Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Combining Amino Acids and Carbohydrates into Readily Biodegradable, Task Specific Ionic Liquids

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Experimental Section

Synthesis of ILs

Materials

N-[2-(ᴅ-glucopyranosyl)ethyl]-*N*,*N*,*N*-trimethylammonium bromide was synthesized according to an established literature procedure.[1] L-glycine, L-leucine, L-serine, L-arginine, L-tyrosine, L-histidine, L-tryptophan and benzaldehyde were purchased from Sigma-Aldrich. Anion exchange resin (DOWEX® 1×8, 100-200 mesh) was purchased from Acros Organics.

General procedure for carbohydrate/amino acid ionic liquid [Carb][AAIL] synthesis

N-[2-(ᴅ-glucopyranosyl)ethyl]-*N*,*N*,*N*-trimethylammonium hydroxide aqueous solution was prepared from N-[2-(ᴅ-glucopyranosyl)ethyl]-N,N,N-trimethylammonium bromide (7.8 mmol) using anion exchange resin (DOWEX®).

The *N*-[2-(ᴅ-glucopyranosyl)ethyl]-*N*,*N*,*N*-trimethylammonium hydroxide aqueous solution was added dropwise to a 1.2 molar excess of the corresponding amino acid (9.3 mmol) in absolute ethanol (100 mL). The mixture was stirred until no dark brown precipitate formed upon testing with $AgNO_3$ (12–48 h). After solvent removal (50 °C, 20 mmbar), the residue was dissolved in methanol. The solid amino acid excess was separated and the solvent was evaporated yielding a viscous liquid (67–87%).

[Carb][Gly] yield: 86%. ^{1}H NMR (400 MHz, CD_3OD) δ 4.39 (d, J = 7.8 Hz, 1H), 4.36 (m, 1H), 4.11 (m, 1H), 3.94 (dd, J = 11.8, 2.2 Hz, 1H), 3.73 – 3.66 (m, 3H), 3.43 – 3.29 (m, 4H), 3.26 (s, 9H), 3.25 – 3.18 (m, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ

180.02, 104.21, 78.27, 78.08, 74.86, 71.53, 67.02, 64.17, 62.68, 54.80, 54.76, 54.72, 46.03.

[Carb][Leu] yield: 83%. ^{1}H NMR (400 MHz, CD_3OD) δ 4.33 (d, J = 7.8 Hz, 1H), 4.32 – 4.27 (m, 1H), 4.08 – 3.98 (m, 1H), 3.89 (dd, J = 11.8, 2.2 Hz, 1H), 3.67 – 3.60 (m, 3H), 3.38 – 3.21 (m, 4H), 3.20 (s, 9H), 3.17 (m, 1H), 1.74 (m, 1H), 1.57 (m, 1H), 1.36 (m, 1H), 0.92 (dd, J = 7.5, 6.6 Hz, 6H). ^{13}C NMR (101 MHz, CD_3OD) δ 182.65, 104.22, 78.28, 78.09, 74.86, 71.53, 67.02, 64.17, 62.68, 55.98, 54.79, 54.75, 54.71, 45.91, 26.07, 23.69, 22.45.

[Carb][Ser] yield: 82%. ^{1}H NMR (400 MHz, CD_3OD) δ 4.39 (d, J = 8.0 Hz, 1H), 4.36 (m, 1H), 4.14 – 4.04 (m, 1H), 3.94 (dd, J = 11.8, 2.2 Hz, 1H), 3.85 (dd, J = 11.8, 4.4 Hz, 2H), 3.69 (m, 3H), 3.42 – 3.27 (m, 4H), 3.26 (s, 9H), 3.23 (m, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 178.11, 104.21, 78.27, 78.08, 74.86, 71.53, 67.03, 65.31, 64.17, 62.68, 58.90, 54.79, 54.76, 54.72.

[Carb][Arg] yield: 67%. ^{1}H NMR (400 MHz, CD_3OD) δ 4.28 (d, J = 7.8 Hz, 1H), 4.25 (m, 1H), 4.04 – 3.93 (m, 1H), 3.83 (dd, J = 11.8, 2.2 Hz, 1H), 3.62 – 3.55 (m, 3H), 3.32 – 3.17 (m, 7H), 3.15 (s, 9H), 3.14 – 3.08 (m, 2H), 1.63 – 1.50 (m, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ 182.52, 104.27, 78.31, 78.20, 74.93, 71.61, 67.03, 64.16, 62.72, 56.95, 54.79, 54.75, 54.71, 49.85, 42.37, 33.48, 26.45.

[Carb][Hist] yield: 74%. ^{1}H NMR (400 MHz, CD_3OD) δ 7.58 (d, J = 1.0 Hz, 1H), 6.88 (d, J = 1.0 Hz, 1H), 4.37 (d, J = 7.8 Hz, 1H), 4.33 (m, 1H), 4.06 (m, 1H), 3.92 (dd, J = 11.8, 2.2 Hz, 1H), 3.67 (m, 3H), 3.46 (dd, J = 8.0, 4.7 Hz, 1H), 3.39 (m, 1H), 3.34 – 3.31 (m, 2H), 3.27 (m, 1H), 3.22 (s, 9H), 3.07 (ddd, J = 14.7, 4.7, 0.8 Hz, 1H), 2.81 (dd, J = 14.7, 8.0 Hz, 1H) ^{13}C NMR (101 MHz, CD_3OD) δ 181.18, 135.99, 134.16, 120.52, 104.22, 78.28, 78.08, 74.86, 71.53, 66.98, 64.17, 62.67, 57.55, 54.79, 54.76, 54.72, 33.39.

[Carb][Trp] yield: 87%. ^{1}H NMR (400 MHz, CD_3OD) δ 7.75 – 7.69 (dt, J =8.0, 1.8 Hz, 1H), 7.36 (dt, J = 8.0, 1,8 Hz, 1H), 7.18 (s, 1H), 7.11 (ddd, J = 8.0, 7.8, 1.2 Hz, 1H), 7.04 (ddd, J = 8.0, 7.8, 1.2 Hz, 1H), 4.36 (d, J = 7.8 Hz, 1H), 4.33 – 4.25 (m, 1H), 4.06 – 3.97 (m, 1H), 3.93 (dd, J = 11.8, 2.0 Hz, 1H), 3.69 (dd, J = 11.8, 2.0 Hz, 1H), 3.65 (dd, J = 8.4, 4.4 Hz, 1H), 3.62 – 3.56 (m, 2H), 3.43 – 3.38 (m, 1H), 3.36 – 3.25 (m, 3H), 3.24 – 3.19 (m, 1H), 3.17 (s, 9H), 3.04 – 2.96 (m, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 180.28, 138.22, 128.97, 124.68, 122.41, 119.77, 119.65, 112.25, 111.80, 104.19, 78.25, 78.06, 74.85, 71.52, 66.94, 64.13, 62.65, 57.72, 54.74, 54.71, 54.67, 31.64.

