85 Hz, 4xCH), 138.82 (4xC-NO<sub>2</sub>), 142.43 (2xC-NH-).

**<sup>19</sup>F NMR** (376 MHz, Acetone-*d*<sub>6</sub>) δ ppm -63.44 (s, 2xCF<sub>3</sub>).

**FTIR** (ATR) (cm<sup>-1</sup>): 3351.23, 3102.59, 3062.69, 2955.16, 2929.02, 2874.92, 2115.20, 1861.68, 1738.39, 1635.35, 1577.00, 1537.86, 1516.18, 1449.40, 1409.83, 1370.48, 1357.31, 1279.51, 1249.25, 1166.62, 1125.66, 1065.49, 1005.11, 963.70, 944.44, 919.59, 899.35, 832.37, 787.08, 766.69, 759.17, 737.42, 723.81, 706.58, 670.13, 653.76, 642.41, 588.68, 531.37, 503.67, 452.49, 425.79.

***N',N'*-Bis(2,6-dinitro-4-(trifluoromethyl)phenyl)pentane-1,5-diamine (Cad-CNBF)**



**Yields:** 0.5462 g, 96%

**Melting point** 134-136 °C

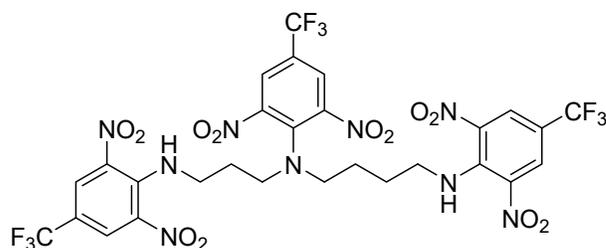
**<sup>1</sup>H NMR** (400 MHz, Acetone-*d*<sub>6</sub>) δ ppm 1.47 – 1.57 (m, 2 H), 1.82 (dt, *J*=14.82, 7.26 Hz, 4 H), 3.07 – 3.15 (m, 4 H), 8.52 (s, 4 H), 8.58 (br. s., 2 H).

**<sup>13</sup>C NMR** (101 MHz, Acetone-*d*<sub>6</sub>) δ ppm 24.40 (CH<sub>2</sub>), 30.03 (2xCH<sub>2</sub>), 47.21 (2xCH<sub>2</sub>), 115.89 (q, *J*=35.6 Hz, 2xC-CF<sub>3</sub>), 123.95 (q, *J*=270.5 Hz, 2xCF<sub>3</sub>), 129.77 (q, *J*=3.90 Hz, 4xCH), 138.71 (4xC-NO<sub>2</sub>), 142.50 (2xC-NH-).

**<sup>19</sup>F NMR** (376 MHz, Acetone-*d*<sub>6</sub>) δ ppm -63.41 (s, 2xCF<sub>3</sub>).

**FTIR** (ATR) (cm<sup>-1</sup>): 3340.55, 3064.59, 2940.78, 1850.99, 1738.46, 1636.56, 1573.50, 1541.42, 1514.09, 1437.54, 1408.88, 1363.96, 1271.30, 1226.04, 1202.60, 1167.78, 1124.59, 954.64, 935.85, 914.95, 896.40, 781.86, 765.20, 727.19, 707.57, 643.01, 535.80, 513.37, 478.20, 451.69.

***N',N'*-Bis(2,6-dinitro-4-(trifluoromethyl)phenyl)-*N'*-(3-((2,6-dinitro-4-(trifluoromethyl)phenyl)amino)propyl)butane-1,4-diamine (Spd-CNBF)**



**Yields:** 0.8032 g, 95%

**Melting point** 164-167 °C

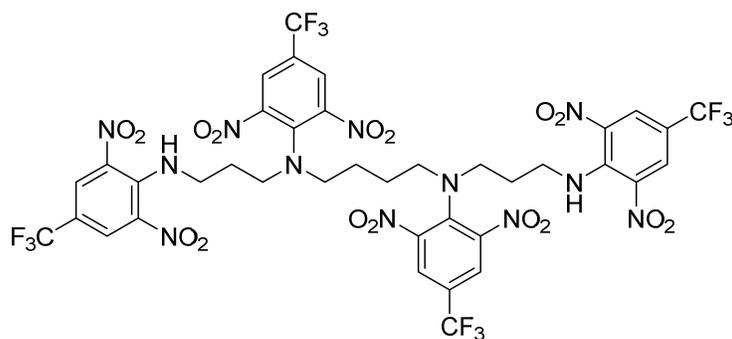
**<sup>1</sup>H NMR** (400 MHz, Acetone-*d*<sub>6</sub>) δ ppm 1.68 - 1.82 (m, 4 H), 2.09 - 2.17 (m, 2 H), 3.06 - 3.19 (m, 6 H), 3.22 (t, *J*=6.75 Hz, 2 H), 8.31 (d, *J*=0.59 Hz, 2 H), 8.46 (m, 3 H, 2xCH, NH), 8.49 - 8.55 (m, 3 H, 2xCH, NH).

**<sup>13</sup>C NMR** (101 MHz, Acetone-*d*<sub>6</sub>) δ ppm 25.42 (CH<sub>2</sub>), 27.62 (CH<sub>2</sub>), 28.57 (CH<sub>2</sub>), 45.10 (CH<sub>2</sub>), 47.03 (CH<sub>2</sub>), 49.61 (CH<sub>2</sub>), 52.08 (CH<sub>2</sub>), 116.02 (q, *J*=35.8 Hz, C-CF<sub>3</sub>), 116.12 (q, *J*=35.5 Hz, C-CF<sub>3</sub>), 123.25 (q, *J*=35.8 Hz, C-CF<sub>3</sub>), 123.50 (q, *J*=271.6 Hz, CF<sub>3</sub>), 123.86 (q, *J*=270.5 Hz, CF<sub>3</sub>), 123.93 (q, *J*=270.9 Hz, CF<sub>3</sub>), 127.89 (q, *J*=3.08 Hz, 2xCH), 129.75 (q, *J*=3.47 Hz, 2xCH), 129.79 (q, *J*=3.85 Hz, 2xCH), 138.69 (2xC-NO<sub>2</sub>), 138.73 (2xC-NO<sub>2</sub>), 141.62 (2xC-NO<sub>2</sub>), 142.40 (C-NH-), 142.42 (C-NH-), 146.80 (C-N).

**<sup>19</sup>F NMR** (376 MHz, Acetone-*d*<sub>6</sub>) δ ppm -63.81 (s, CF<sub>3</sub>), -63.49 (s, CF<sub>3</sub>), -63.45 (s, CF<sub>3</sub>).

**FTIR** (ATR) (cm<sup>-1</sup>): 3341.68, 3077.99, 2969.85, 2929.71, 2324.19, 2113.34, 2014.65, 1996.40, 1738.71, 1637.71, 1578.90, 1523.81, 1474.11, 1448.46, 1433.47, 1411.40, 1365.44, 1303.60, 1278.15, 1228.93, 1181.74, 1129.58, 1105.84, 996.21, 948.22, 910.32, 900.51, 877.51, 793.51, 783.71, 765.22, 740.45, 724.25, 711.31, 660.81, 641.79, 582.55, 515.14, 451.54, 431.22.

***N*<sup>1</sup>,*N*<sup>1'</sup>-(Butane-1,4-diyl)bis(*N*<sup>1</sup>,*N*<sup>3</sup>-bis(2,6-dinitro-4-(trifluoromethyl)phenyl)propane-1,3-diamine) (Spm-CNBF)**



**Yields:** 1.0565 g, 93%

**Melting point** 205-208 °C

**<sup>1</sup>H NMR** (400 MHz, Acetone-*d*<sub>6</sub>) δ ppm 1.57 – 1.67 (m, 4 H), 2.11 (quin, *J*=6.68 Hz, 4 H), 3.01 – 3.08 (m, 4 H), 3.11 – 3.22 (m, 8 H), 8.27 (d, *J*=0.59 Hz, 4 H), 8.45 (s, 6 H).

**<sup>13</sup>C NMR** (101 MHz, THF-*d*<sub>8</sub>) δ ppm 25.65 (2xCH<sub>2</sub>), 28.86 (2xCH<sub>2</sub>), 45.10 (2xCH<sub>2</sub>) 49.78 (2xCH<sub>2</sub>), 52.44 (2xCH<sub>2</sub>), 116.54 (q, *J*=35.8 Hz, 2xC-CF<sub>3</sub>), 123.69 (q, *J*=272.0 Hz, 2xCF<sub>3</sub>), 123.98 (q, *J*=35.8 Hz, 2xC-CF<sub>3</sub>), 124.10 (q, *J*=270.9 Hz, 2xCF<sub>3</sub>), 127.82 (q, *J*=3.47 Hz, 4xCH), 129.75 (q, *J*=3.85 Hz, 4xCH), 138.88 (4xC-NO<sub>2</sub>), 141.56 (4xC-NO<sub>2</sub>), 142.28 (2xC-NH-), 147.28 (2xC-NH-).

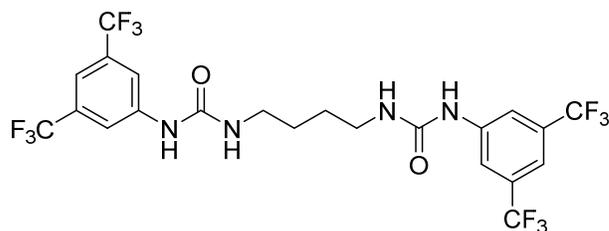
**<sup>19</sup>F NMR** (376 MHz, Acetone-*d*<sub>6</sub>) δ ppm -63.80 (s, 2xCF<sub>3</sub>), -63.50 (s, 2xCF<sub>3</sub>).

**<sup>19</sup>F NMR** (376 MHz, THF-*d*<sub>8</sub>) δ ppm -64.06 (s, 2xCF<sub>3</sub>) -63.71 (s, 2xCF<sub>3</sub>).

**FTIR** (ATR) (cm<sup>-1</sup>): 3313.20, 3089.31, 2969.78, 2947.66, 2110.38, 2014.74, 1738.55, 1636.82, 1580.92, 1536.65, 1464.43, 1434.75, 1414.18, 1366.13, 1351.30, 1314.11, 1279.28, 1230.02, 1217.44, 1192.93, 1167.23, 1121.32, 1021.37, 953.00, 919.04, 897.32, 819.36, 791.31, 765.25, 730.14, 710.47, 669.53, 659.70, 611.38, 539.92, 520.44, 488.19, 453.90.

## PA-s-BPI

**1,1'-(Butane-1,4-diyl)bis(3-(3,5-bis(trifluoromethyl)phenyl)urea) (Put-BPI)**



**Yields:** 0.1346 g, 90%

**Melting point** 229-231 °C

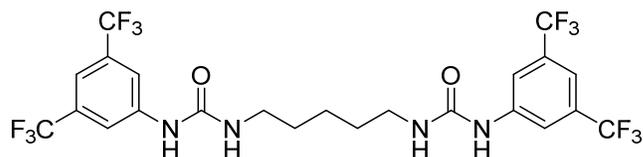
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 1.40 – 1.54 (m, 4 H), 3.05 – 3.19 (m, 4 H), 6.51 (t, *J*=5.72 Hz, 2 H), 7.52 (s, 2 H), 8.07 (s, 4 H), 9.15 – 9.24 (m, 2 H).

**<sup>13</sup>C NMR** (101 MHz, DMSO-*d*<sub>6</sub>) δ ppm 27.02 (2xCH<sub>2</sub>), 38.96 (2xCH<sub>2</sub>), 113.28 (m, 2xCH), 117.14 (m, 4xCH), 123.36 (q, *J*=272.4 Hz, 4xCF<sub>3</sub>), 130.55 (q, *J*=32.4 Hz, 4xC-CF<sub>3</sub>), 142.64 (2xC-NH-), 155.87 (2xC=O).

**<sup>19</sup>F NMR** (376 MHz, DMSO-*d*<sub>6</sub>) δ ppm -62.69 (4xCF<sub>3</sub>).

**FTIR** (ATR) (cm<sup>-1</sup>): 3338.27, 3115.77, 2942.46, 1654.09, 1561.43, 1473.54, 1439.27, 1386.76, 1272.33, 1257.13, 1172.79, 1126.44, 1095.26, 1029.32, 999.67, 940.85, 911.24, 877.52, 846.36, 763.74, 700.05, 679.19, 656.85, 625.46.

**1,1'-(Pentane-1,5-diyl)bis(3-(3,5-bis(trifluoromethyl)phenyl)urea) (Cad-BPI)**



**Yields:** 0.1481 g, 92%

**Melting point** 218-221 °C

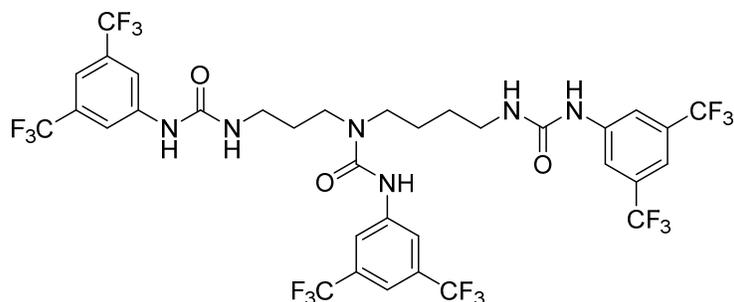
**<sup>1</sup>H NMR** (400 MHz, Acetone-*d*<sub>6</sub>) δ ppm 1.37 - 1.47 (m, 2 H), 1.58 (quin, *J*=7.26 Hz, 4 H), 3.25 (q, *J*=6.75 Hz, 4 H), 6.13 (t, *J*=4.84 Hz, 2 H), 7.50 (s, 2 H), 8.14 (s, 4 H), 8.54 (s, 2 H).

**<sup>13</sup>C NMR** (101 MHz, Acetone-*d*<sub>6</sub>) δ ppm 24.88 (CH<sub>2</sub>), 30.57 (2xCH<sub>2</sub>), 40.52 (2xCH<sub>2</sub>), 114.73 (sept, *J*=3.85 Hz, 2xCH), 118.49 (q, *J*=3.85 Hz, 4xCH), 124.61 (q, *J*=271.7 Hz, 4xCF<sub>3</sub>), 132.45 (q, *J*=32.8 Hz, 4xC-NH-), 143.80 (2xC-NH-), 155.84 (2xC=O).

**<sup>19</sup>F NMR** (376 MHz, Acetone-*d*<sub>6</sub>) δ ppm -64.63 (s, 4xCF<sub>3</sub>).

**FTIR** (ATR) (cm<sup>-1</sup>): 3327.81, 3119.05, 2937.36, 2863.96, 1655.49, 1569.13, 1473.96, 1439.54, 1387.70, 1271.38, 1171.11, 1126.91, 1039.30, 1015.93, 936.12, 913.67, 875.77, 849.66, 699.46, 679.39, 663.31, 641.16.

