SUPPLIMENTARY INFORMATION

Chitosan Supported Ionic Liquid, a Multifaceted Catalyst for Streamlined and Efficient Synthesis of Carboxylic, Amino acid and Carbohydrate Esters

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Materials

All the reactions were performed in an oven-dried round bottomed flask. Solvents, reagents and chemicals used for reactions in this paper were purchased from Sigma-aldrich/Spectrochem Pvt. Ltd. and used without any further purification unless it is specified otherwise. Double distilled water was used for the preparation of all aqueous solutions. Reactions were monitored by thin-layer chromatography (TLC). TLC was performed using E. Merck pre-coated silica plates (60F-254) with 0.25 mm thickness and visualized using short-wave UV light or developing agents.

Instrumentation

The structural validation of synthesised compounds was based on 1HNMR, 13CNMR, mass spectroscopy. Nuclear magnetic resonance (NMR) was acquired at 400 MHz and 100 MHz for 1H NMR and 13C NMR respectively using a JEOL JNM-ECS 400 spectrometer instrument with DMSO-d6 and CDCl3 as solvents. TMS was taken as the reference in NMR, and data were processed with its delta software. Coupling constant (J) is reported in Hertz and chemical shift values are reported in ppm for 1H NMR, and multiplicities are as follows: s (singlet), d (doublet), dd (doubledoublet), t (triplet) and m (multiplet). 13C CP-MAS was obtained through JEOL ECZR at 600 MHz. High resolution mass spectroscopy was generated by XEVO G2-XS QTOF spectrometer, Thermo Fisher Scientific Q Exactive spectrometer, Impact HD (Bruker) ESI QTOF high resolution mass spectrometer.

FT-IR experiments were carried out in the range of 400-4000 cm-1 (Thermo Scientific; Model: INCOLET iS50) spectrometer. The powder X-ray diffraction (PXRD) studies were performed on Bruker diffractometer (D8 Discover) at room temperature and 2θ range 0°−100° (scanning rate = 2°/min, λ = 0.15406 nm, 40 kV, 40 mA). The thermal stability of ionic liquid was determined using a PerkinElmer Pyris diamond TGA/ differential thermal analyser. For obtaining the data, the sample was heated from room temperature to 1000 °C in N_2 atmosphere at a heating rate of 10 °C min^{-1} and gas flow of 200 mL min^{-1}. Carl Zeiss, India (Jeol Japan Mode: JSM 6610LV) was used to obtain the SEM images.

Table S1. Comparison of the present work with previous literature for the esterification of acid to their corresponding esters.

Entry	Catalyst	Solvent	Temperature	Time	Yield(%)	Ref
1	Triphosgene	DCM	40°C	2h	95%	S[1]
2	TMSCl	-	RT	24h	89%	S[2]
3	[Pd(cinnamyl)Cl]$_2$, IBnF·HBr	1,4-dioxane	100°C	36h	75%	S[3]
4	Pd(PPh$_3$)$_4$		140°C	27h	64%	S[4]
5	(CN-OA-m)	DMSO	-40°C, white LED	14h	92%	S[5]
6	Sulfated Zirconium Catalyst	-	60 °C	6h	75%	S[6]
7	silicotungstic acid; $H_4SiW_{12}O_{40}\cdot nH_2O$(STA)	-	98 °C(reflux)	4h	91%	S[7]
8	N,N'-diisopropylcarbodiimide	Water	RT	4h	92%	S[8]
9	XtalFluor-E	TFE in CH_2Cl_2	RT	16h	84%	S[9]
10	[Ir(cod)Cl]$_2$	CH_2Cl_2	RT	12h	88%	S[10]
11	PPh$_3$/I$_2$	Acetonitrile	Reflux, MW	30 mins	93%	S[11]
12	Silica-IL	Cyclohexane	Reflux, 93 °C	3h	86%	S[12]
13	[Bmim][dca]	-	60 °C	120h	65%	S[13]
14	IL	-	85 °C	3h	91.5%	S[14]
15	**Chitosan-IL$_6$**	-	**RT**	**30**	**96%**	**P.**

				mins		**W.**

Table S2. Optimization of reaction conditions for the amount of catalyst using benzoic acid **A1** and ethanol **B1** as the model substrate.[a]

Entry	**Catalyst (mg)**	**Yield(%)[b]**
1	Chitosan-IL_6 (5mg)	92
2	**Chitosan-IL_6 (10mg)**	**96**
3	Chitosan-IL_6 (15mg)	96
4	Chitosan-IL_6 (20mg)	96

[a]Reaction conditions: Benzoic acid A1 (1 mmol), ethanol B1 (1 mmol), catalyst, room temperature for 30 mins. [b]Isolated yield.

Gram scale synthesis.

For the practical application of the produced esters, we synthesised a few value-added compounds on a gram scale (Figure S1) [15,16]. The reactions were conducted at a scale of 100 mmol using 50 mg of the catalyst. The reactions proceeded easily with yields of 85% for diisopropyl azodicarboxylate over a period of 6 hours, and 86% for methyl nicotinate over a period of 5 hours. Considering esters of amino acids, methyl cysteinate produced a 93% yield over the course of 8 hours, whereas glucose pentaacetate produced 92% yield over the course of 12 hours. These results demonstrate the proposed protocol's practicality and operational simplicity even at higher reaction scales.