[Carb][Tyr] yield: 76%. ^{1}H NMR (400 MHz, CD_3OD) δ 7.03 (d, J = 8.5 Hz, 1H), 6.68 (d, J = 8.5 Hz, 1H), 4.37 (d, J = 7.8 Hz, 1H), 4.34 – 4.28 (m, 1H), 4.12 – 3.99 (m, 1H), 3.93 (dd, J = 11.8, 2.2 Hz, 1H), 3.68 (dd, J = 11.8, 5.9 Hz, 1H), 3.64 (m, 2H), 3.40 (m, 1H), 3.37 – 3.25 (m, 4H), 3.22 (s, 9H), 3.02 (dd, J = 13.5, 4.8 Hz, 1H), 2.65 (dd, J = 13.5, 8.4 Hz, 1H).^{13}C NMR (101 MHz, CD_3OD) δ 181.78, 160.76, 131.32, 128.30, 117.69, 104.22, 78.27, 78.08, 74.87, 71.55, 66.99, 64.16, 62.68, 59.15, 54.78, 54.75, 54.72, 42.05.

Table 1. Comparison of Knoevenagel process performance indicators achieved in the presence of different amino acid catalysts.

Substrates	Catalyst	Catalyst loading	Solvent	Temp	Reaction Time	Yield [%]	Ref.
Cinnamaldehyde + acetyl acetone	Glycine	20%mol	DMSO	RT	1h	15	[2]
Benzaldehyde +malononitrile	Glycine	20%mol	[6-mim] [PF_6]	RT	22h	77	[3]
Benzaldehyde +malononitrile	Glycine	20%mol	[MMIm] [MSO_4]	RT	70 min	98	[4]
Benzaldehyde + malononitrile	ILs of amino acid amides	30%mol	Solvent-free	RT	30 min	97	[5]
Benzaldehyde + cyanoacetate	[Chol][Gly]	1%mol	Solvent-free	RT	3h	74	[6]
Benzaldehyde +malononitrile	[TBA][Leu]	2.5%mol	water	RT	30 min	89	[7]
Benzaldehyde + malononitrile	[Carb][Gly] [Carb][Trp]	10%mol	water	RT	30 min 15 min	94 92	This work

Figure 1. Biodegradation of carbohydrate/amino acid based Ils.