**3-(3,5-Bis(trifluoromethyl)phenyl)-1-(4-(3-(3,5-bis(trifluoromethyl)phenyl)ureido)butyl)-1-(3-(3-(3,5-bis(trifluoromethyl)phenyl)ureido)propyl)urea (Spd-BPI)**



**Yields:** 0.1546 g, 90%

**Melting point** 120-124 °C



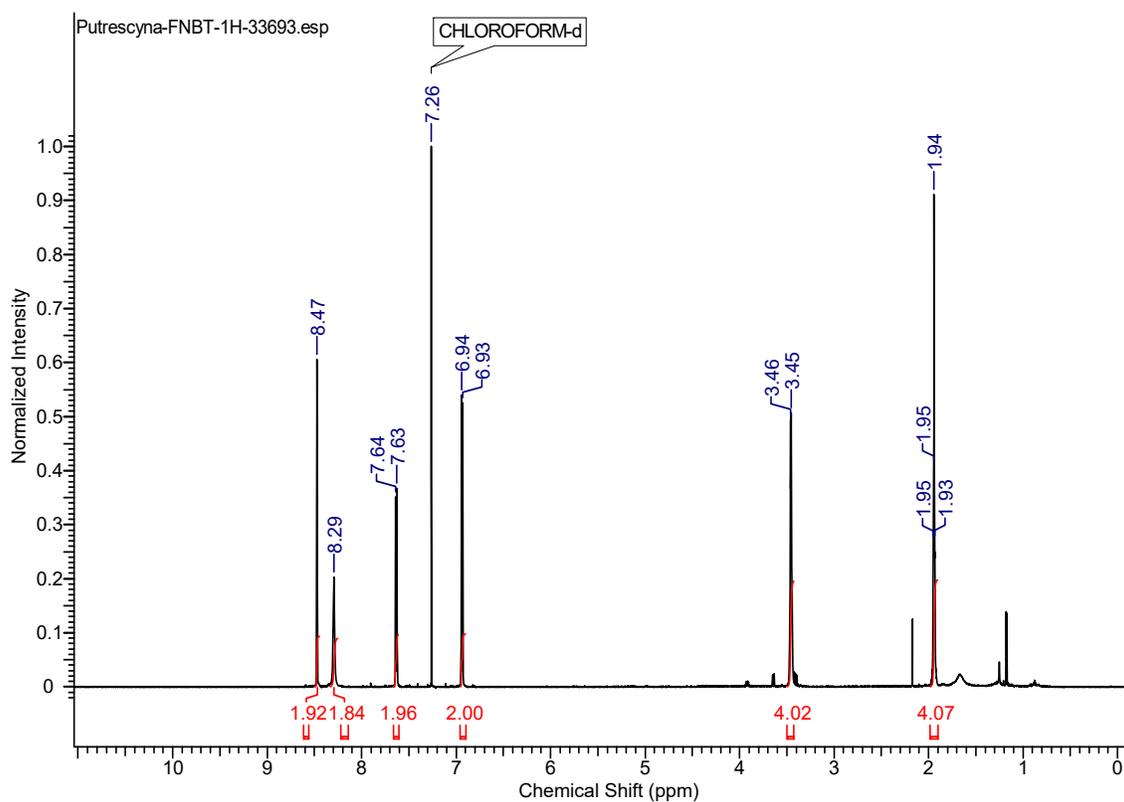
**<sup>13</sup>C NMR** (101 MHz, Acetone-*d*<sub>6</sub>) δ ppm 26.24 (2xCH<sub>2</sub>), 29.73 (2xCH<sub>2</sub>), 37.99 (2xCH<sub>2</sub>), 45.15 (2xCH<sub>2</sub>), 47.21 (2xCH<sub>2</sub>), 114.86 (m, 2xCH), 115.51 (m, 2xCH), 118.59 (m, 4xCH), 120.49 (m, 4xCH), 124.58 (q, *J*=272.0 Hz, 8xCF<sub>3</sub>), 132.16 (q, *J*=32.8 Hz, 4x $\underline{\text{C}}$ -CF<sub>3</sub>), 132.47 (q, *J*=32.8 Hz, 4x $\underline{\text{C}}$ -CF<sub>3</sub>), 143.63 (2x $\underline{\text{C}}$ -NH-), 143.65 (2x $\underline{\text{C}}$ -NH-), 156.14 (2xC=O), 156.21 (2xC=O).

**<sup>19</sup>F NMR** (376 MHz, DMSO-*d*<sub>6</sub>) δ ppm -62.78 (s, 4xCF<sub>3</sub>), -62.69 (s, 4xCF<sub>3</sub>).

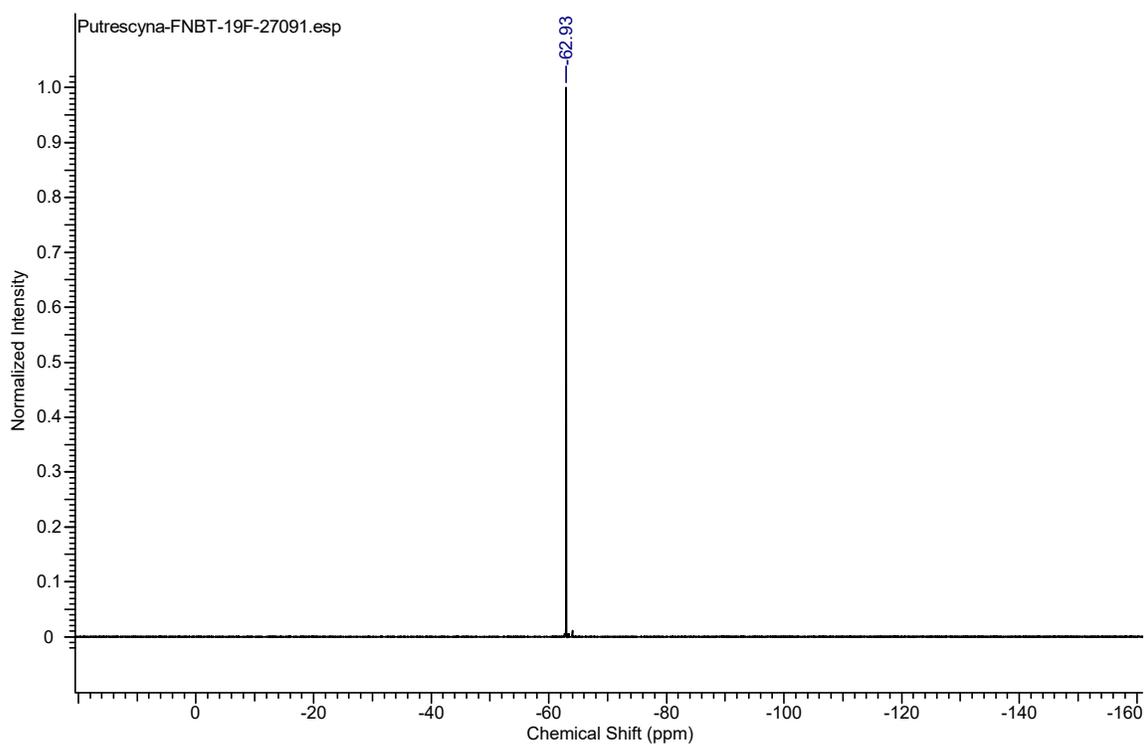
**<sup>19</sup>F NMR** (376 MHz, Acetone-*d*<sub>6</sub>) δ ppm -64.57 (s, 4xCF<sub>3</sub>), -64.65 (s, 4xCF<sub>3</sub>).

**FTIR** (ATR) (cm<sup>-1</sup>): 3311.12, 3115.62, 2942.14, 1640.51, 1539.43, 1472.32, 1442.34, 1374.70, 1273.73, 1168.66, 1119.52, 1001.62, 941.52, 880.32, 842.29, 756.51, 732.03, 700.90, 680.88, 629.06.

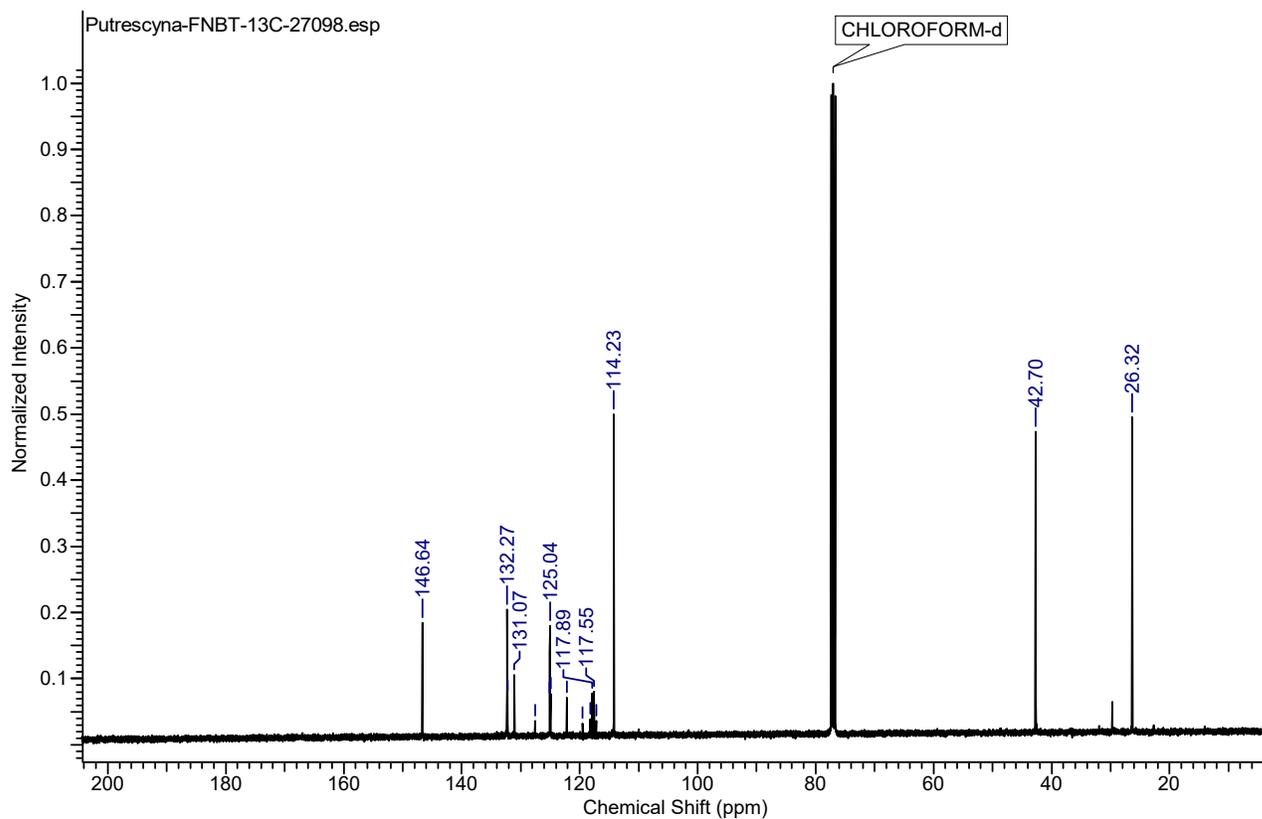
### Put-FNBT (<sup>1</sup>H NMR)



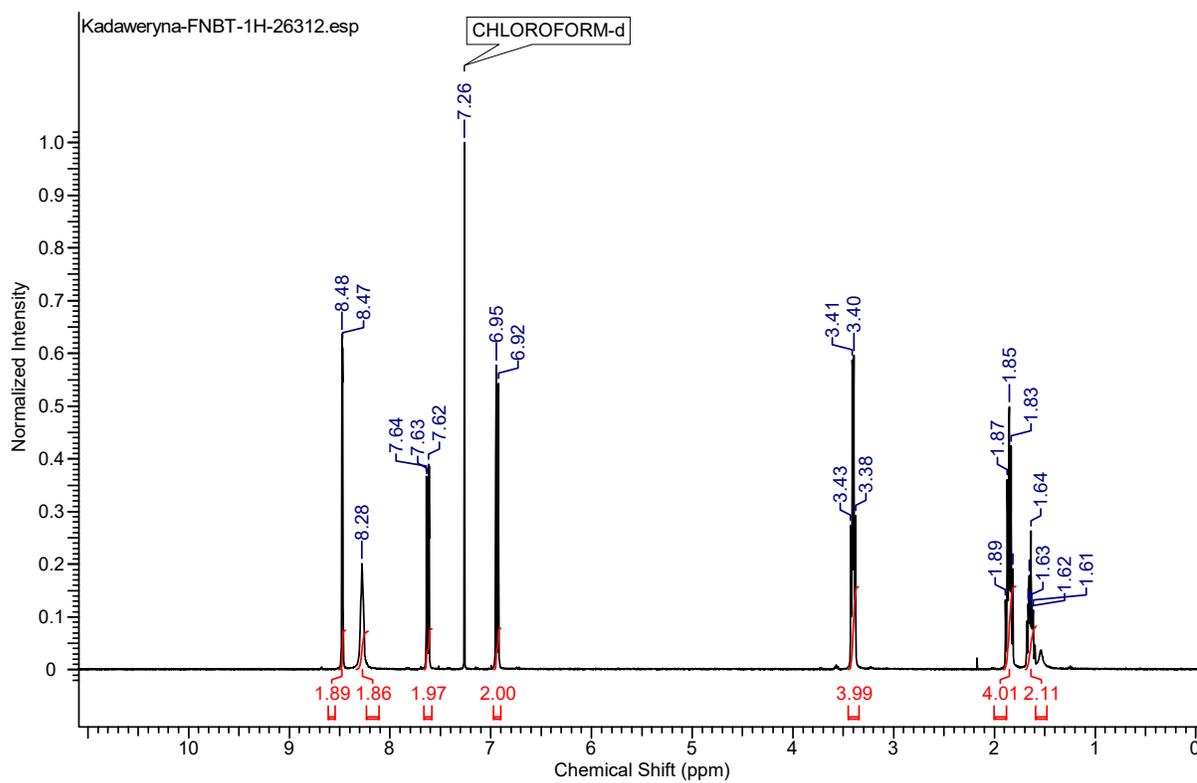
### Put-FNBT (<sup>19</sup>F NMR)



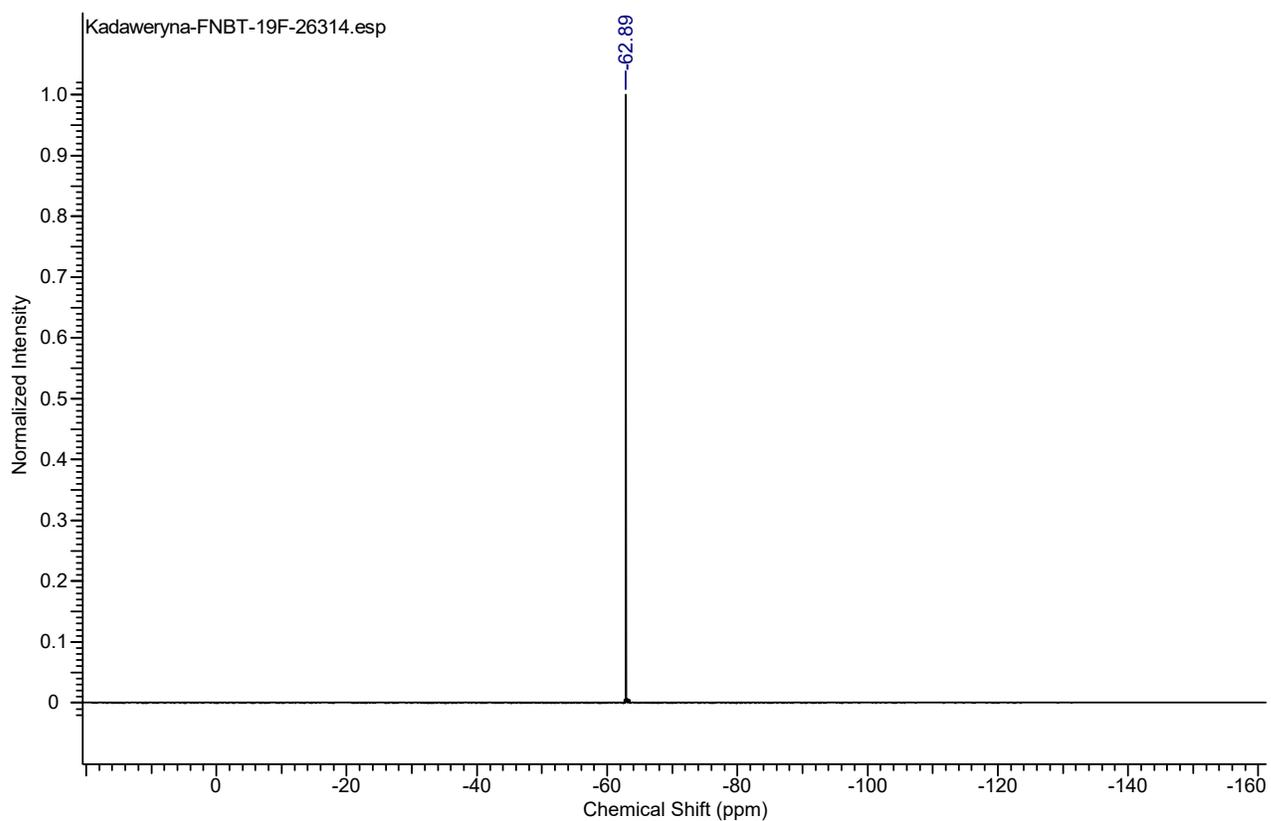
### Put-FNBT (<sup>13</sup>C NMR)