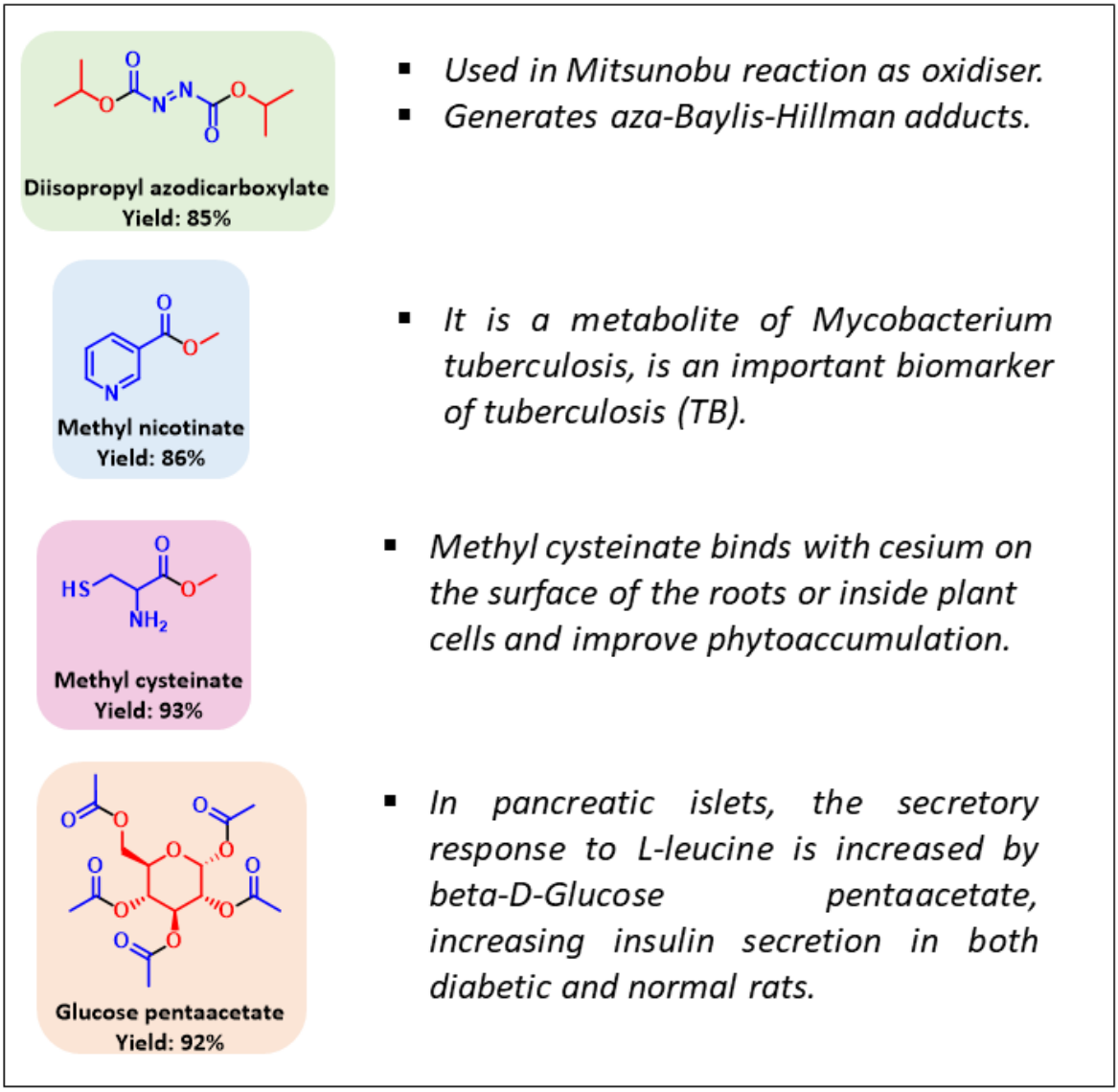


Figure S1. Practical application of a few value-added esters synthesized in gram scale.