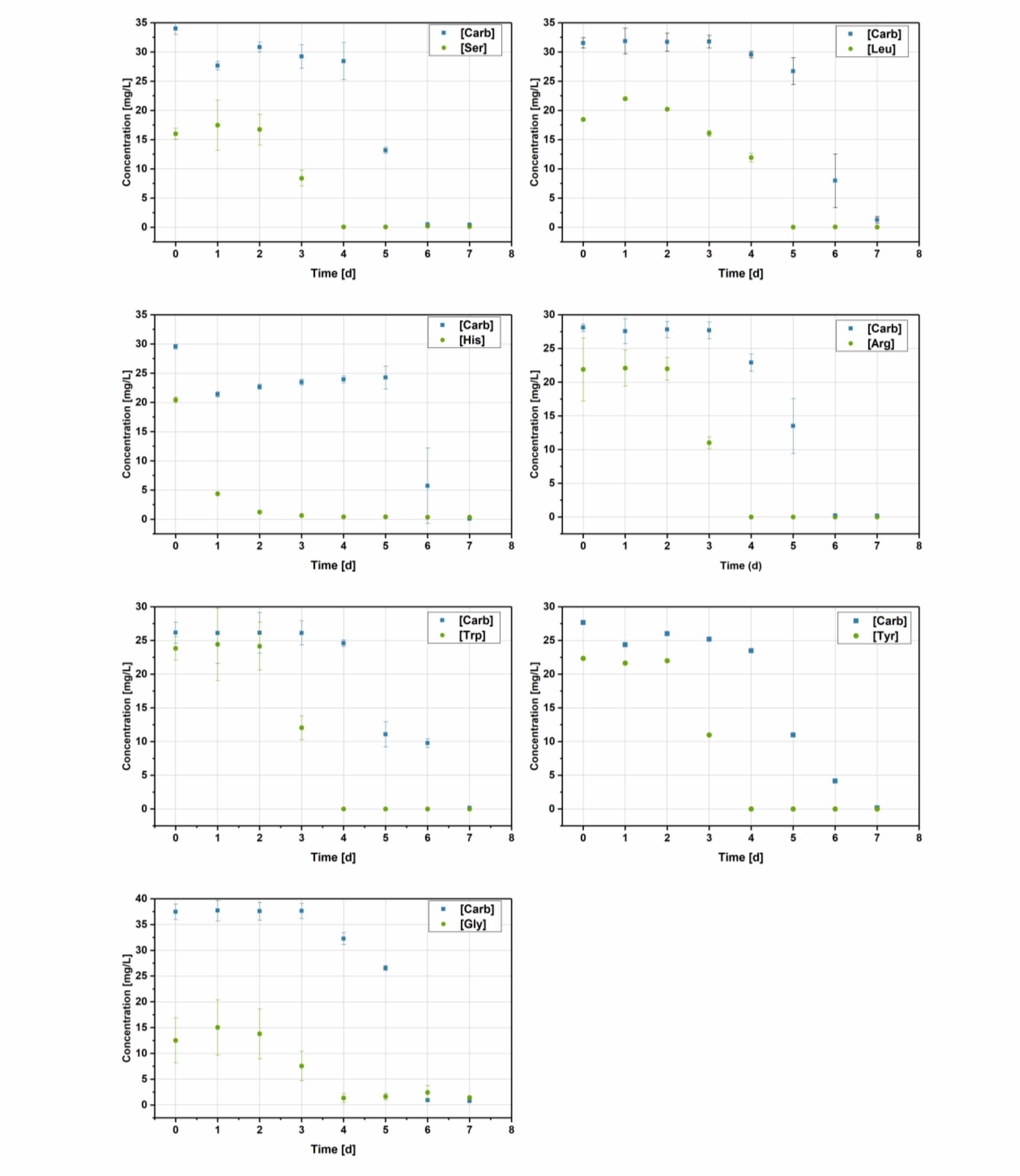
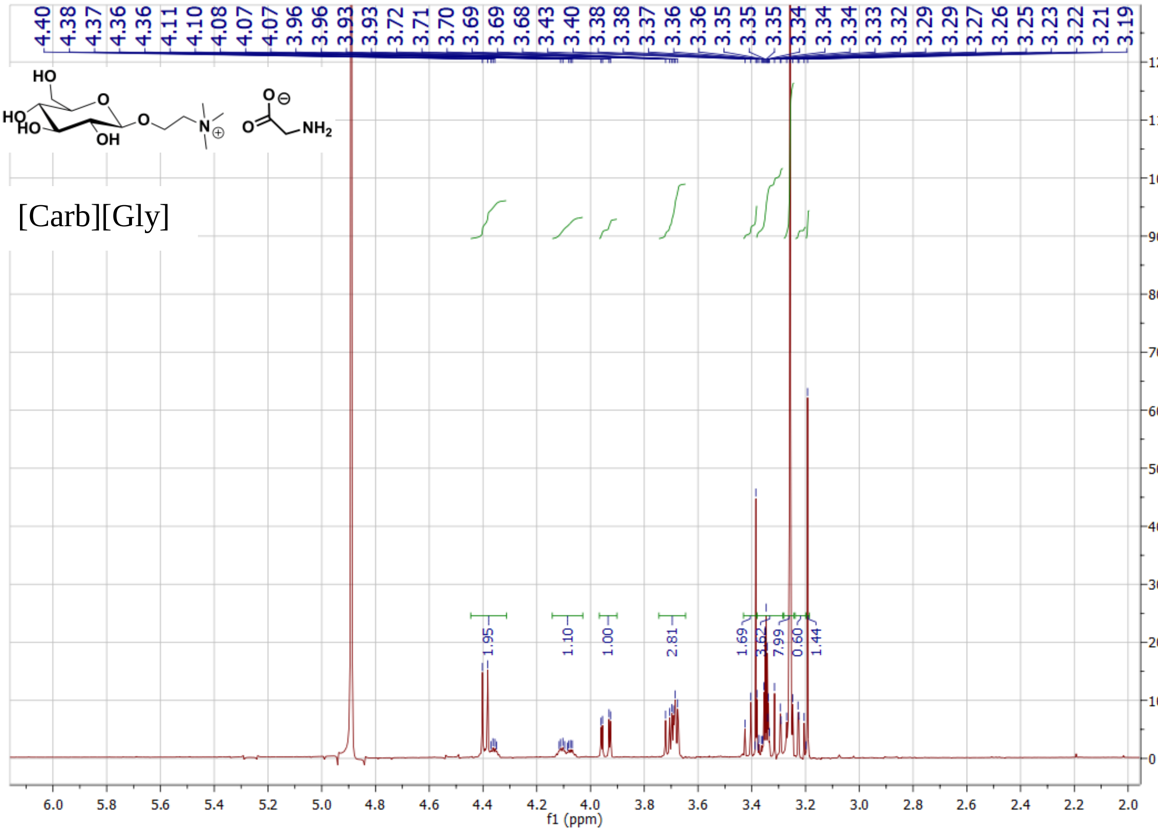