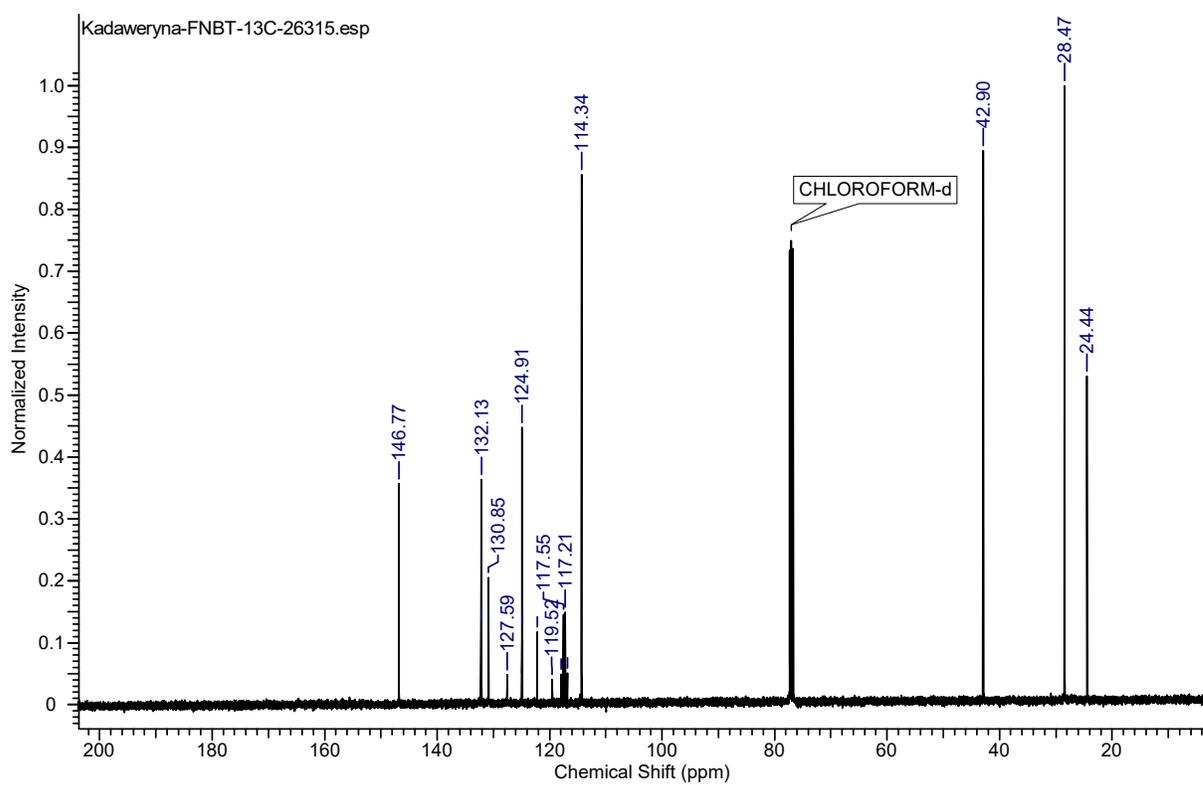
### Cad-FNBT (<sup>1</sup>H NMR)



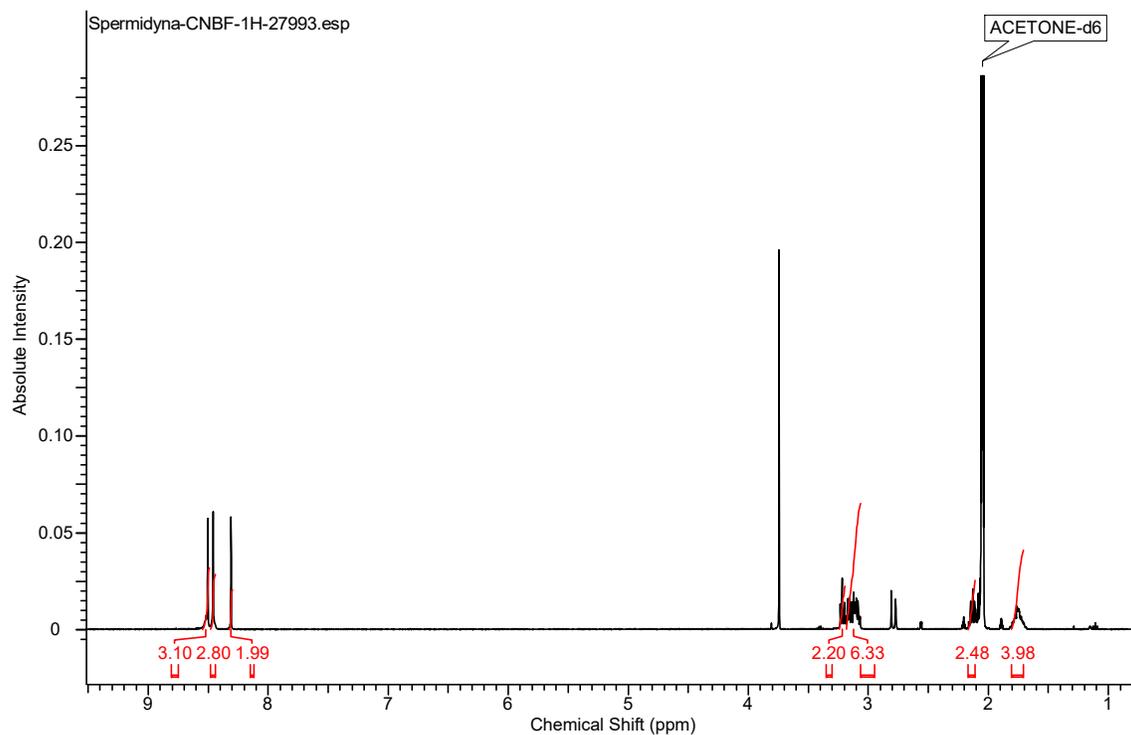
### Cad-FNBT (<sup>19</sup>F NMR)



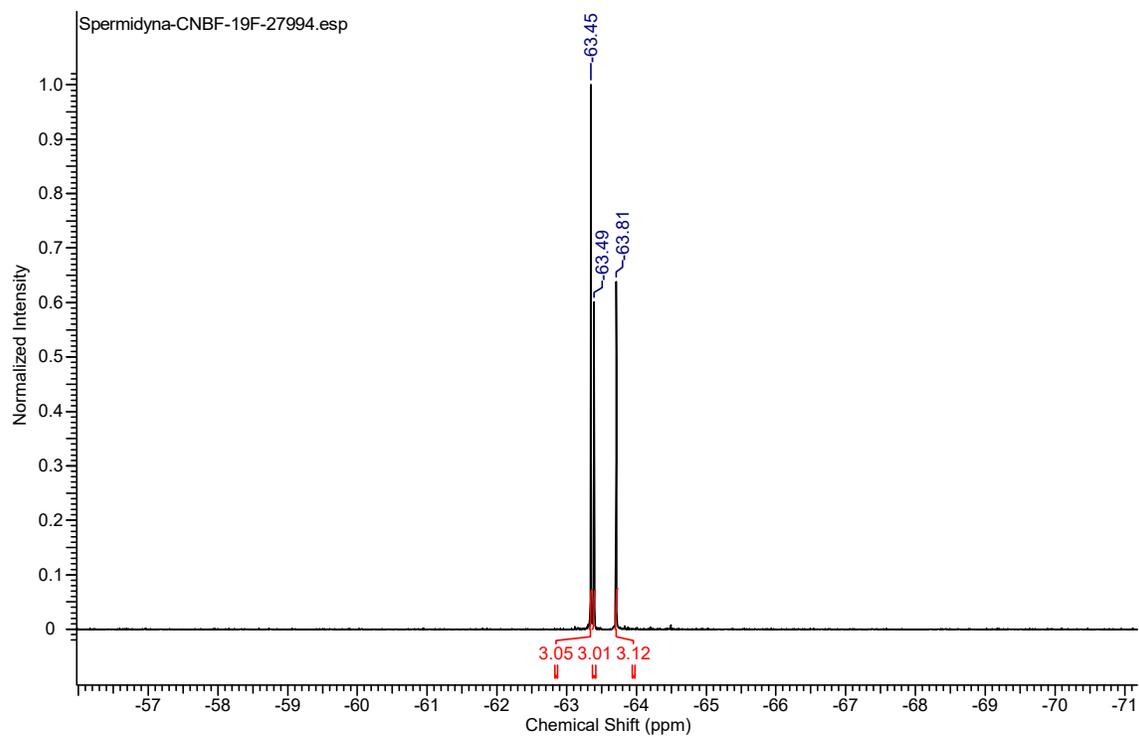
### Cad-FNBT (<sup>13</sup>C NMR)



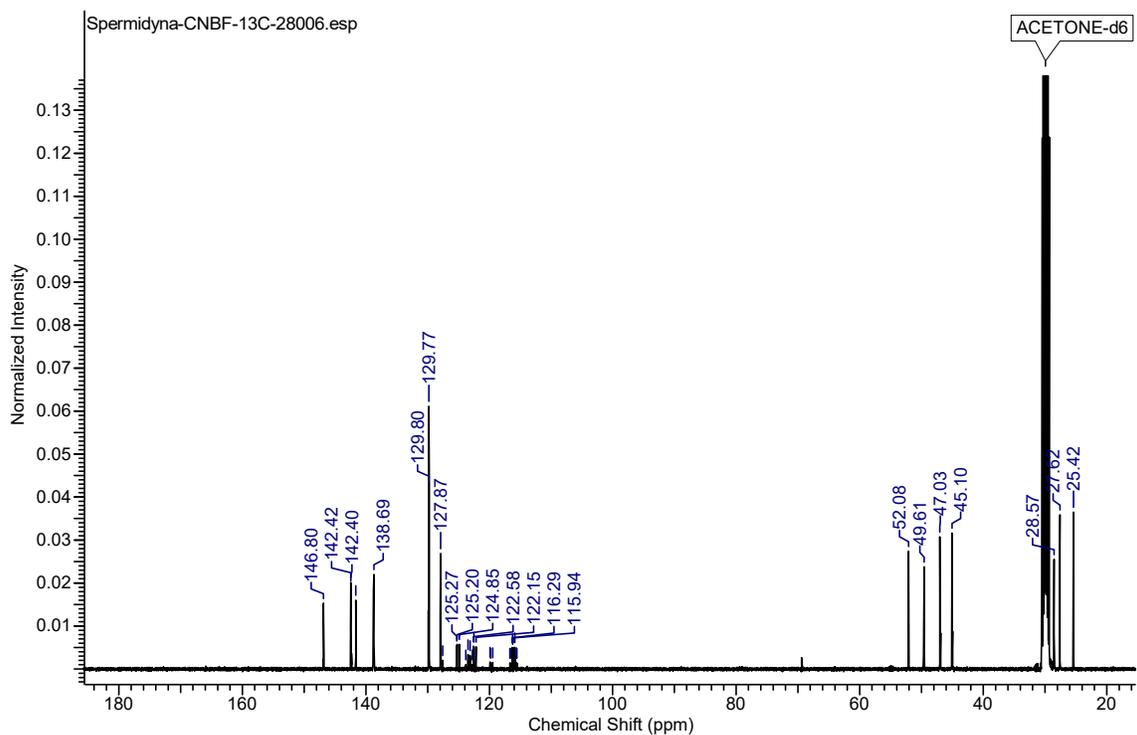
### Spd-CNBF (<sup>1</sup>H NMR)



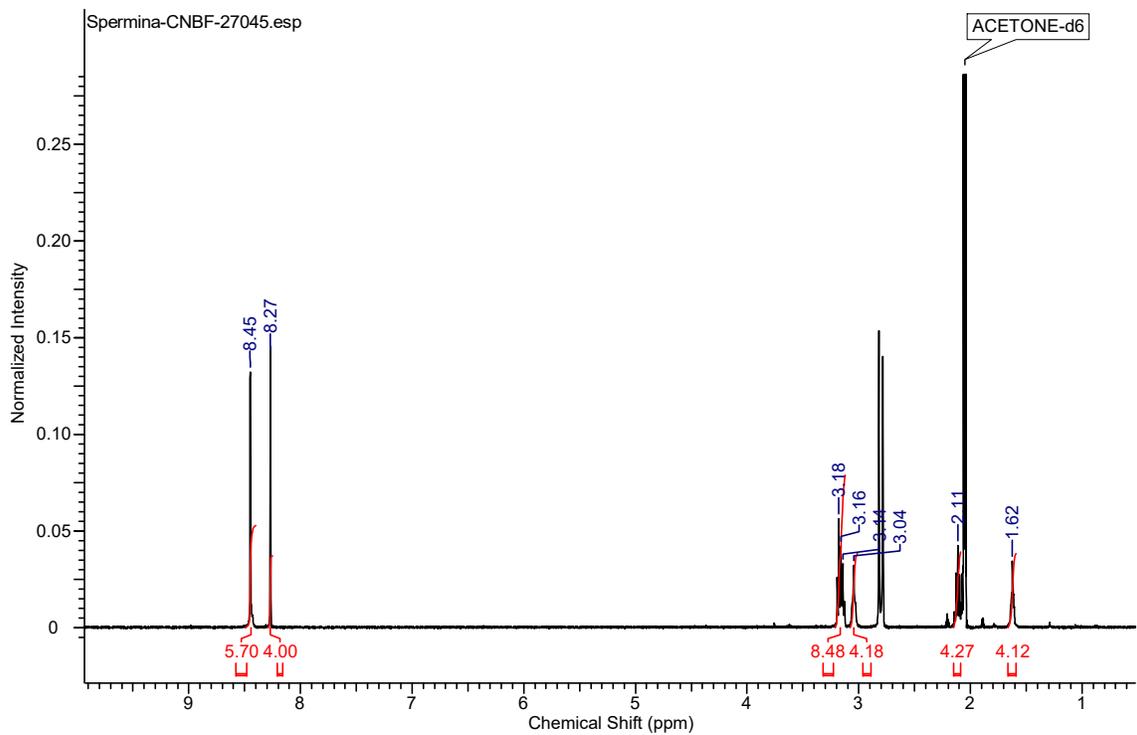
### Spd-CNBF (<sup>19</sup>F NMR)