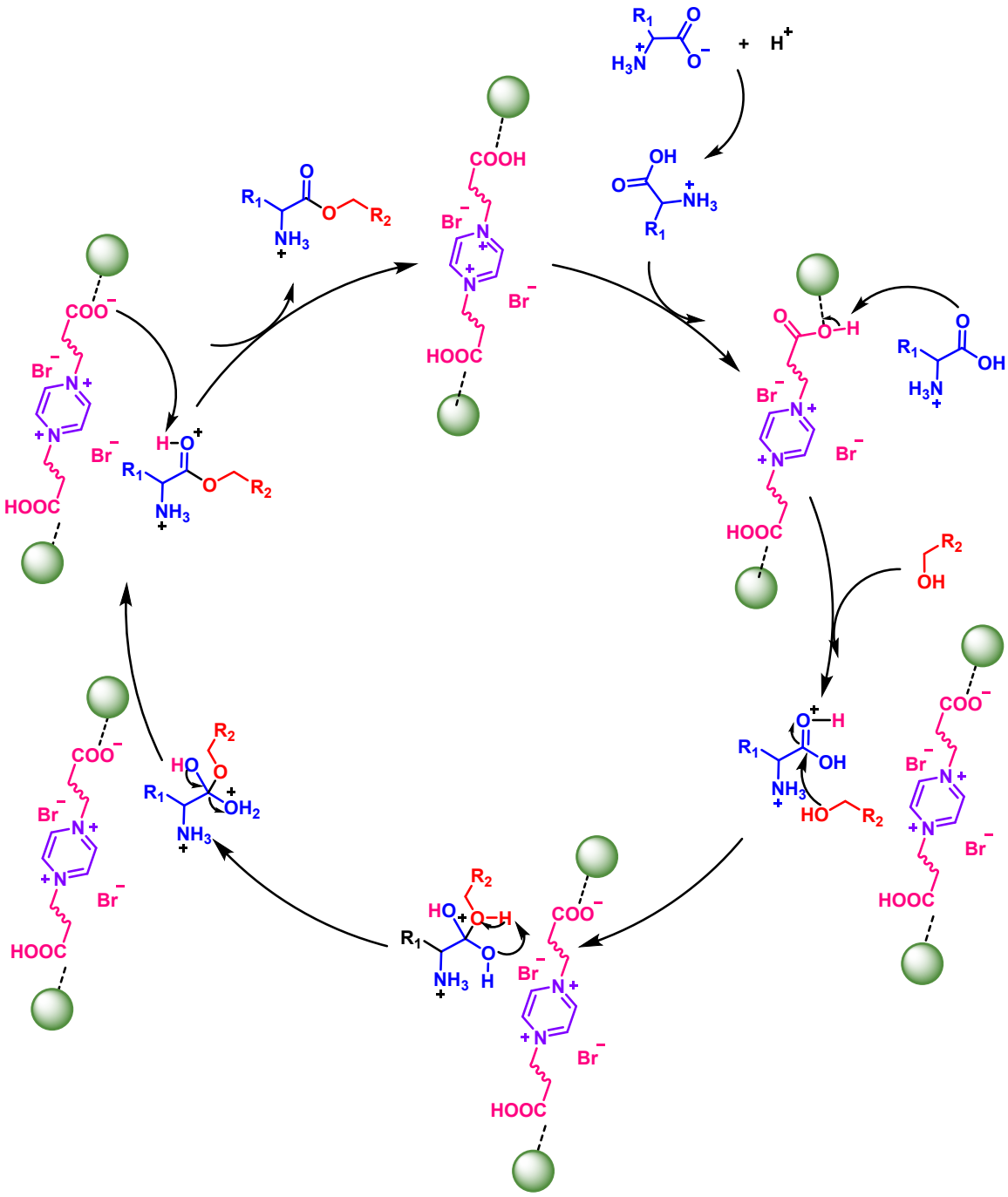


Figure S2. Plausible mechanism for Chitosan-IL_6 catalysed selective esterification of glycine amino acid and ethanol to ethyl glycinate.

To capture an insight into the reaction route of Chitosan-IL_6 catalysed esterification of amino acid we hereby present a feasible mechanism (Figure S2) from theoretical dimensions. We here consider glycine D1 and ethanol B to obtain ethyl glycinate E1. At the starting acetic acid protonates the oxygen of glycine which is in zwitter ion form. The oxygen of carbonyl then extracts a proton from the carboxylic group of Chitosan-IL_6, which is followed by the interaction of ethanolic OH with the carbonyl C of glycine. This leads to proton exchange between glycine and ethanol molecules and followed by the elimination of water molecule.

Finally, the desorption of glycinate from Chitosan-IL_6 results in the synthesis of the desired product and continuing the active use of the catalyst in further cycles.