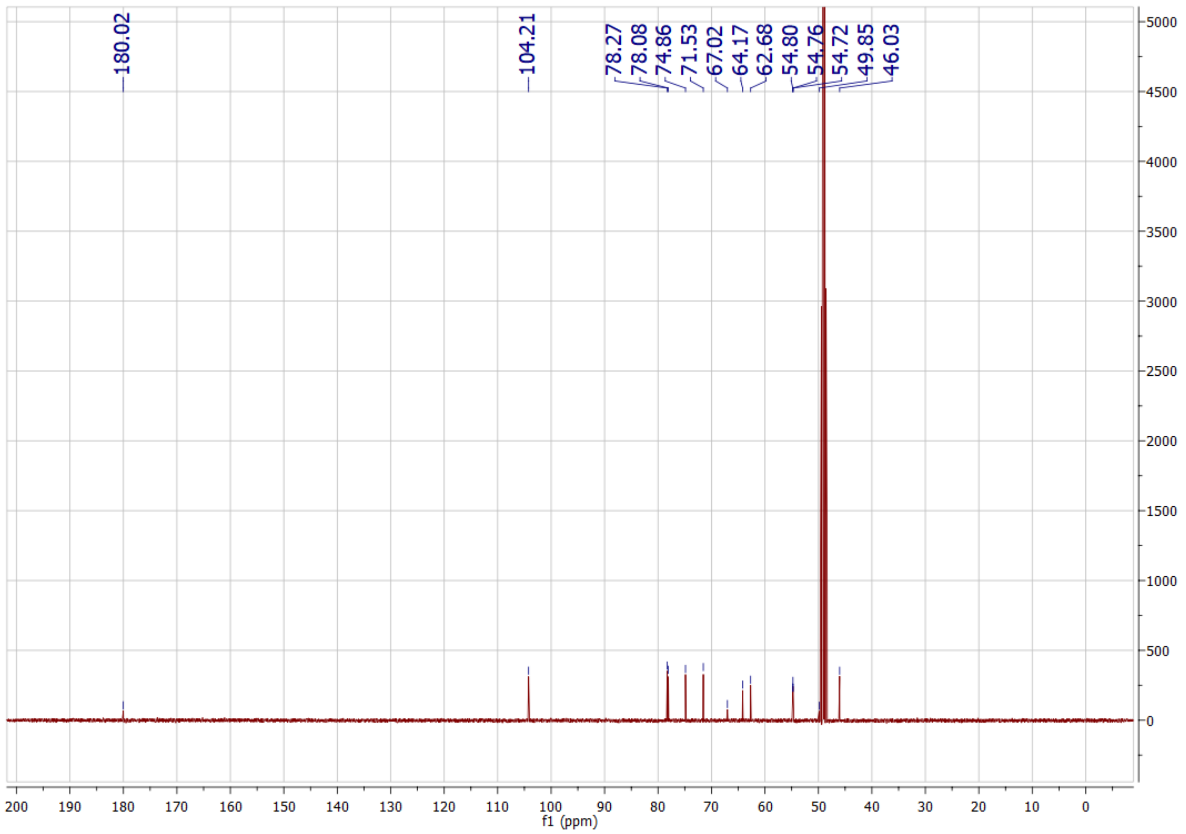
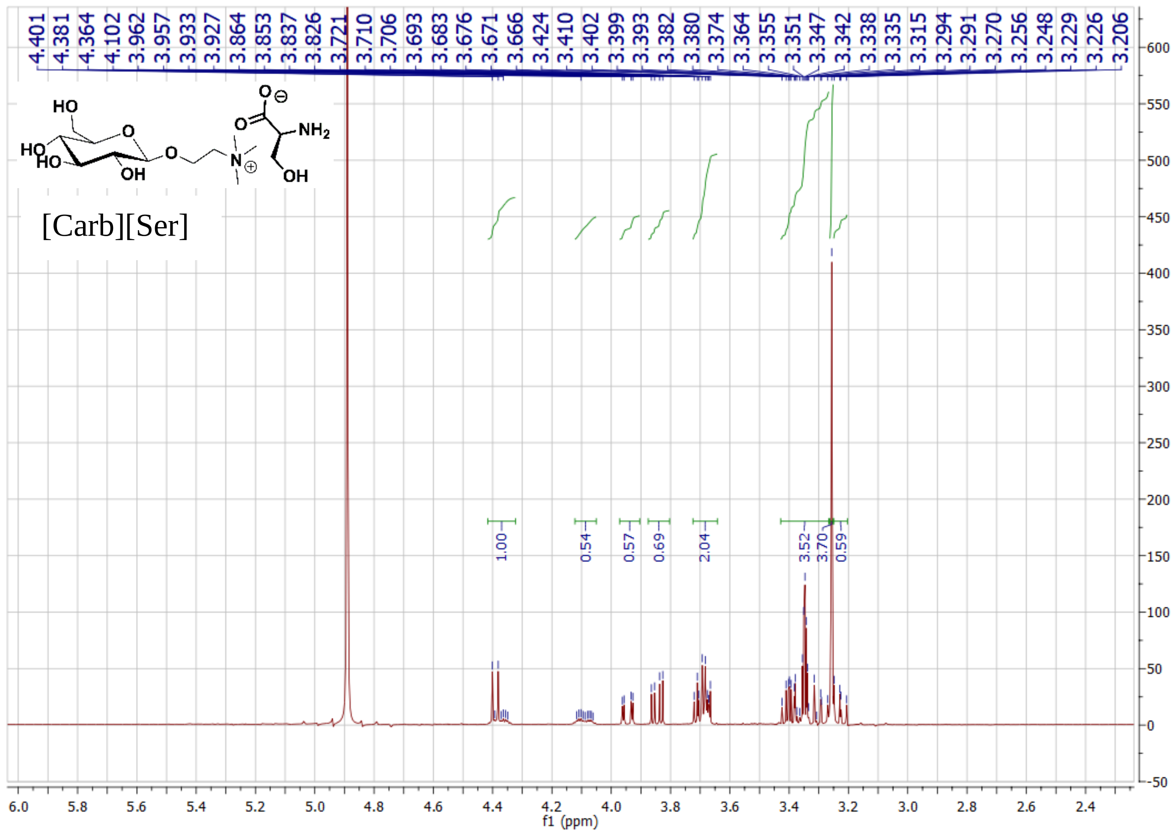