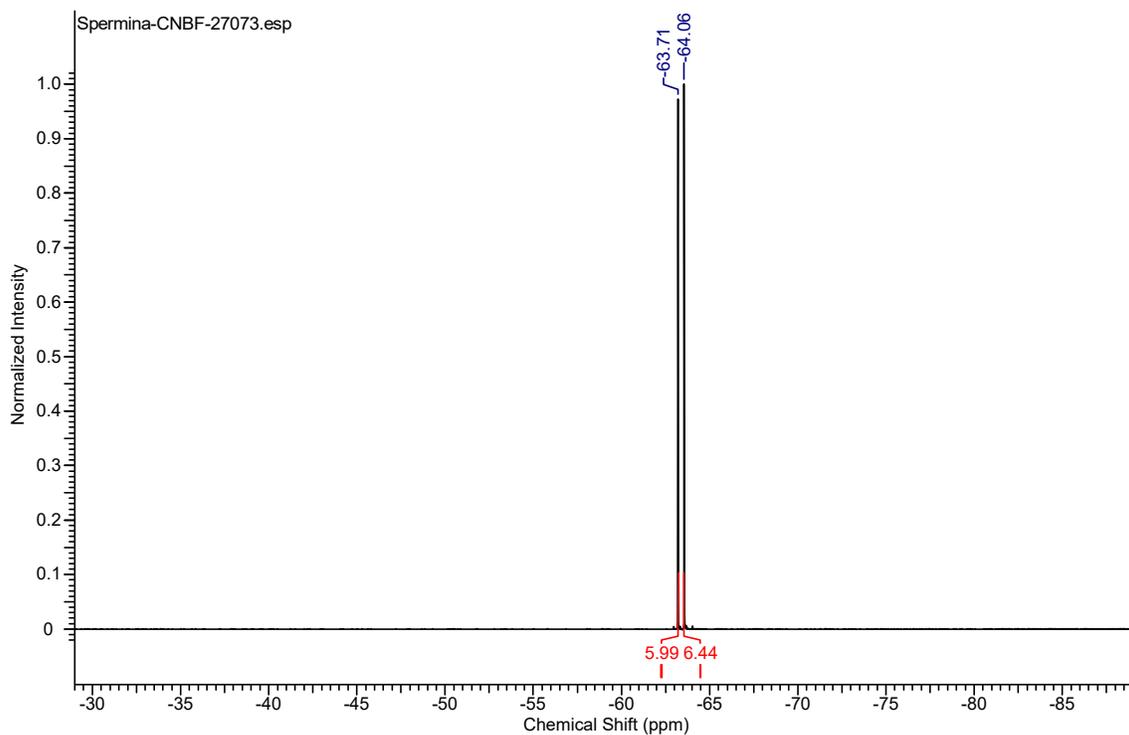
### Spd-CNBF (<sup>1</sup>H NMR)



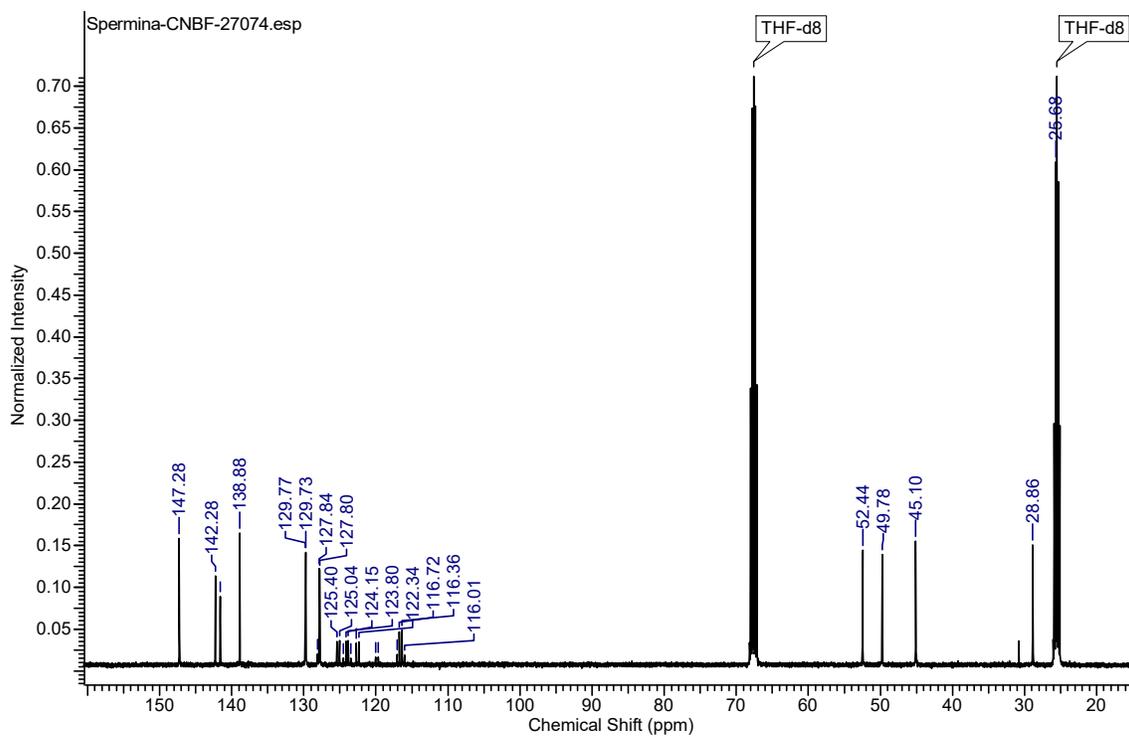
### Spm-CNBF (<sup>1</sup>H NMR)



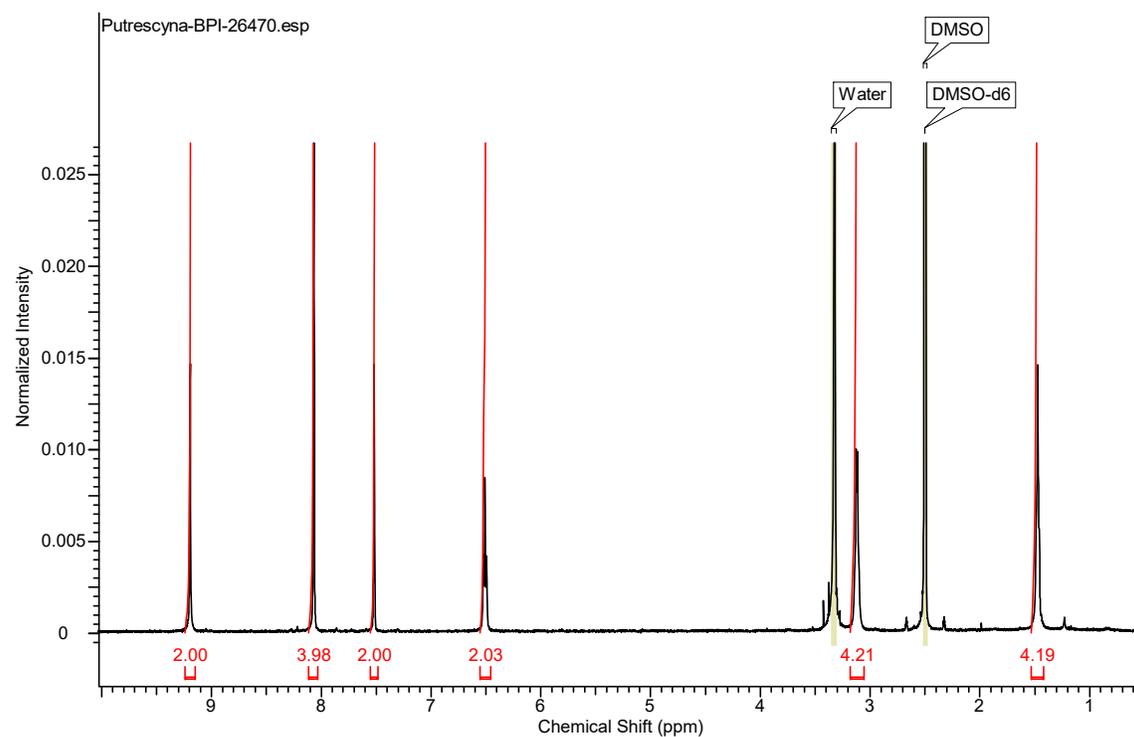
### Spm-CNBF (<sup>19</sup>F NMR)



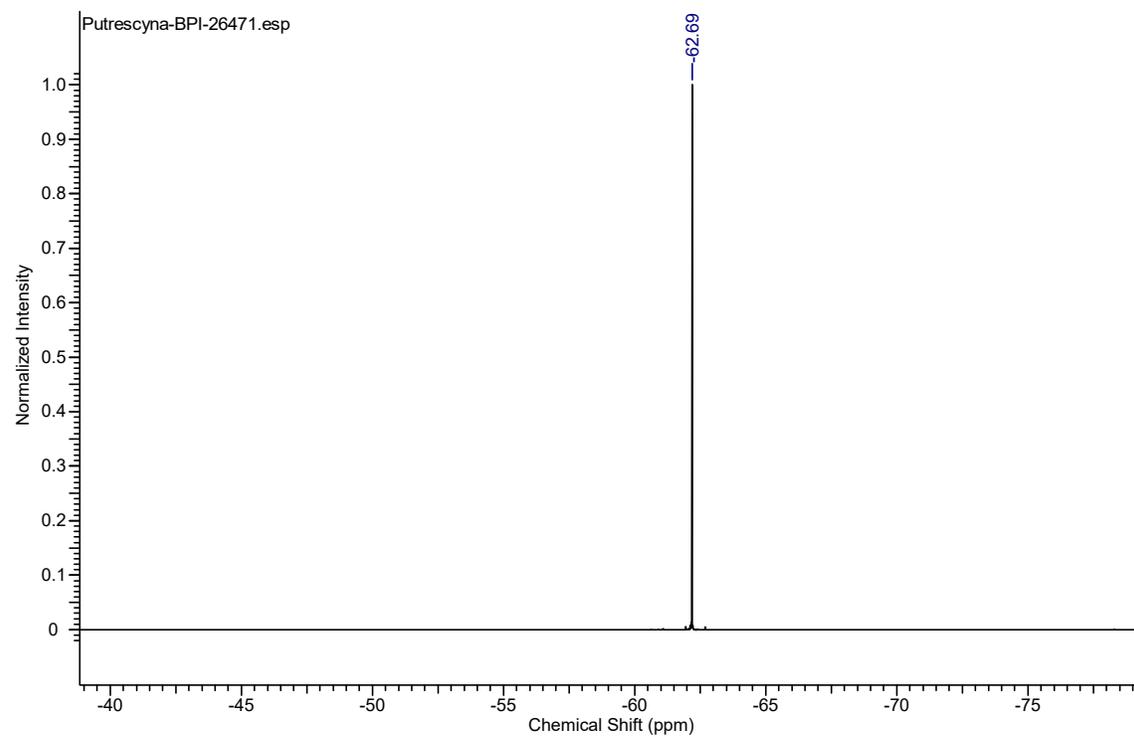
### Spm-CNBF (<sup>13</sup>C NMR)



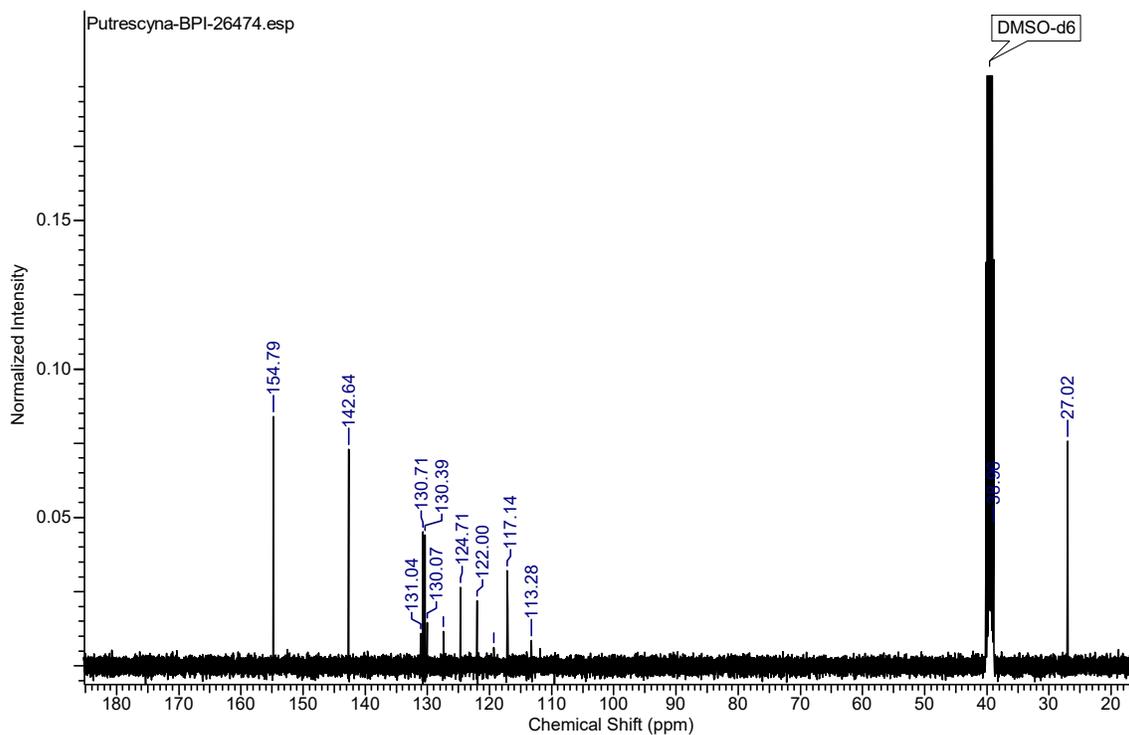
### Put-BPI ( $^1\text{H}$ NMR)