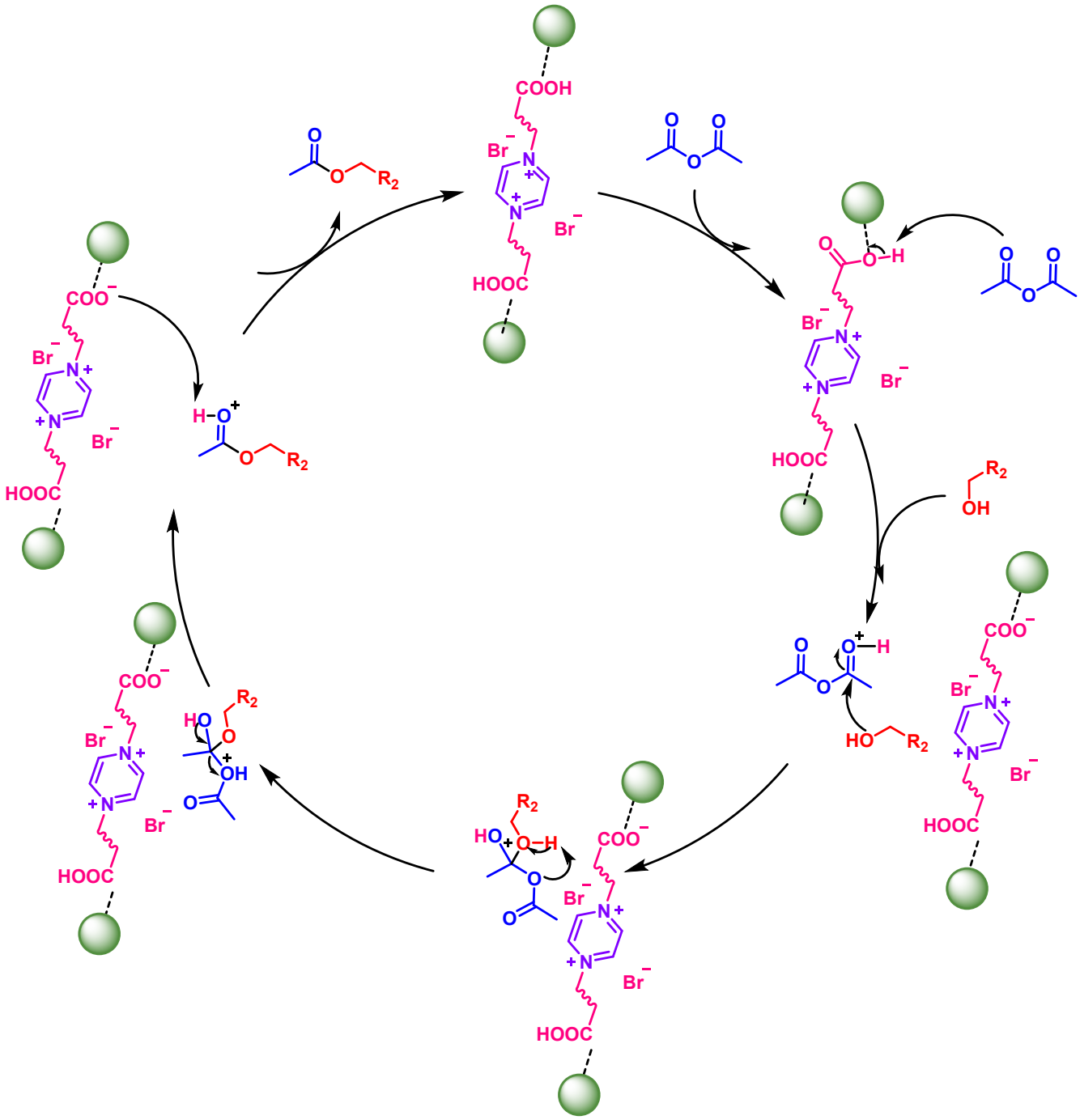


Figure S3. Plausible mechanism for Chitosan-IL_6 catalysed selective esterification of acetic anhydride and carbohydrate to carbohydrate esters.

Figure S3 outlines a plausible mechanistic pathway for the Chitosan-IL_6 catalysed esterification of carbohydrates based on the discussed controlled reactions. The oxygen of

one of the carbonyl C interacts with the ionic liquid first, followed by the interaction of OH of carbohydrate. This causes a proton transfer from carbohydrate OH to acetic anhydride's oxygen. This is followed by the loss of acetic acid and final desorption of the ester moiety from the catalyst to obtain the desired product.

Table S3. Recyclability test of Chitosan IL_6 catalyzed esterification of benzoic acid and ethanol to ethyl benzoate **C1**.[a]

Catalytic run	**Yield(%)[b]**
1	96
2	96
3	96
4	96
5	96
6	95
7	95
8	94
9	93
10	93

[a]Reaction conditions: Carboxylic acid (1 mmol), alcohol (1 mmol), Chitosan-IL_6 (10 mg) under neat conditions at RT for appropriate time. [b]Isolated yield.

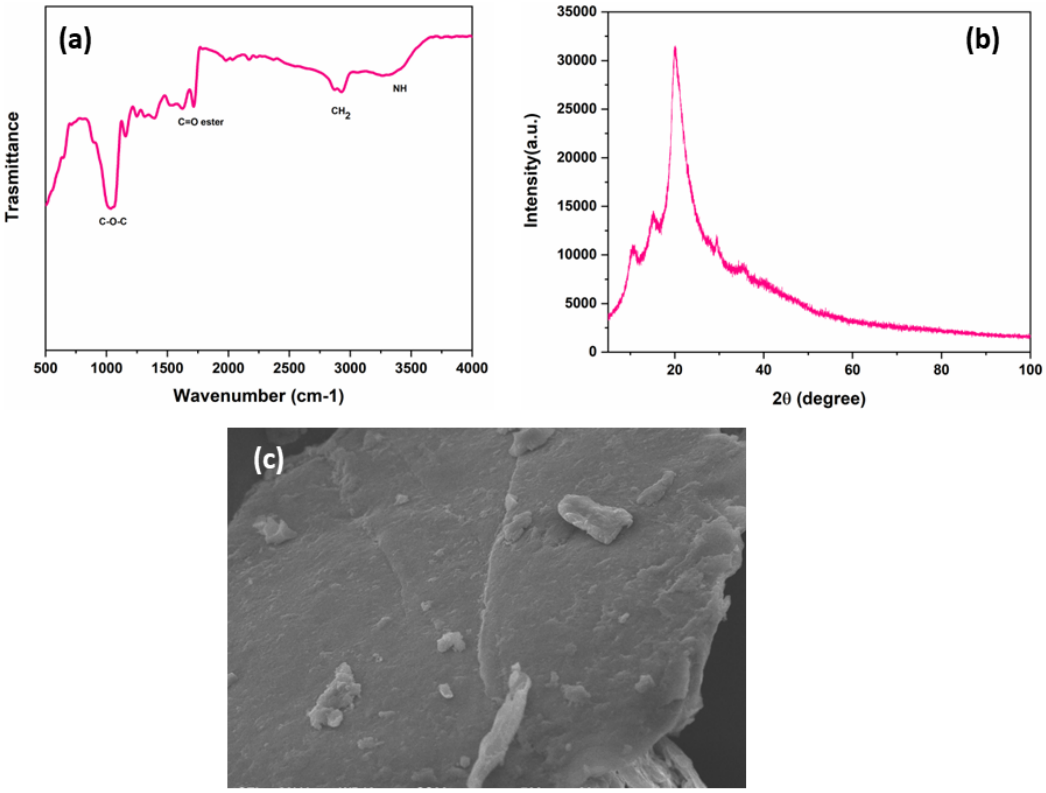


Figure S4. IR (a), XRD (b) and SEM(c) image of reused catalyst.