Figure 2. ^{1}H and ^{13}C NMR spectra of the [Carb][AAIL]s.



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3.683
3.676
3.671
3.666
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3.402
3.399
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3.380
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3.291
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3.248
3.229
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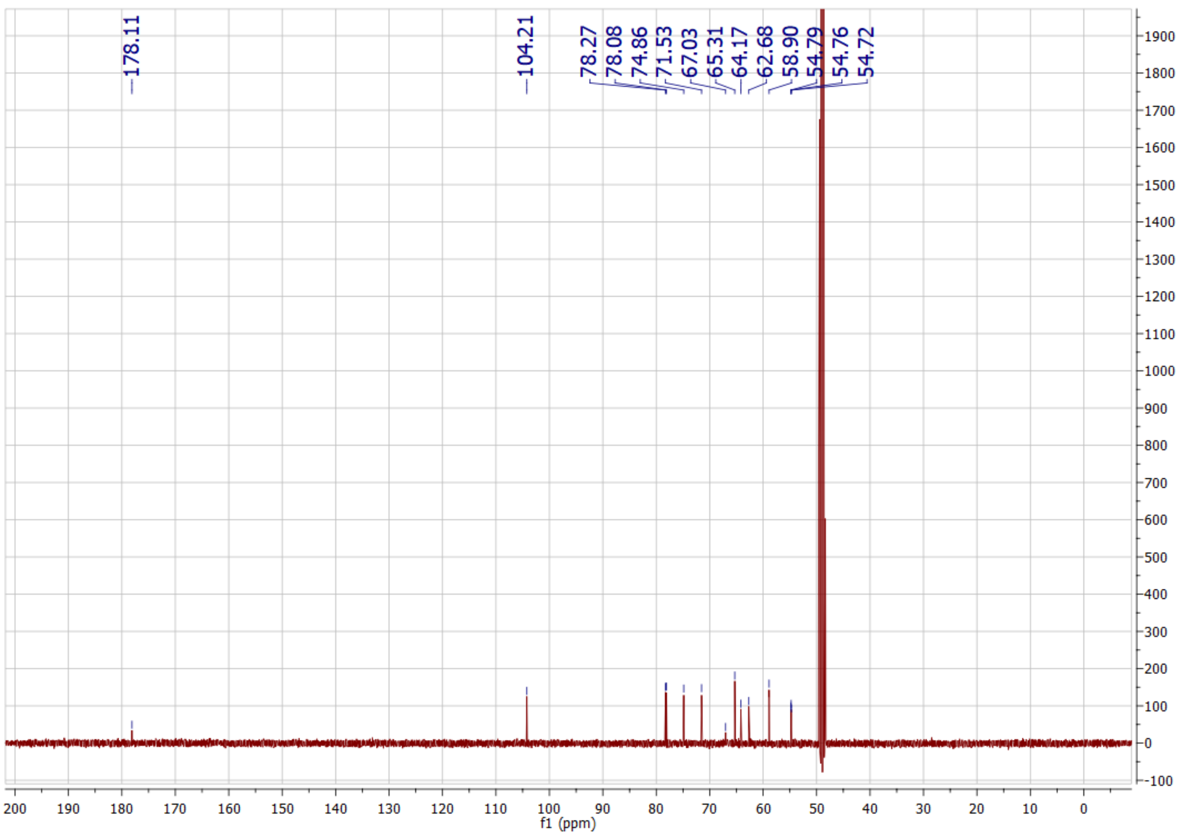
3.70
0.59
f1 (ppm)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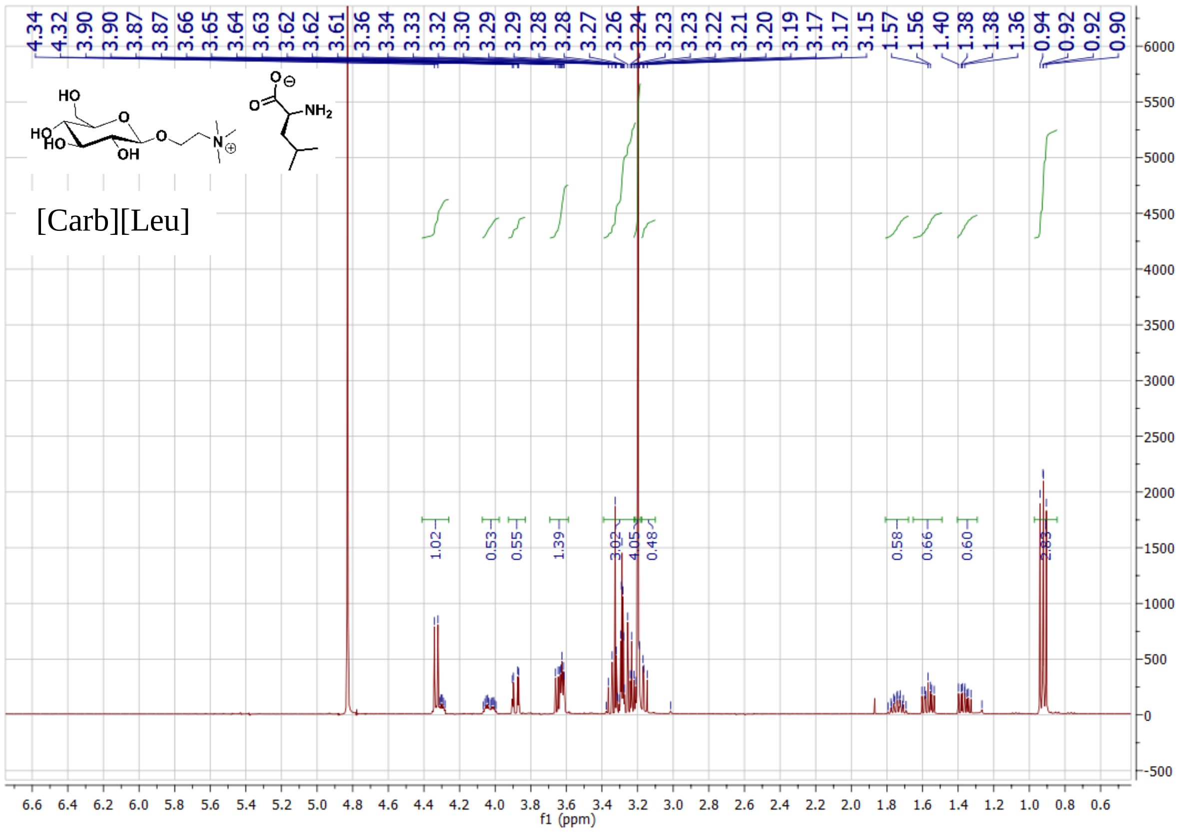
54.72
f1 (ppm)



[Carb][Leu]
4.34 4.32 3.90 3.90 3.87 3.87 3.66 3.65 3.64 3.63 3.62 3.62 3.61 3.36 3.34 3.33 3.32 3.30 3.29 3.29 3.28 3.28 3.27 3.26 3.24 3.23 3.23 3.22 3.21 3.20 3.19 3.17 3.17 3.15 1.57 1.56 1.40 1.38 1.38 1.36 0.94 0.92 0.92 0.90
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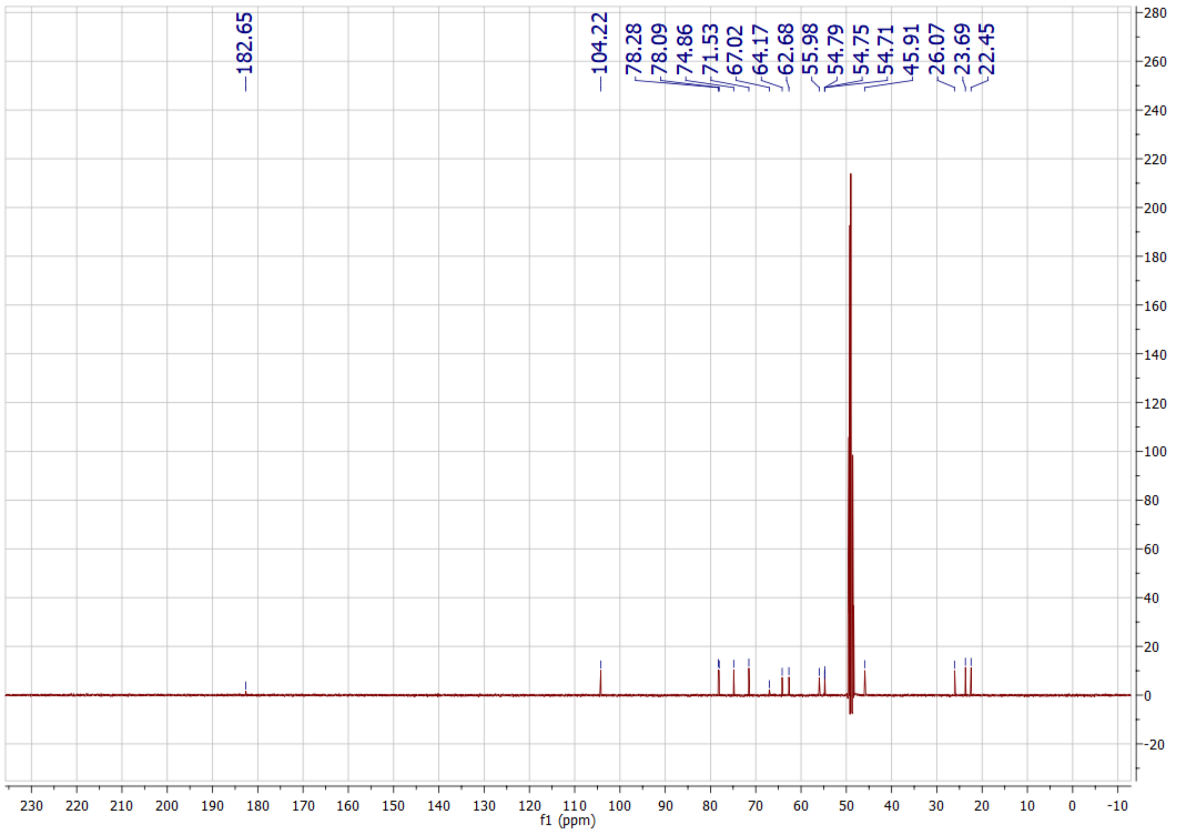
f1 (ppm)