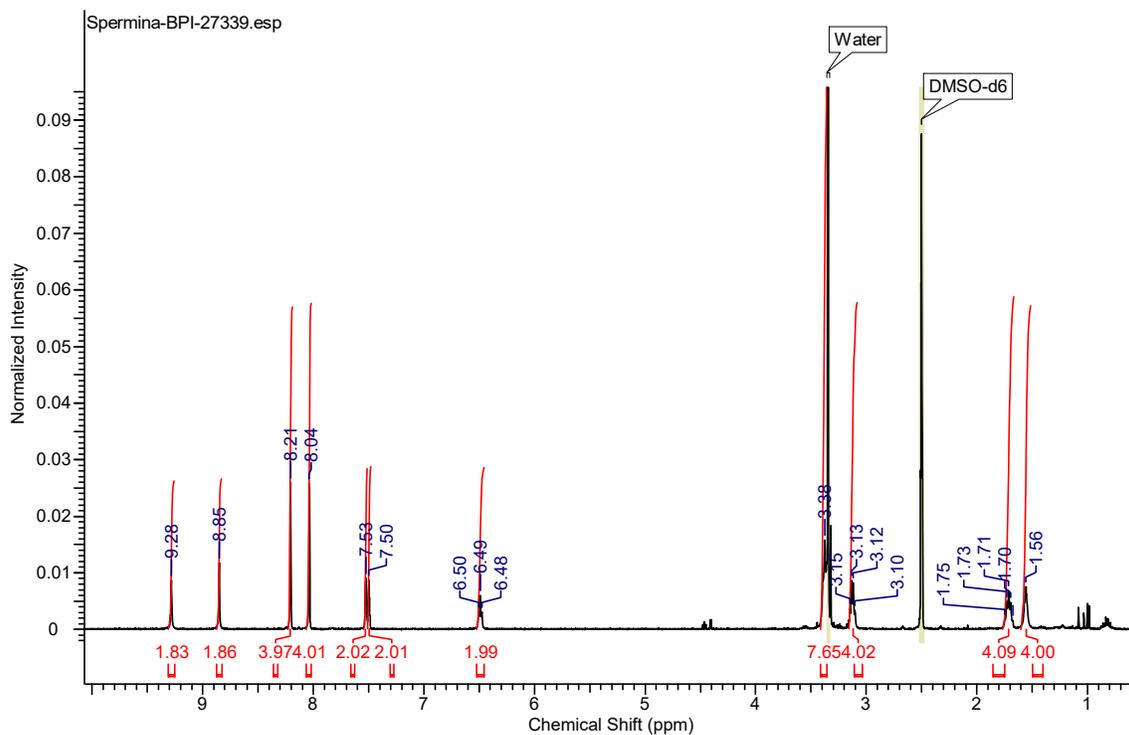
### Put-BPI ( $^{19}\text{F}$ NMR)



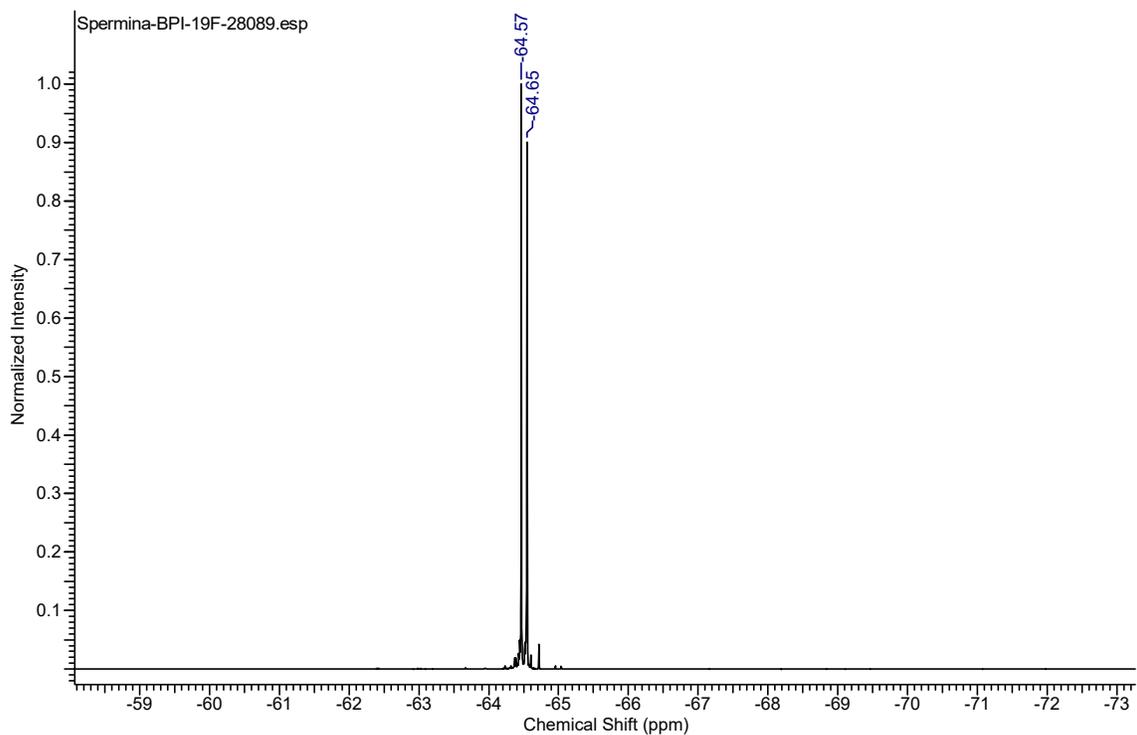
### Put-BPI (<sup>13</sup>C NHR)



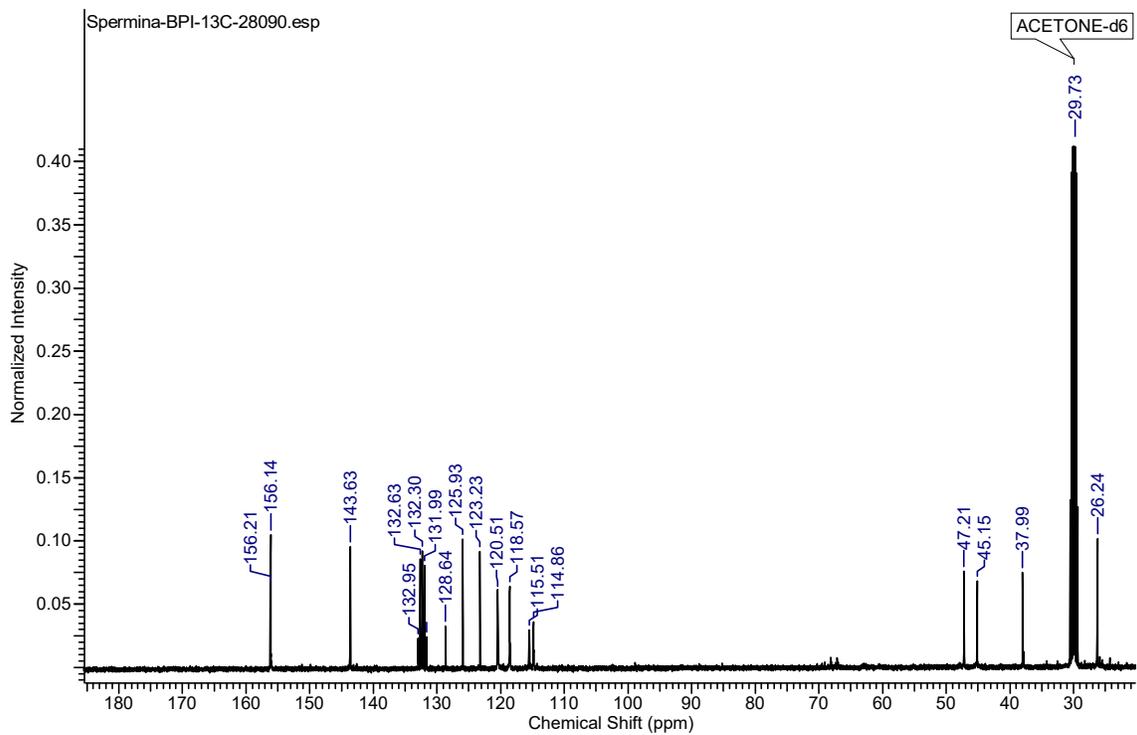
### Spm-BPI (<sup>1</sup>H NMR)