Determination of acidity of Chitosan-IL$_6$

The density of total acidic sites on Chitosan-IL$_6$ was calculated by back acid–base titration[17]. First, 100 mg of Chitosan-IL$_6$ was added to 10 mL of freshly prepared 0.05 N NaOH solution and the resulting mixture was stirred for 3 h at RT. Subsequently, the mixture was centrifuged at 8000 rpm for 2 min and washed two times with double distilled water. The filtrate containing excess NaOH solution was then back titrated with freshly prepared 0.1 N HCl solution till neutralization point, monitored by using phenolphthalein indicator to evaluate the total concentration of acidic sites in Chitosan-IL$_6$.

Calculation of acidic strength of Chitosan-IL$_6$

It was found that 1.3 mL of 0.1 N HCl was required to reach the neutralization point.

V_{NaOH} X S_{NaOH} = V_{HCl} X S_{HCl}

V_{NaOH} X 0.05 = 1.3 X 0.1

V_{NaOH} = 2.6 mL

Therefore, the volume of NaOH required to neutralize the acidic sites in Chitosan-IL_6 = (10-2.6) mL = 7.4 mL.

V_{NaOH} X S_{NaOH} = $V_{Chitosan\text{-}IL6}$ X $S_{Chitosan\text{-}IL6}$

7.4 X 0.05 =10 X $S_{Chitosan\text{-}IL6}$

$S_{Chitosan\text{-}IL6}$ = 0.037 N

The equivalent weight of carboxylic acid group (-COOH) is 45.

That is, 1000 mL of 1 N Chitosan-IL_6 would contain 45 g free carboxylic acid sites.

So, 10 mL of 0.037 N Chitosan-IL_6 solution contains 0.01665 g free carboxylic acid sites.

0.01665 g free carboxylic acid sites= 0.37 mmol free carboxylic acid sites.

100 mg sample of Chitosan-IL_6 contains 0.37 mmol free carboxylic acid.

Thus, 1000 mg sample of Chitosan-IL_6 would contain 3.7 mmol free carboxylic acid sites.

That is, total acid sites in Chitosan-IL_6 = 3.7 mmol g^{-1}.

Calculation of TOF of Chitosan-IL_6

1000 mg (1g) of Chitosan-IL_6 contains 3.7 mmol acid sites

To determine TOF [18] of Chitosan-IL_6 we considered the model reaction of benzoic acid **A1** (1mmol) and ethanol **B1** (1mmol) in the presence of 10 mg of catalyst (Chitosan-IL_6) at RT to yield ethyl benzoate **C1**.

As the yield of this product is 96%,

The turn over number (**TON**) of C1 is = $\frac{mmol\ of\ product}{mmol\ of\ active\ sites\ in\ catalyst}$

1g Chitosan-IL_6 has 3.7 mmol active sites, so 10 mg of Chitosan-IL_6 has = 0.037 mmol active sites.

TON = $\frac{0.96}{0.037}$ = 25.94 (as the yield of product is 96%, mmol of product = 0.96)

And turn over frequency (TOF) of C1 is = $\frac{TON}{Reaction\ time} = \frac{25.94}{30/60} h^{-1} = 51.88\ h^{-1}$

Table S4. TOF values Chitosan-IL_6 for the products **C1-C29**[a]

Entry	Product Code	Yield (%)[b]	Time (h)	TOF (h^{-1})
1	C1	96	0.5	51.88
2	C2	95	0.58	44.26
3	C3	94	0.58	43.80
4	C4	92	0.58	42.87
5	C5	98	0.42	63.06
6	C6	97	0.42	62.42
7	C7	97	0.42	62.42
8	C8	99	0.33	81.08
9	C9	98	0.33	80.26
10	C10	96	0.5	51.88
11	C11	97	0.42	62.42
12	C12	97	0.42	62.42
13	C13	89	0.66	36.44
14	C14	90	0.66	36.85
15	C15	93	0.66	38.08
16	C16	85	0.83	27.68
17	C17	89	0.83	28.98
18	C18	90	0.75	32.43

19	C19	92	0.75	33.15
20	C20	84	0.83	27.35
21	C21	90	0.83	29.31
22	C22	89	0.83	28.98
23	C23	88	0.83	28.65
24	C24	86	0.83	28.00
25	C25	86	0.83	28.00
26	C26	87	0.83	28.33
27	C27	90	0.83	29.31
28	C28	85	0.83	27.68
29	C29	89	0.83	28.98

[a]Reaction conditions: Carboxylic acid (1 mmol), alcohol (1mmol), Chitosan-IL_6 (10 mg) under neat conditions at RT for appropriate time. [b]Isolated yield