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104.22
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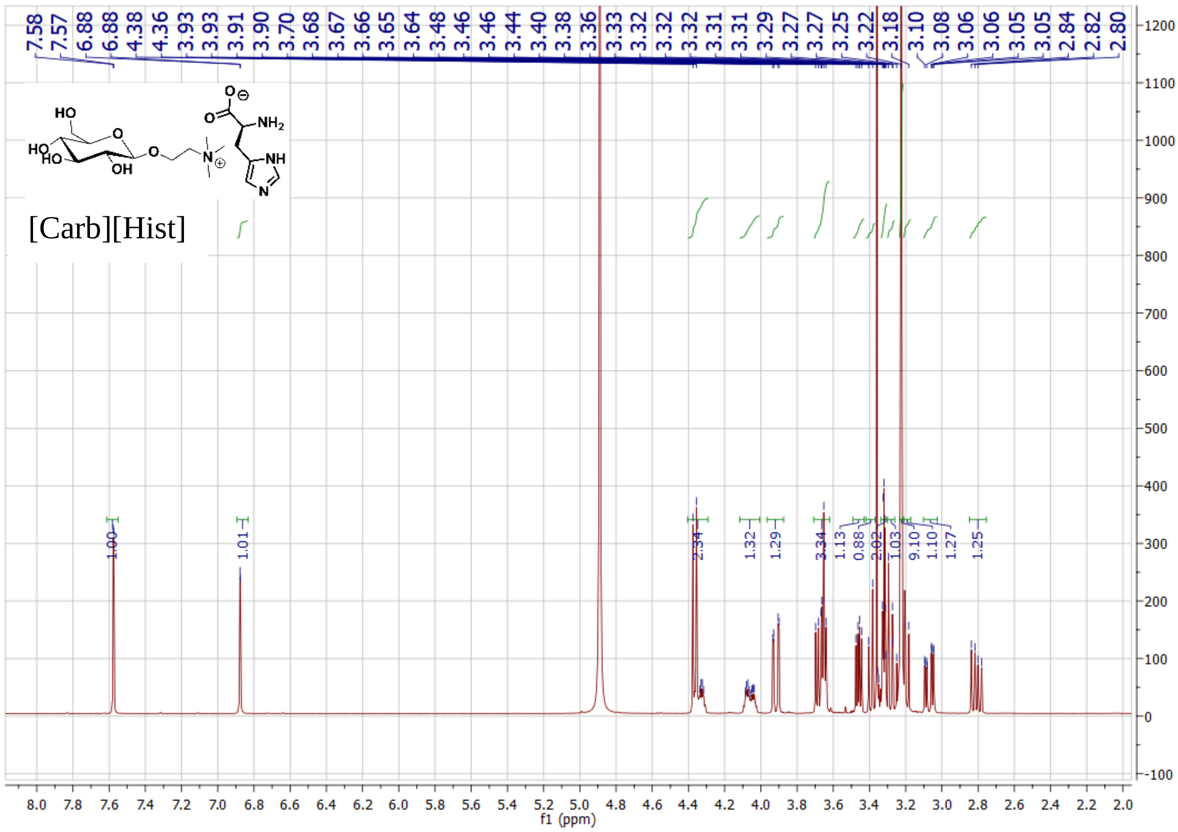
f1 (ppm)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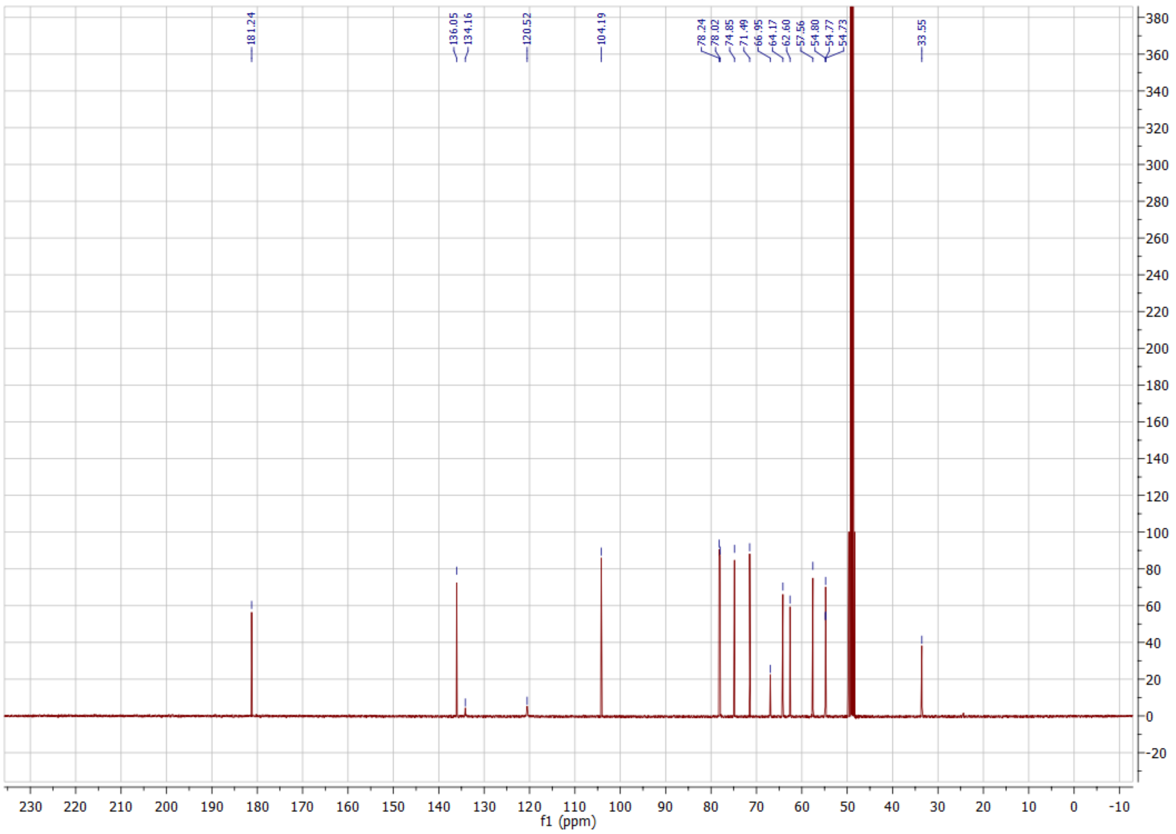
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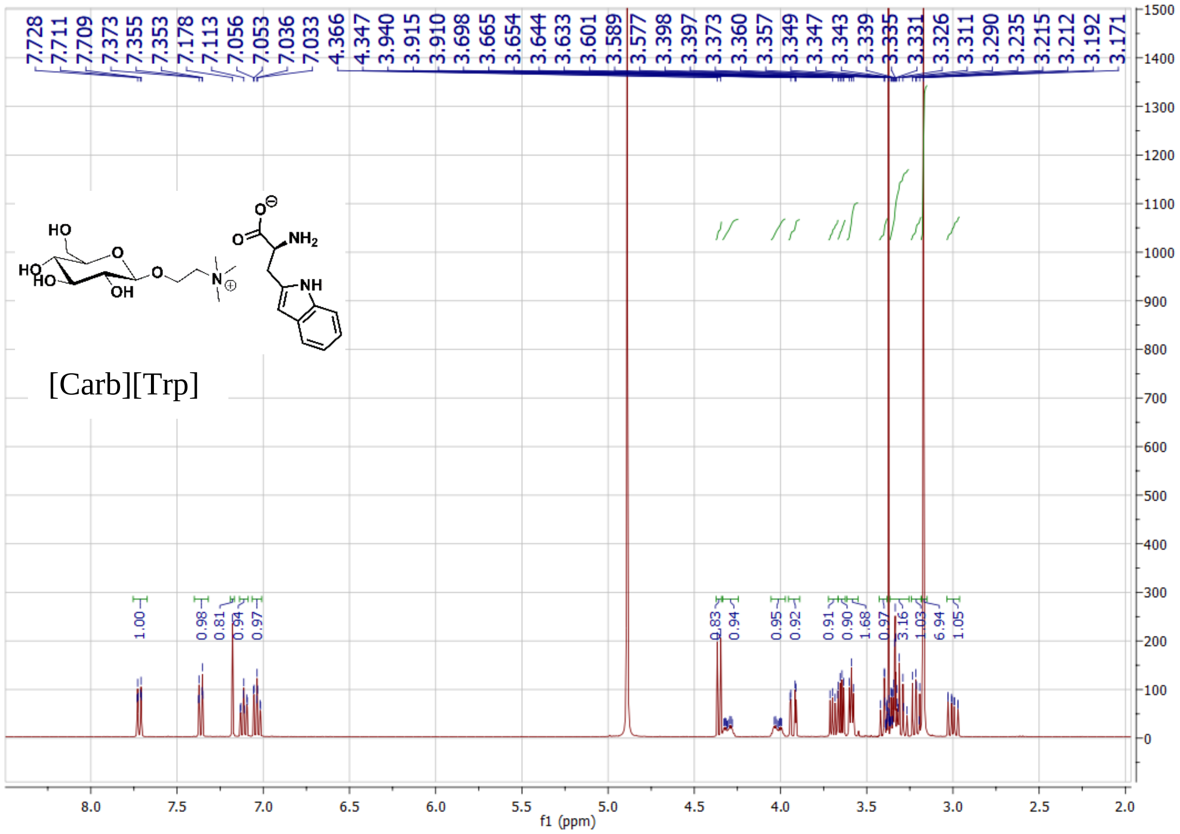