### Spm-BPI (<sup>19</sup>F NMR)

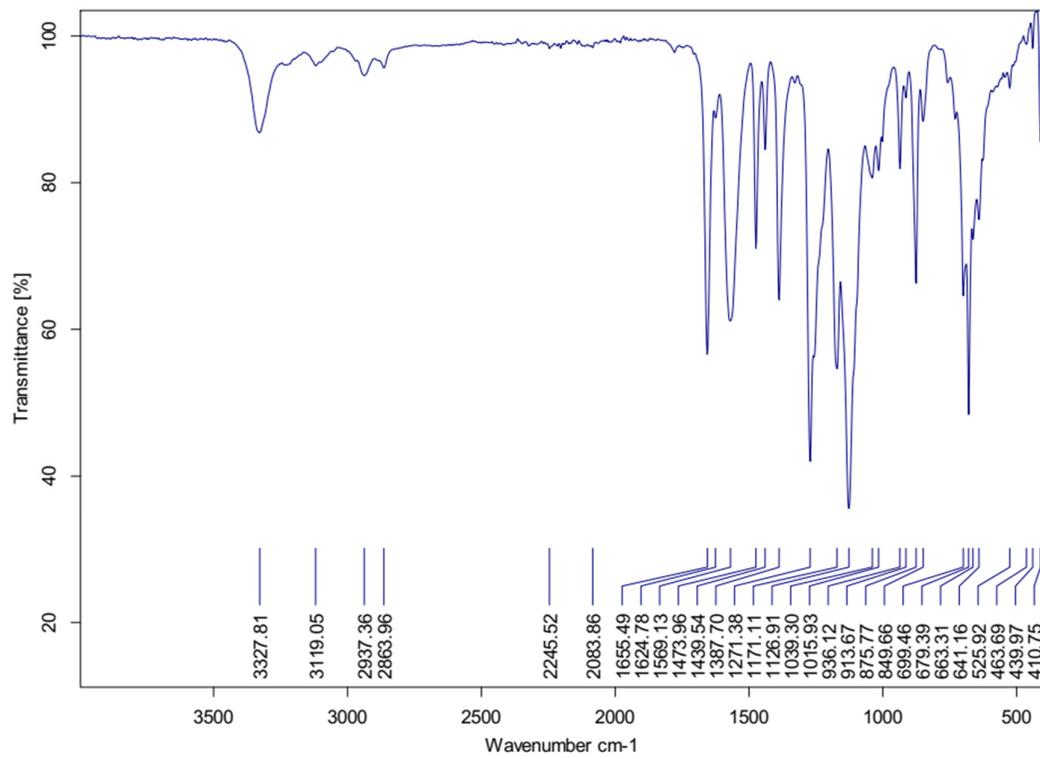


### Spm-BPI (<sup>13</sup>C NMR)

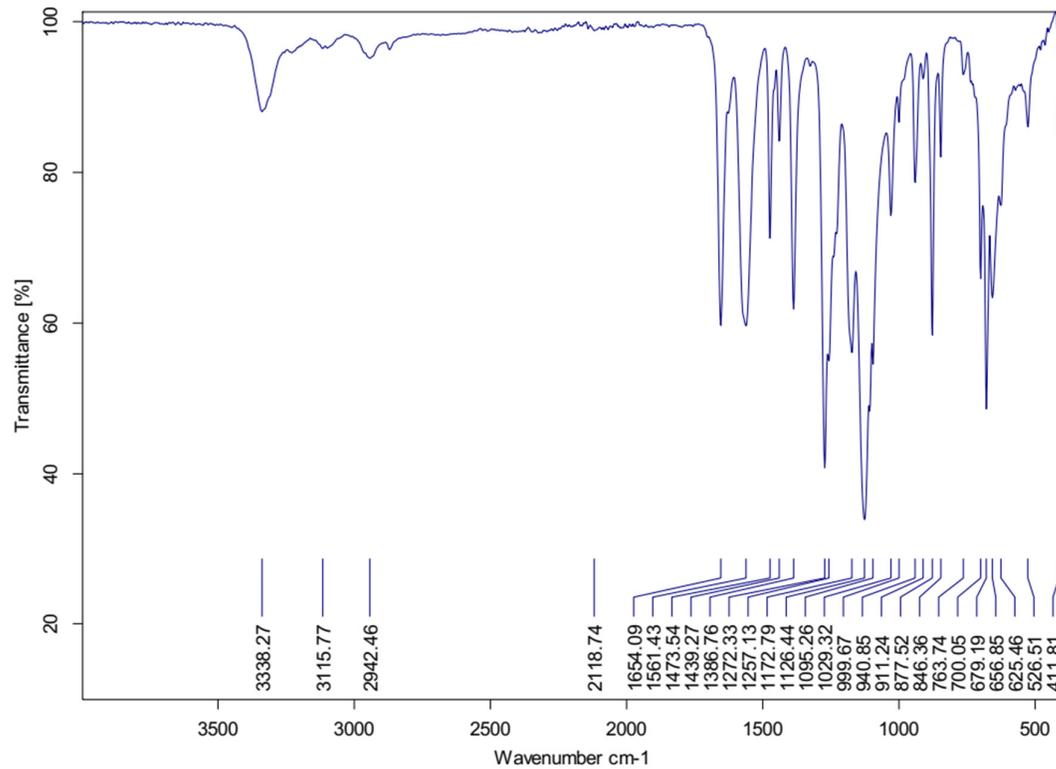


# IR-ATR spectra

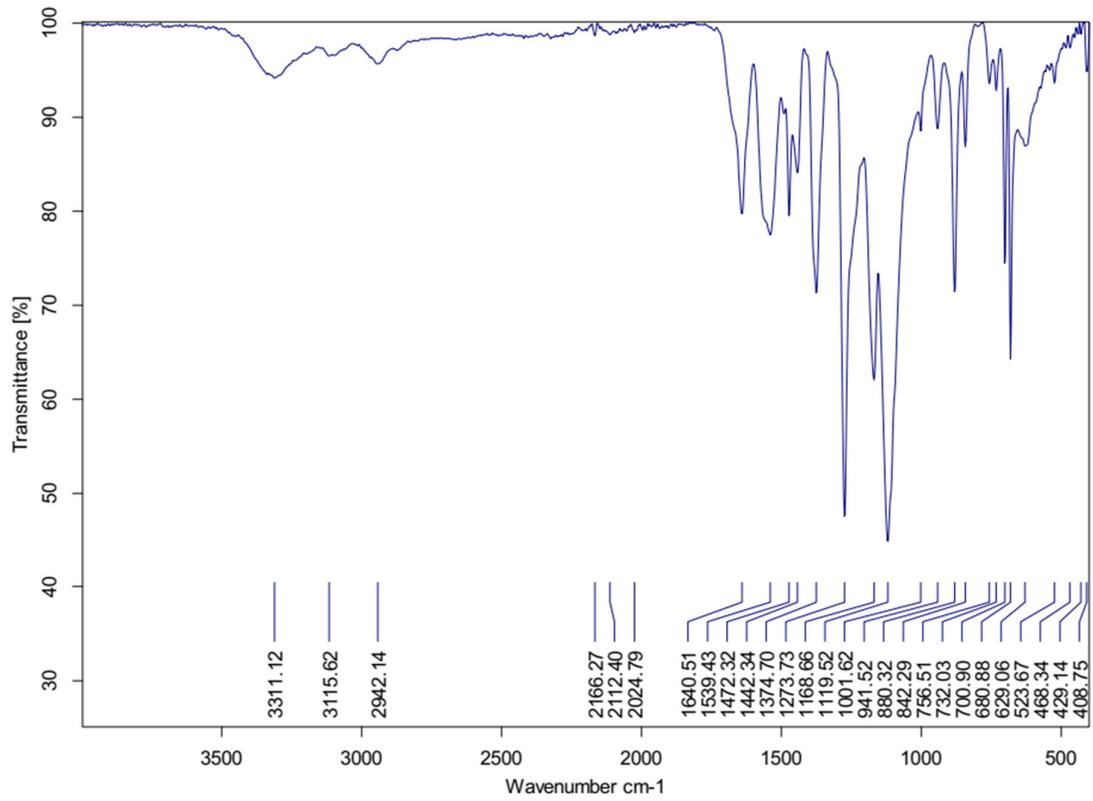
## Cad-BPI



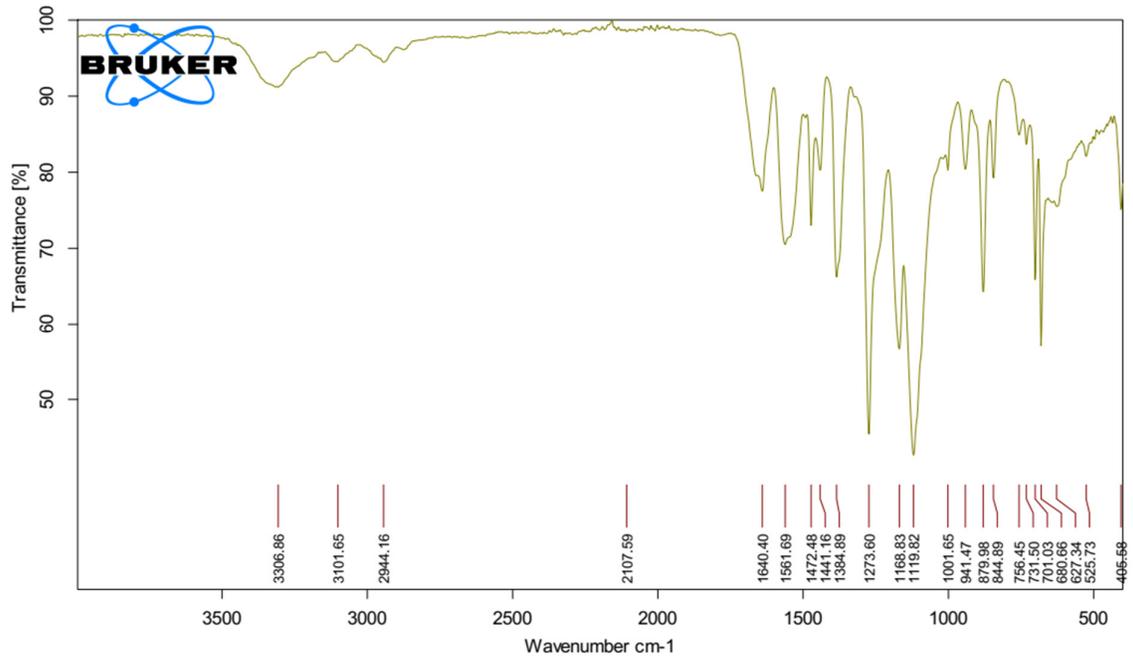
## Put-BPI



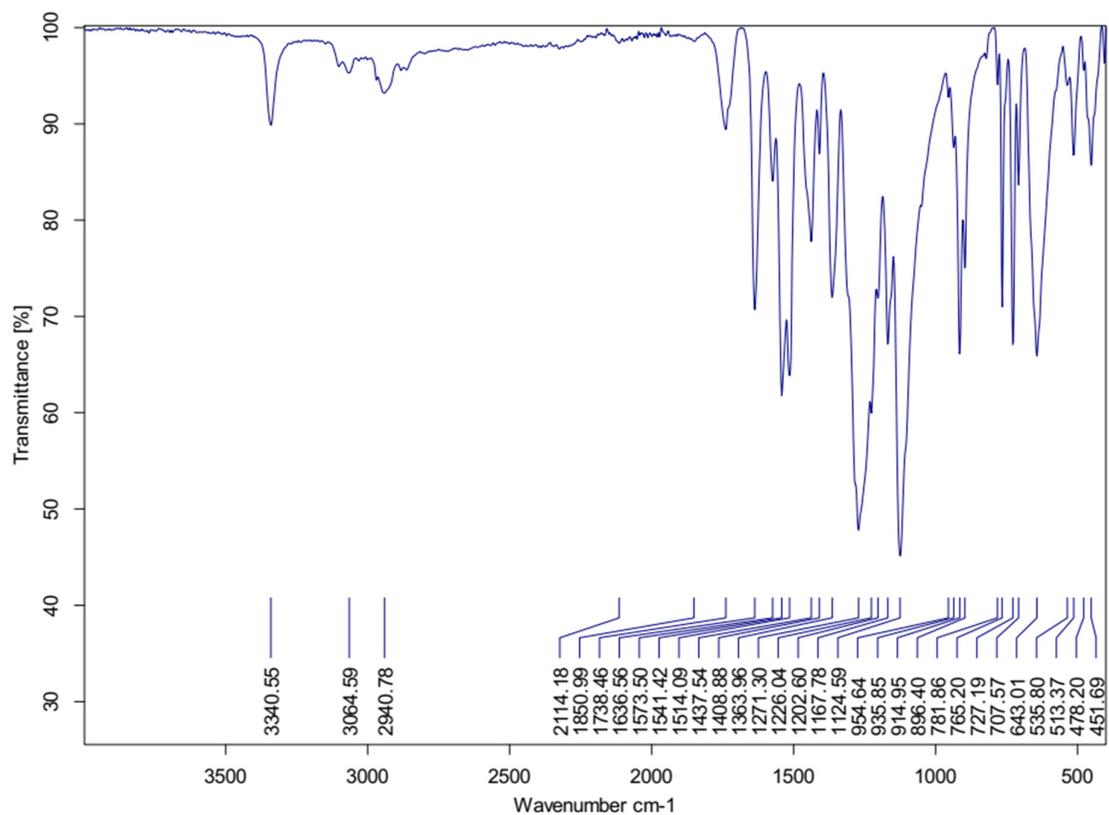
### Spm-BPI



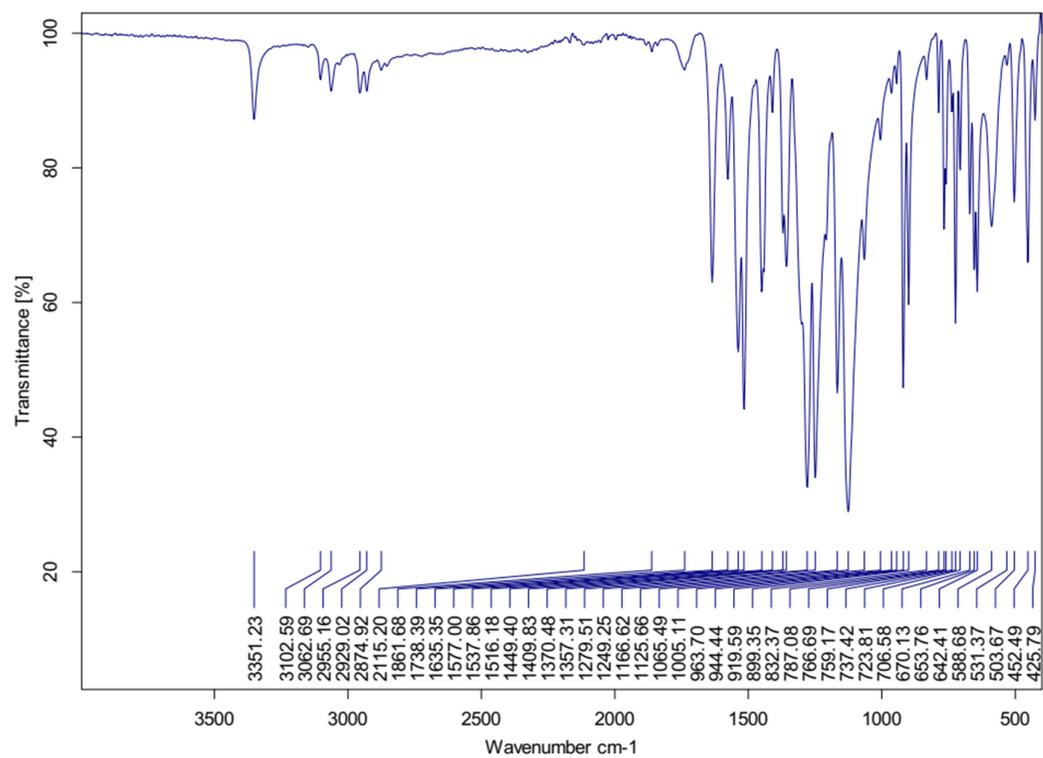
### Spd-BPI



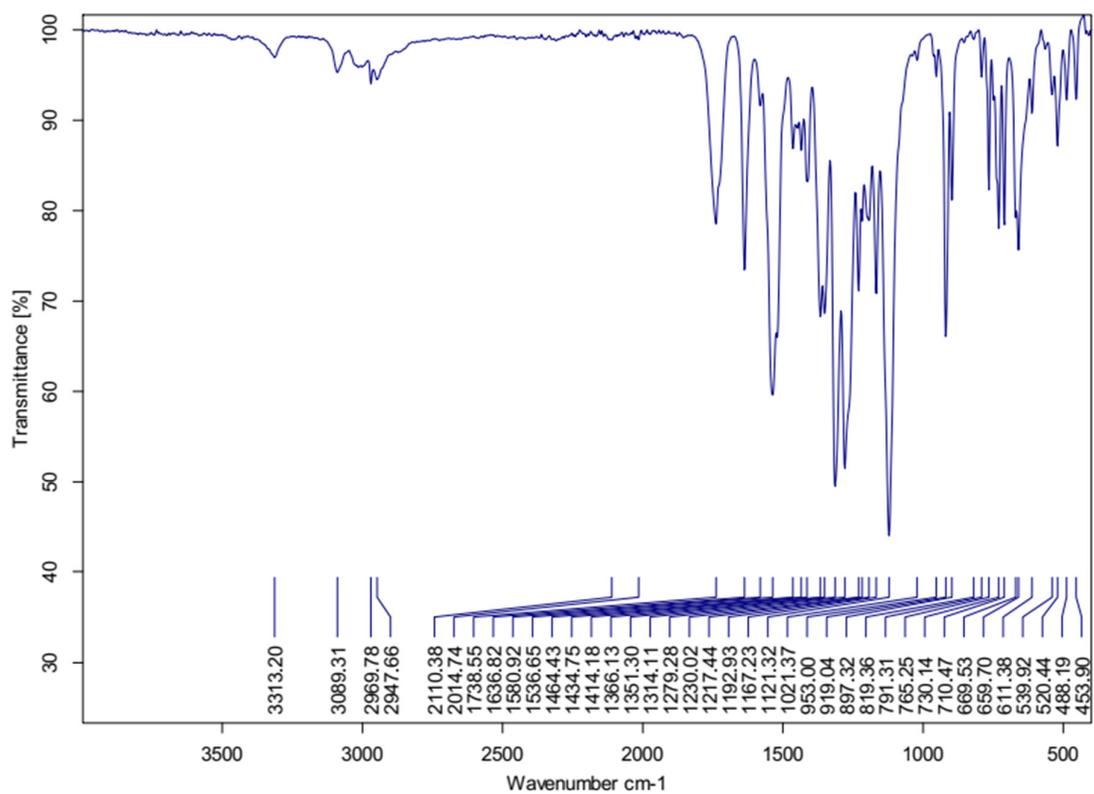
### Cad-CNBF



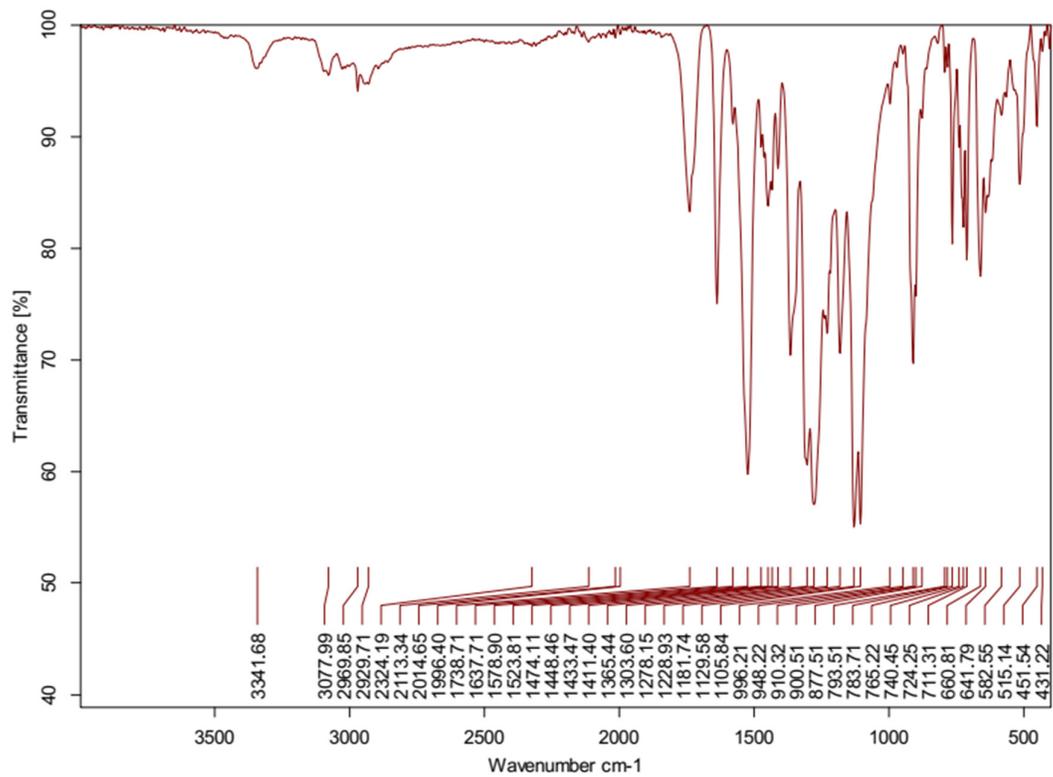
### Put-CNBF



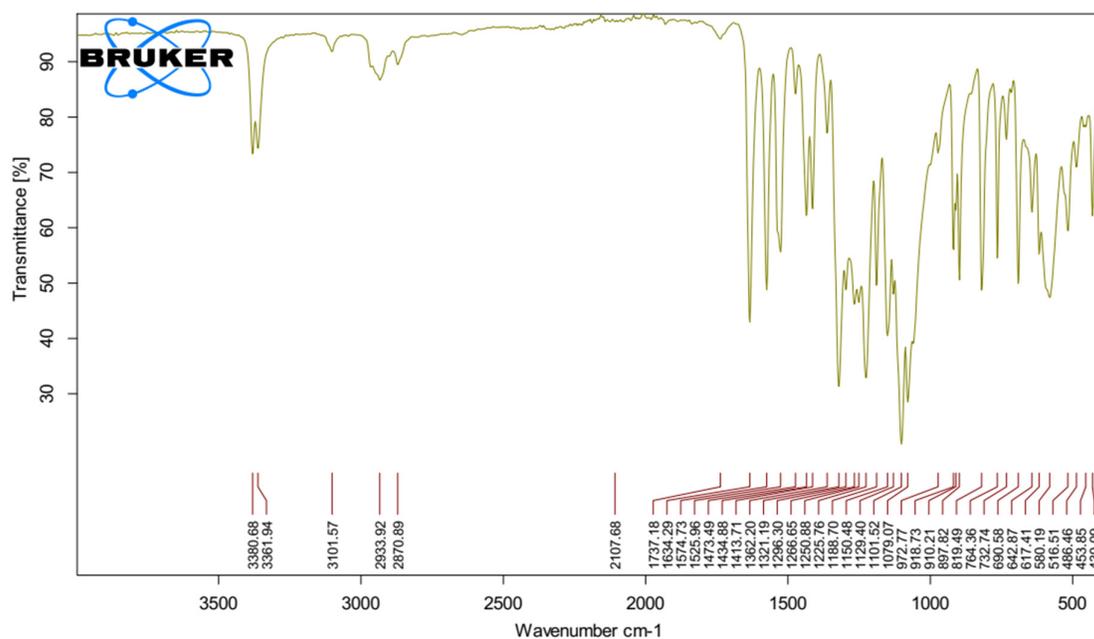
### Spm-CNBF



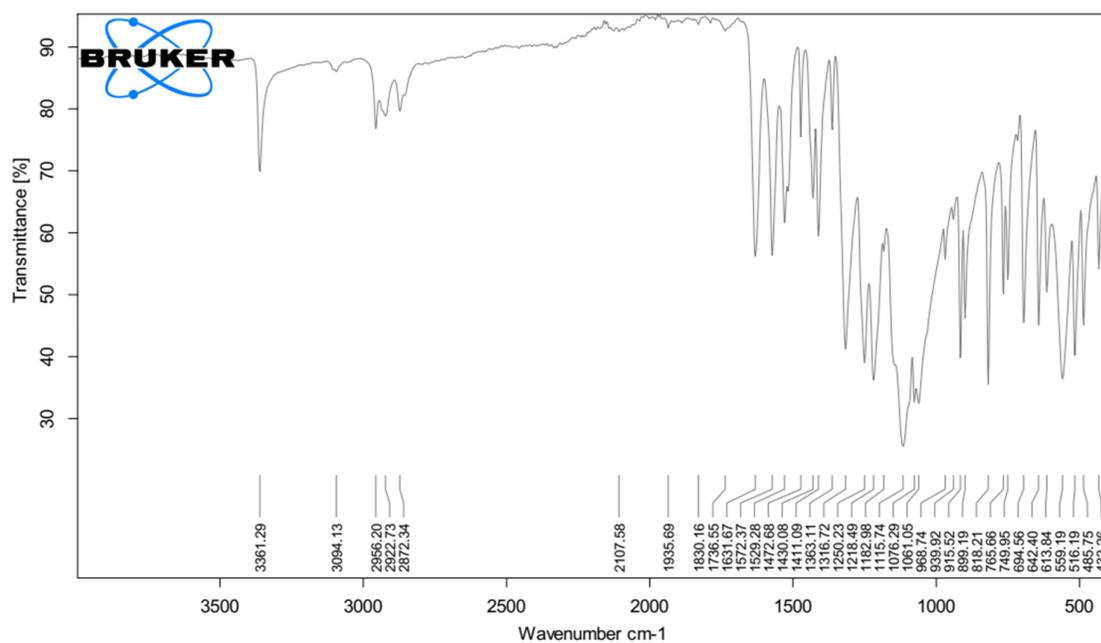
### Spd-CNBF



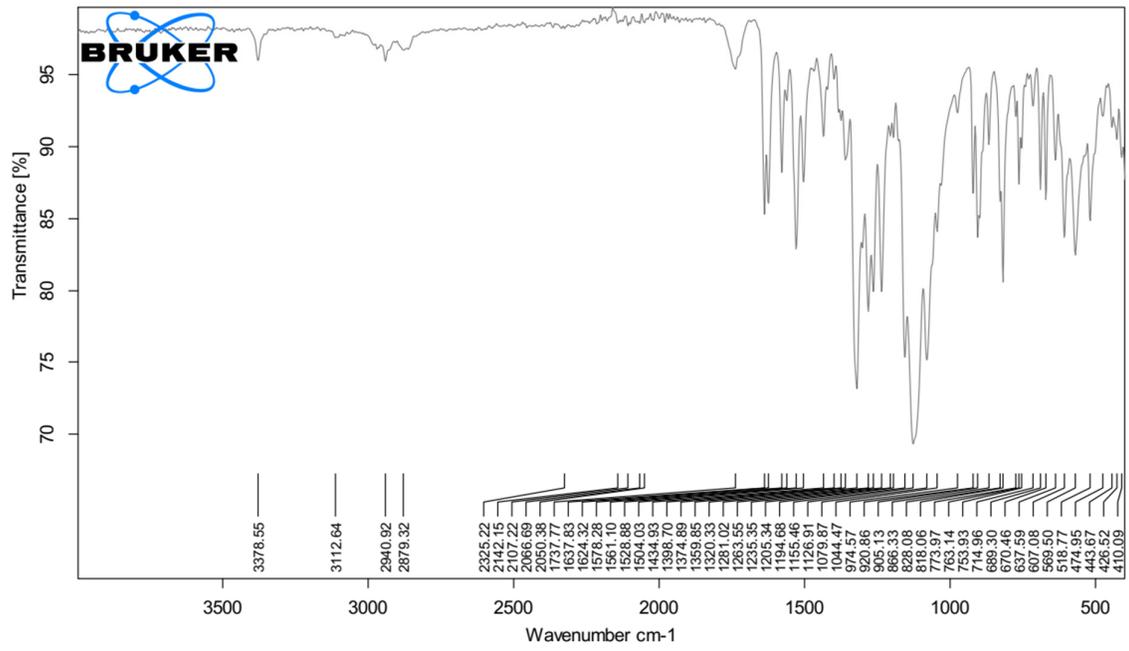
## Cad-FNBT



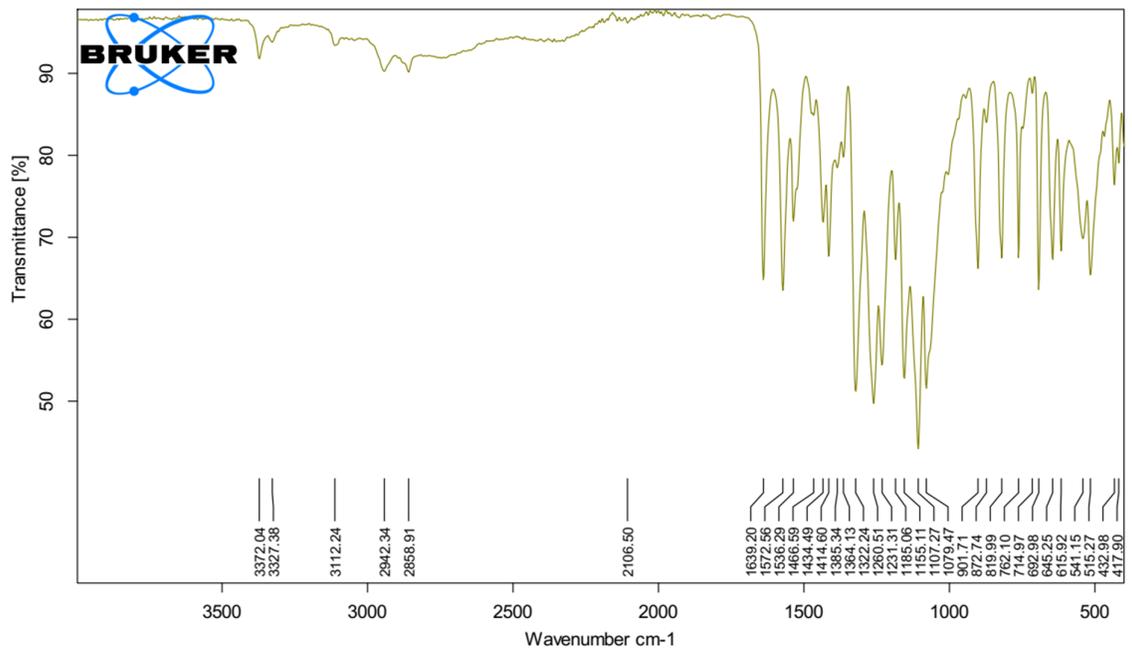
## Put-FNBT



### Spm-FNBT



### Spd-FNBT



**Table S1.** The results of the data collections and refinement for Cad-FNBT; Put-FNBT; Spm-FNBT and Spd-CNBF.

Identification code	Spm-FNBT	Cad-FNBT	Put-FNBT	Spd-CNBF
Empirical formula	C <sub>38</sub> H <sub>34</sub> F <sub>12</sub> N <sub>8</sub> O <sub>8</sub>	C <sub>19</sub> H <sub>18</sub> F <sub>6</sub> N <sub>4</sub> O <sub>4</sub>	C <sub>18</sub> H <sub>16</sub> F <sub>6</sub> N <sub>4</sub> O <sub>4</sub>	C <sub>28</sub> H <sub>22</sub> F <sub>9</sub> N <sub>9</sub> O <sub>12</sub>
Formula weight	958.73	480.37		
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength [Å]	1.54184	1.54184	1.54184	0.7999
Crystal system, space group	Triclinic, P-1	Monoclinic, P2(1)/n	Triclinic, P-1	Triclinic, P-1
Unit cell dimensions [Å]	a = 7.9650(3)	a = 9.93377(12)	a = 4.9668(2)	a = 7.9750(16) Å
and [°]	$\alpha$ = 71.646(3)	$\alpha$ = 90°	$\alpha$ = 83.837(3)	$\alpha$ = 75.65(3)°.
	b = 11.6008(4)	b = 18.5968(3)	b = 6.5809(3)	b = 11.781(2) Å
	$\beta$ = 83.951(3)	$\beta$ = 100.4050(13) °	$\beta$ = 85.011(3)	$\beta$ = 82.14(3)°
	c = 11.7281(4)	c = 11.49761(16)	c = 14.7689(6)	c = 17.767(4) Å
	$\gamma$ = 73.737(3)	$\gamma$ = 90°	$\gamma$ = 85.340(3)	$\gamma$ = 87.48(3)°
Volume [Å <sup>3</sup> ]	987.23(6)	2089.10(5)	476.87(4)	1601.9(6)

Z, calculated density [Mg/m <sup>3</sup> ]	1, 1.613	4, 1.527	1, 1.624	2, 1.757
Absorption coefficient [mm <sup>-1</sup> ]	1.340	1.267	1.368	0.232
F(000)	490	984	238	860
Crystal size [mm <sup>3</sup> ]	0.260 x 0.050 x 0.050	0.110 x 0.090 x 0.045	0.180 x 0.030 x 0.030	0.170 x 0.050 x 0.030
Theta range for data collection	3.972 to 74.466°.	4.756 to 74.465°.	3.019 to 74.322°.	1.343 to 29.995