Table S5. TOF values Chitosan-IL_6 for the products **D1-D12**[a]

Entry	**Product Code**	**Yield (%)[b]**	**Time (h)**	**TOF (h^{-1})**
1	D1	94	3.5	7.26
2	D2	96	3	8.65
3	D3	94	3.5	7.26
4	D4	96	3	8.65
5	D5	95	3.5	7.33
6	D6	95	3.5	7.33
7	D7	96	3.5	7.41

8	D8	90	3	8.11
9	D9	99	2	13.38
10	D10	98	2	13.24
11	D11	98	2	13.24
12	D12	95	3	8.56

[a]Reaction conditions: Amino acid (1 mmol), alcohol (1mmol), Chitosan-IL_6 (10 mg), acetic acid (3 drops) under neat conditions at RT for appropriate time. [b]Isolated yield.

Table S6. TOF values Chitosan-IL_6 for the products **E1-E7**[a]

Entry	**Product Code**	**Yield (%)[b]**	**Time (h)**	**TOF (h^{-1})**
1	E1	98	1	26.49
2	E2	96	1	25.95
3	E3	96	1	25.95
4	E4	95	1	25.67
5	E5	93	0.83	30.28
6	E6	92	0.83	29.96
7	E7	90	2	12.16

[a]Reaction conditions: Acetic anhydride (4-5 mmol), carbohydrate (1 mmol), Chitosan-IL_6 (10 mg) under neat conditions at RT for appropriate time. [b]Isolated yield.

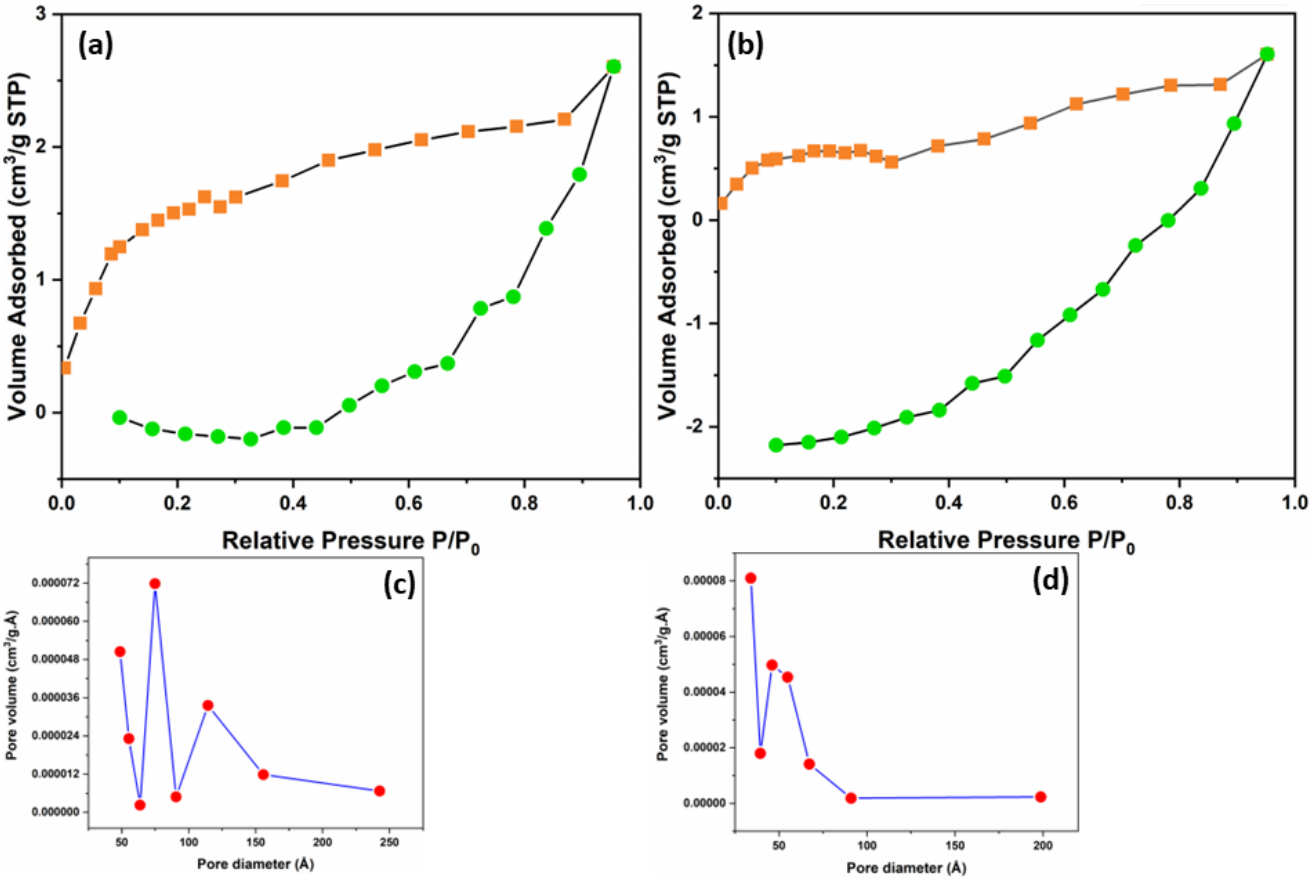
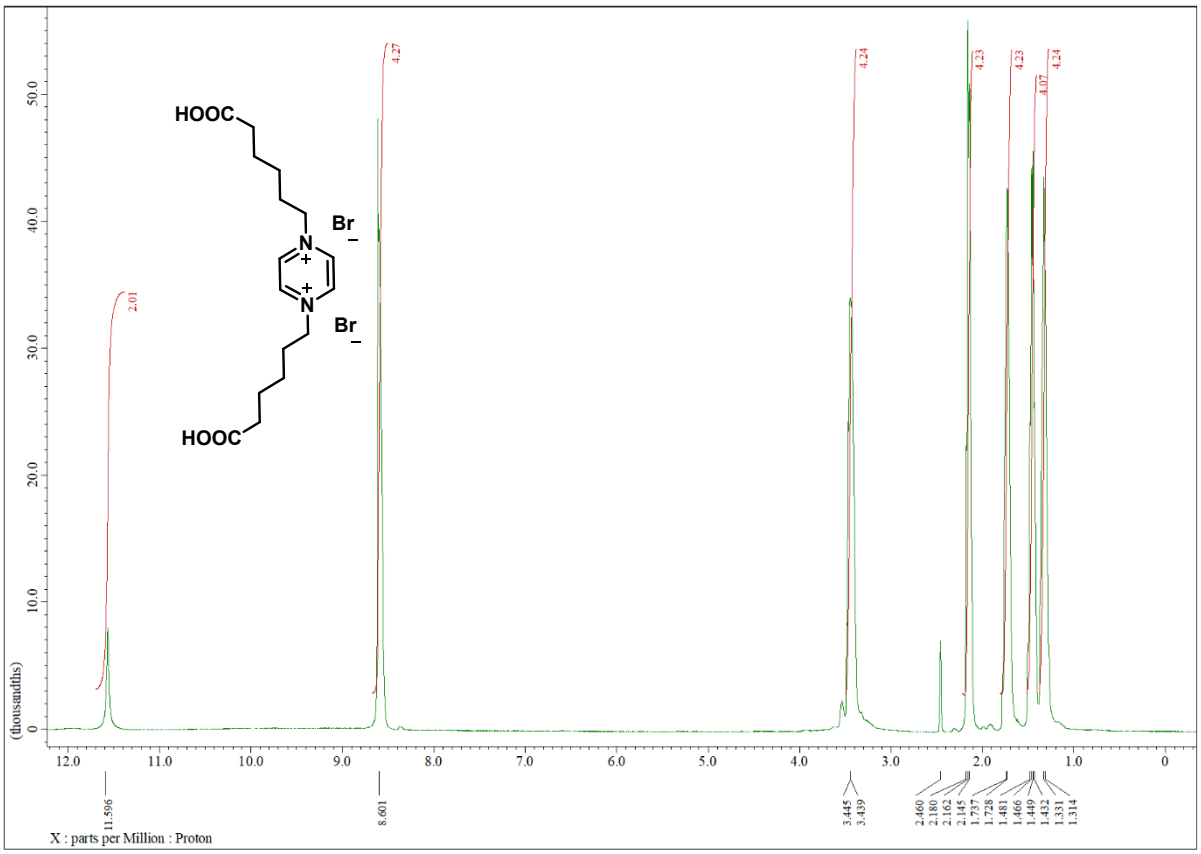