54.73
33.55
f1 (ppm)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0.94
0.95
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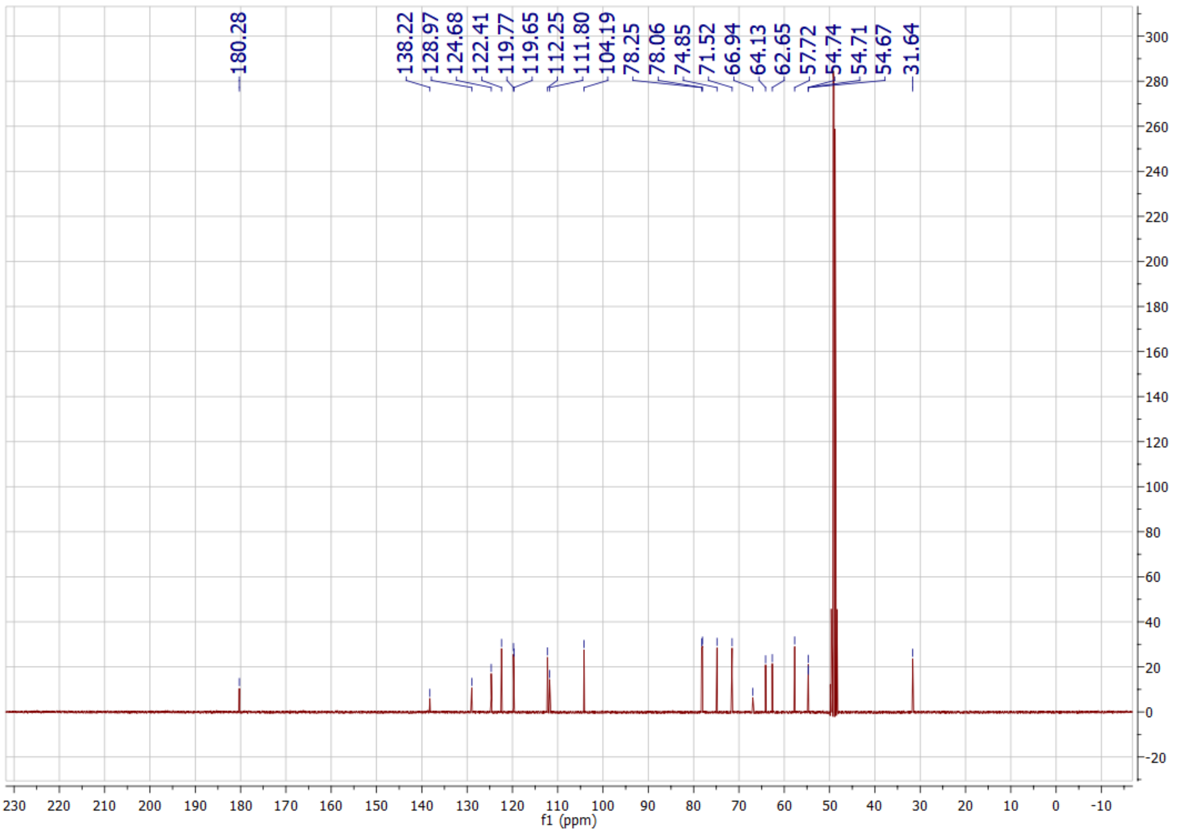
[Carb][Trp]
f1 (ppm)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54.71
54.67