Index ranges	-7<=h<=9 -14<=k<=14 -14<=l<=14	-12<=h<=12 -22<=k<=23 -14<=l<=14	-5<=h<=5 -8<=k<=8 -17<=l<=17	-9<=h<=9 -14<=k<=14 -22<=l<=22
Reflections collected/unique	11806, 3960 [R(int) = 0.0290]	8183, 8183	4577, 1791 [R(int) = 0.0150]	20171, 5885 [R(int) = 0.0344]
Completeness [%] to theta [°]	67.684° 99.9 %	67.684° 96.7%	67.684° 98.4 %	28.681°91.9 %

Absorption correction	Analytical	Analytical	Analytical	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.87553	0.951 and 0.890	1.00000 and 0.88847	0.993 and 0.962
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2	Full-matrix least- squares on F2	Full-matrix least- squares on F2
Data / restraints / parameters	3960 / 0 / 298	8183 / 48 / 326	1791 / 0 / 145	5885 / 12 / 550
Goodness-of-fit on F2	0.969	1.054	1.061	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0929	R1 = 0.0710, wR2 = 0.2045	R1 = 0.0438, wR2 = 0.1223	R1 = 0.0426, wR2 = 0.1164
R indices (all data)	R1 = 0.0408, wR2 = 0.0992	R1 = 0.0857, wR2 = 0.2197	R1 = 0.0472, wR2 = 0.1252	R1 = 0.0453, wR2 = 0.1192
Extinction coefficient	n/a	n/a	n/a	n/a
Largest diff. peak and hole [eÅ <sup>-3</sup> ]	0.364 and -0.359	0.664 and -0.559	0.610 and -0.430	0.620 and -0.556

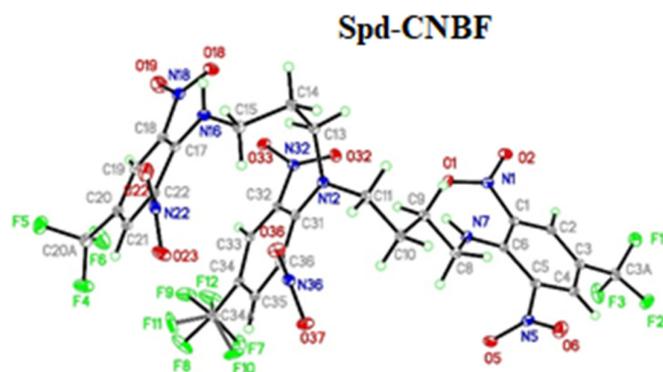
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**Table S2.** Precision and accuracy of the proposed procedures.

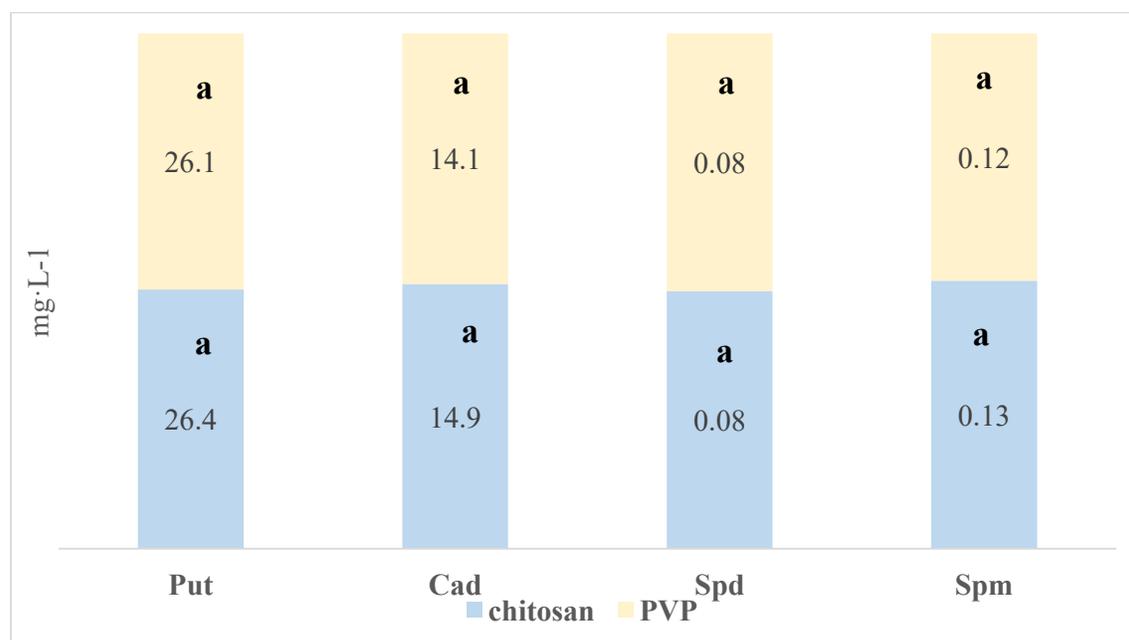
		Put		Cad			Spd			Spm		
X1	X2	Rec	CV	X2	Rec	CV	X2	Rec	CV	X2	Rec	CV
[mg·L <sup>-1</sup> ]	[mg·L <sup>-1</sup> ]	[%]	[%]	[mg·L <sup>-1</sup> ]	[%]	[%]	[mg·L <sup>-1</sup> ]	[%]	[%]	[mg·L <sup>-1</sup> ]	[%]	[%]
CNBF												
5.25	5.16	98.32	0.72	5.02	95.54	3.04	4.88	92.91	1.27	4.958	94.44	3.04
7.50	7.37	98.32	1.19	7.24	96.56	1.38	7.01	93.44	1.35	6.968	92.91	3.69
10.50	10.25	97.64	1.90	10.01	95.29	2.41	9.88	94.09	1.24	9.838	93.69	5.05
15.25	15.01	98.44	0.53	14.45	94.75	3.44	14.50	95.07	2.75	14.84	97.31	1.312
19.20	18.96	98.47	0.51	18.38	95.480	2.13	17.75	92.21	1.34	18.752	97.41	1.32
FNBT												
5.25	5.13	97.79	1.87	5.07	96.49	1.69	5.07	96.61	2.24	5.11	97.33	1.63
7.50	7.41	98.77	0.82	7.35	98.08	1.01	7.21	96.11	0.55	7.35	97.95	1.41
10.50	10.24	97.52	1.67	10.13	96.46	0.97	10.07	95.87	1.16	10.26	97.68	1.39
15.25	15.10	98.99	0.53	15.10	99.03	0.93	15.14	99.25	0.36	15.10	99.03	0.74
19.20	19.10	99.22	0.41	19.11	99.28	0.46	19.07	99.08	0.47	19.12	99.31	0.61

Where: *X1* -experimental concentration, *X2* - found concentration, *Rec* - recovery was calculated as mean value of (experimental concentration/found concentration)·100%, *CV* - coefficient of variation [%]

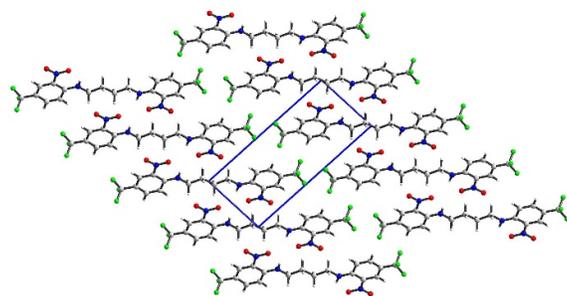




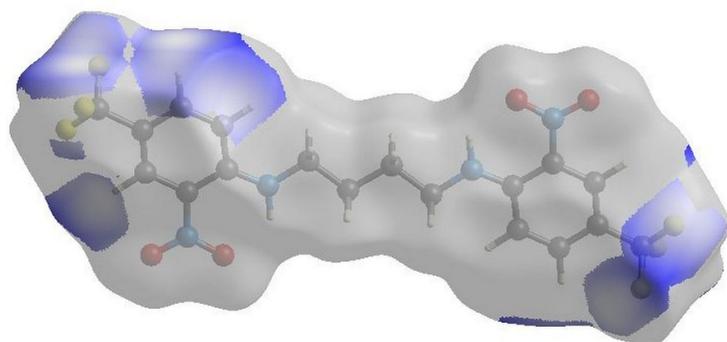
**Figure S1.** Molecular structures of polyamine derivatives.



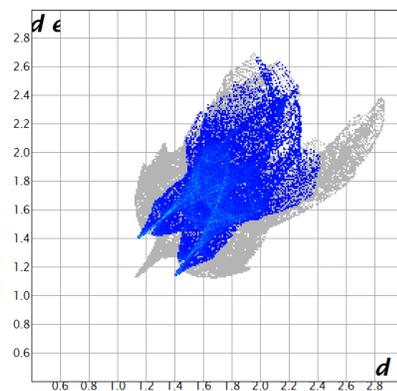
**Figure S2.** Results of biogenic amines chromatographic determination in wine samples after FNBT derivatization (sample 1, Cascade, red sweet wine) and purification procedures with chitosan, and PVP; the letter (a) for the same polyamine indicate no significant differences (one-way ANOVA and Duncan test,  $p < 0.05$ ).



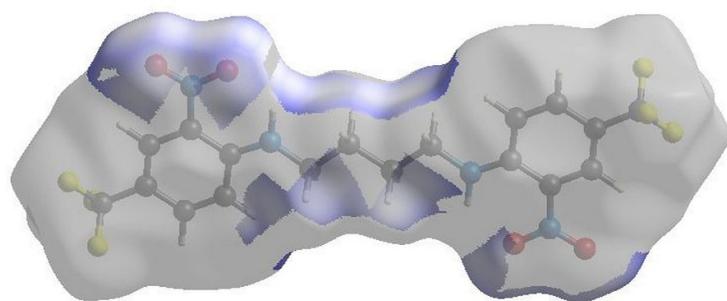
**Figure S3.** Packing of Put-FNBT along *a* axis.



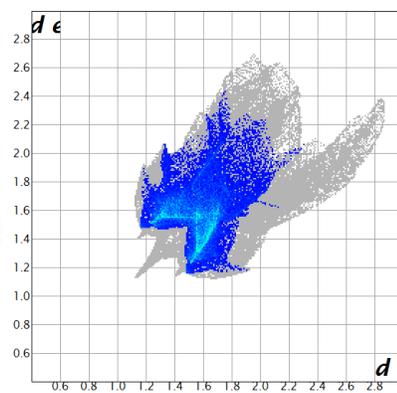
a



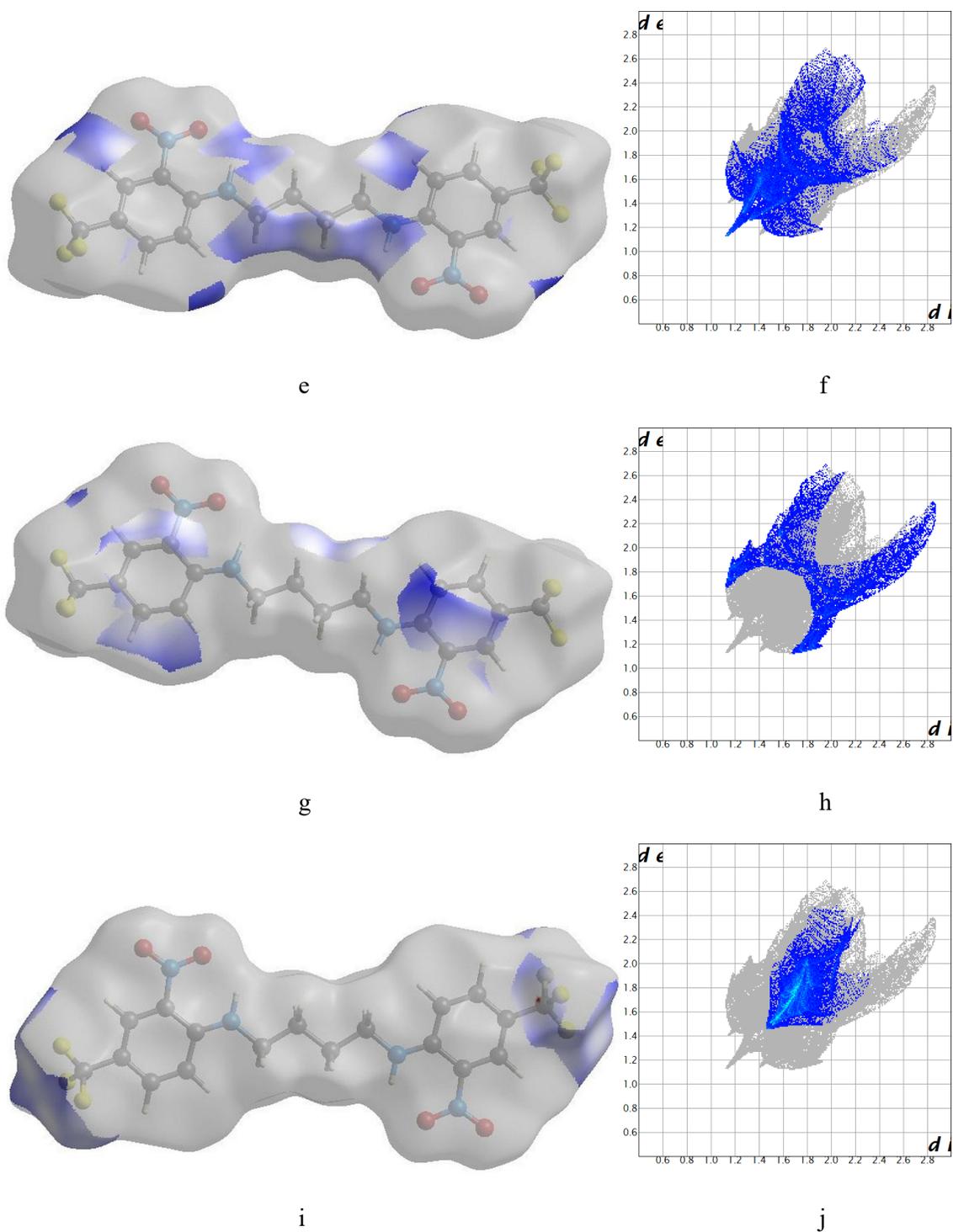
b



c

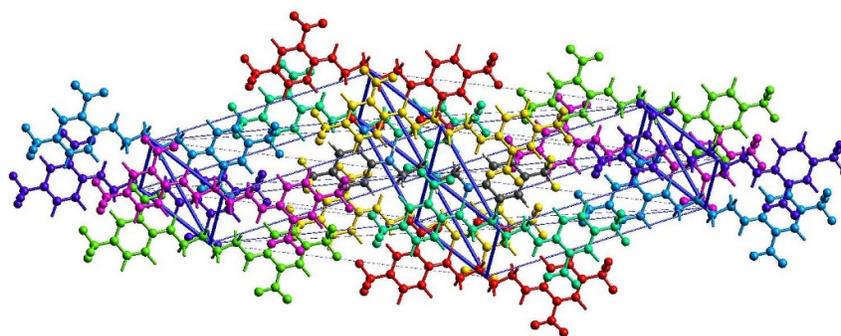


d

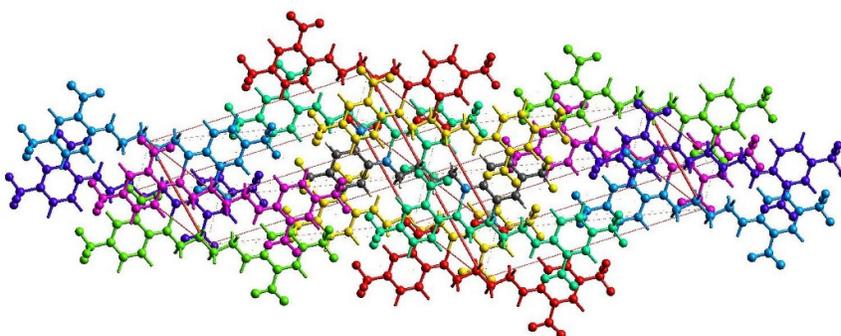


**Figure S4.** Hirshfeld surfaces and fingerprints of selected interactions created in the crystal network of Put-FNBT: Hirshfeld surface (a) and fingerprint (b) for F...H (20.8%), Hirshfeld surface (c; red markers correspond to the spike at 1.25; 0.95) and fingerprint (d) for O...H (24.4%), Hirshfeld surface (e) and fingerprint (f) for H...H (14.8%), Hirshfeld surface (g) and

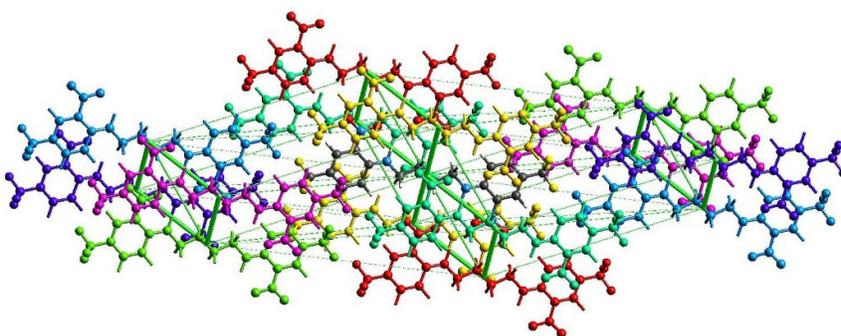
fingerprint (h) for H...C (10.6%), Hirshfeld surface (i) and fingerprint (j) for F...F (14.1%). In brackets, there is given surface area included as a percentage of the total surface area.



a



b



c

	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	8.56	B3LYP/6-31G(d,p)	-33.5	-8.7	-29.5	22.8	-53.5
	4.97	B3LYP/6-31G(d,p)	-1.2	-7.3	-79.9	43.9	-49.2
	17.00	B3LYP/6-31G(d,p)	-9.5	-1.0	-12.5	0.0	-21.6
	6.58	B3LYP/6-31G(d,p)	-15.0	-7.8	-73.9	41.3	-60.5

20.81	B3LYP/6-31G(d,p)	0.3	-0.1	-5.8	0.0	-4.8
20.84	B3LYP/6-31G(d,p)	1.5	-0.1	-7.2	0.0	-4.8
16.80	B3LYP/6-31G(d,p)	-3.1	-0.5	-12.6	0.0	-14.7

**Figure S5.** Interactions energy (total – a, electrostatic – b, dispersion – c) in the crystal network of Put-FNBT are given in kJ/mol. The tube diameter depends on the interactions energy. The color coding and the interactions energy are given in the table (d); R is the distance between molecular centroids in Å.

**Table S3.** Linear regression calibration parameters of BAs determination by RP-HPLC method after derivatives with FNBT (n =3<sup>a</sup>).

	t ± SD	R <sup>2</sup>	DL	QL
	[min]		[mg·L <sup>-1</sup> ]	
Histamine	6.73 ±0.07	0.9991	1.01	3.86
Tyramine	9.71 ±0.02	0.999	1.00	3.34
Tryptamine	13.84 ±0.02	0.9990	1.16	3.87
Phenylethylamine	15.93 ±0.03	0.9995	0.66	2.19

Where: *t* - retention time; *SD* - standard deviation, *R*<sup>2</sup> - coefficient of determination; *n*- number of samples; *DL* (Detection Limit) [mg·L<sup>-1</sup>] = (3 × *s<sub>y/x</sub>*) × *b*<sup>-1</sup>; *QL* (Quantification Limit) [mg·L<sup>-1</sup>] = (10 × *s<sub>y/x</sub>*) × *b*<sup>-1</sup>; <sup>a</sup>- each concentration level was analyzed in triplicate

**Table S4.** Results of aromatic and heterocyclic biogenic amines determination ( $\bar{X} \pm SD$ ) [ $\text{mg}\cdot\text{L}^{-1}$ ] in tested wine samples.

Wine sample	Him	Tym	Try	Phen
Cascade, sweet red wine	7.04±0.05	1.24±0.0	0.10±0.01	0.78±0.01
		1		
Maréchal Foch, sweet red wine	8.62±0.04	1.90±0.0	nd	1.55±0.01
		2		
Agat Donskoy, sweet, red wine (Enovini yeast)	12.4±0.06	3.35±0.0	0.11±0.01	2.96±0.02
		3		
Agat Donskoy, sweet red wine (Bordeaux yeast)	8.70±0.19	0.89±0.0	0.025±0.004	0.43±0.01
		1		
Aurora and Arcadia, sweet white wine	4.90±0.02	7.02±0,1	0.14±0.03	2.94±0.01
		4		
Aurora, semi-sweet white wine elderberry wine	3.63±0.02	nd	0.94±0.03	0.83±0.02
	5.27±0.04	2.06±0.0	nd	2.01±0.03
		1		
chokeberry wine	2.81±0.01	nd	nd	0.51±0.01
apple wine	4.11±0.03	2.51±0.0	nd	0.41±0.01
		4		

Where:  $\bar{X}$  - mean value;  $SD$  – standard deviation, number of independent sample = 3.