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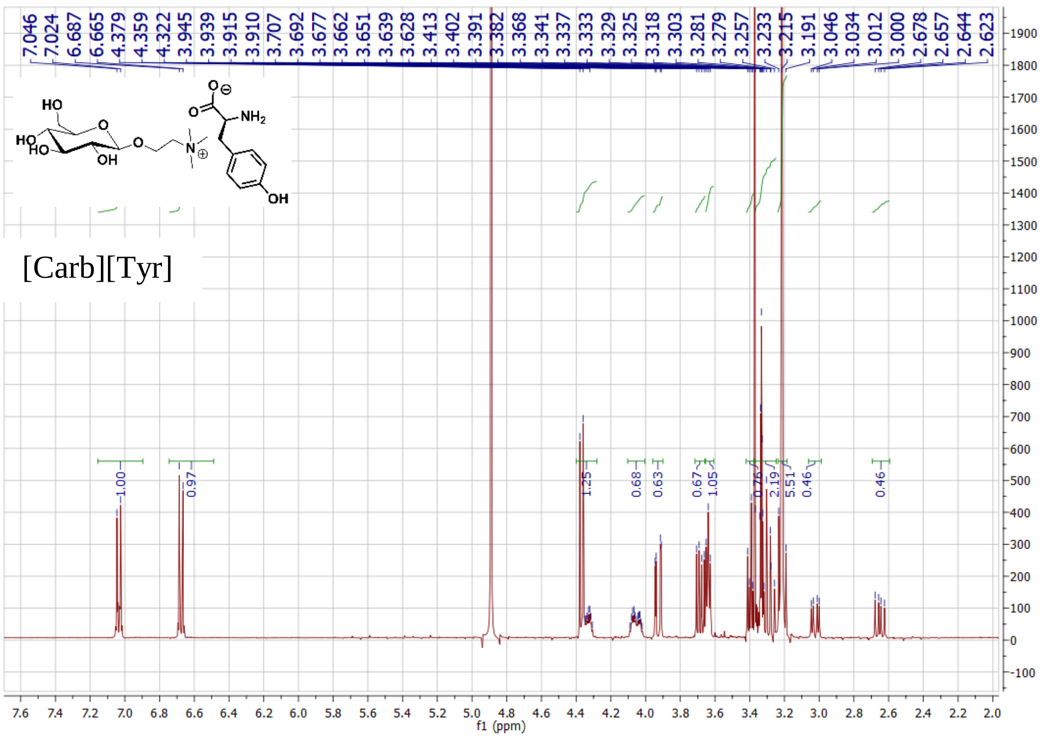
f1 (ppm)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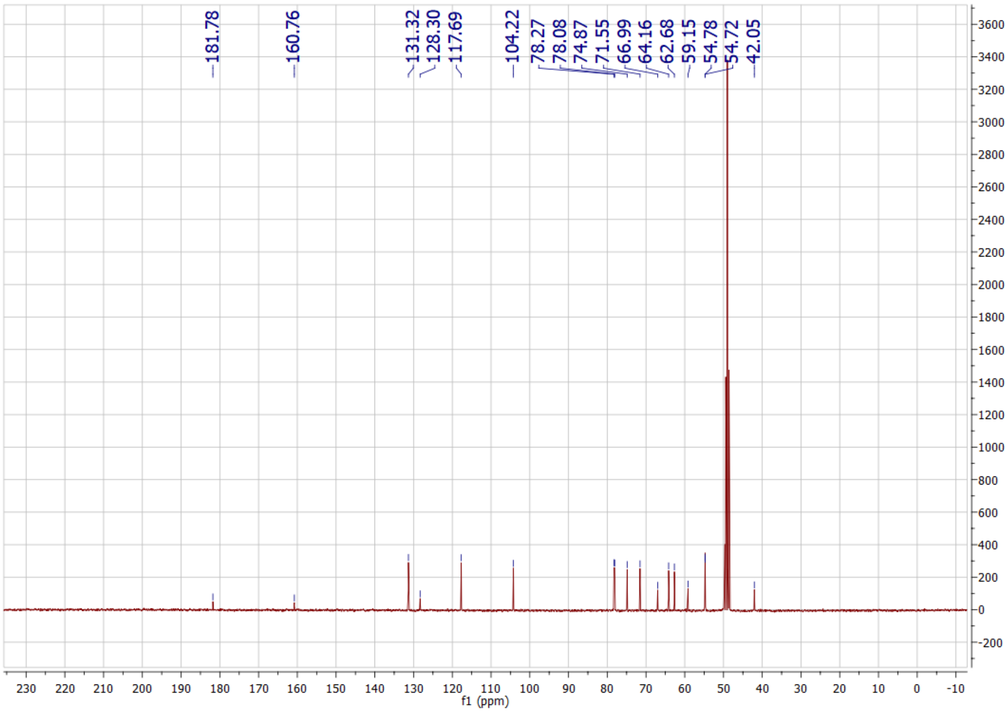
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62.68
59.15
54.78
54.72
42.05
f1 (ppm)

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