Figure S5. N_2 adsorption/desorption isotherm of (a) Chitosan and (b) Chitosan IL_6 and Pore size distribution of (c) Chitosan and (d) Chitosan IL_6

<u>^{1}H NMR, ^{13}C NMR and MS spectra of all compounds.</u>



FigureS6. ^{1}H NMR spectrum of 1,4-bis(5-carboxypentyl)pyrazine-1,4-diium ([BCPPD][Br])

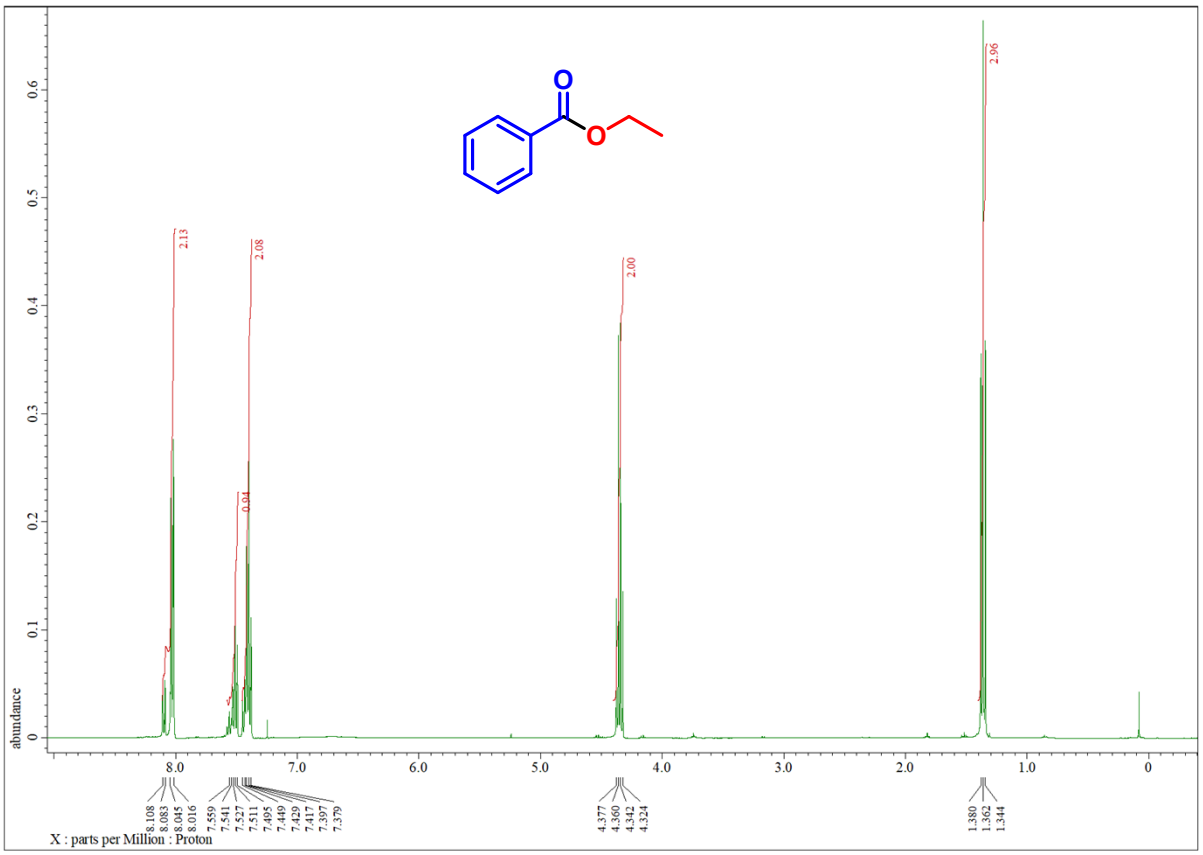


Figure S7. ^{1}H NMR spectrum of Ethyl benzoate **C1.**

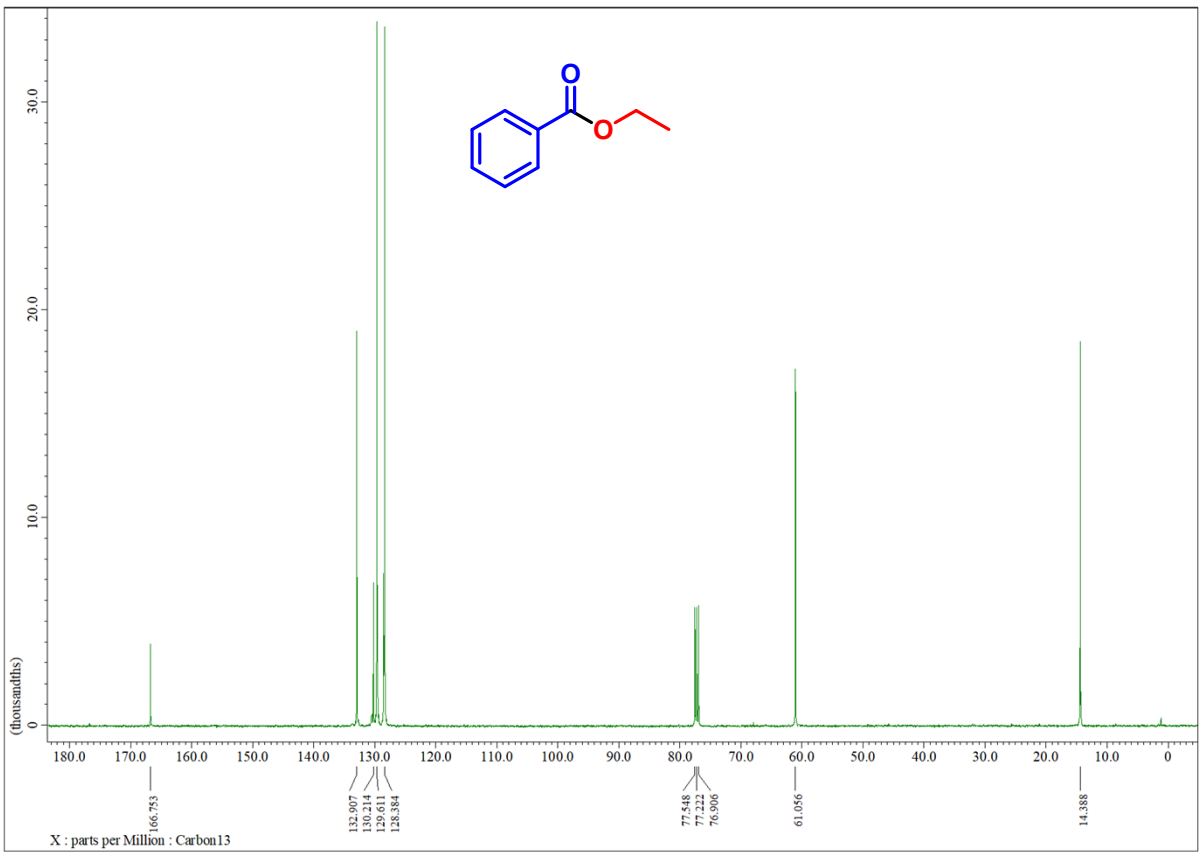


Figure S8. ^{13}C NMR spectrum of Ethyl benzoate **C1.**

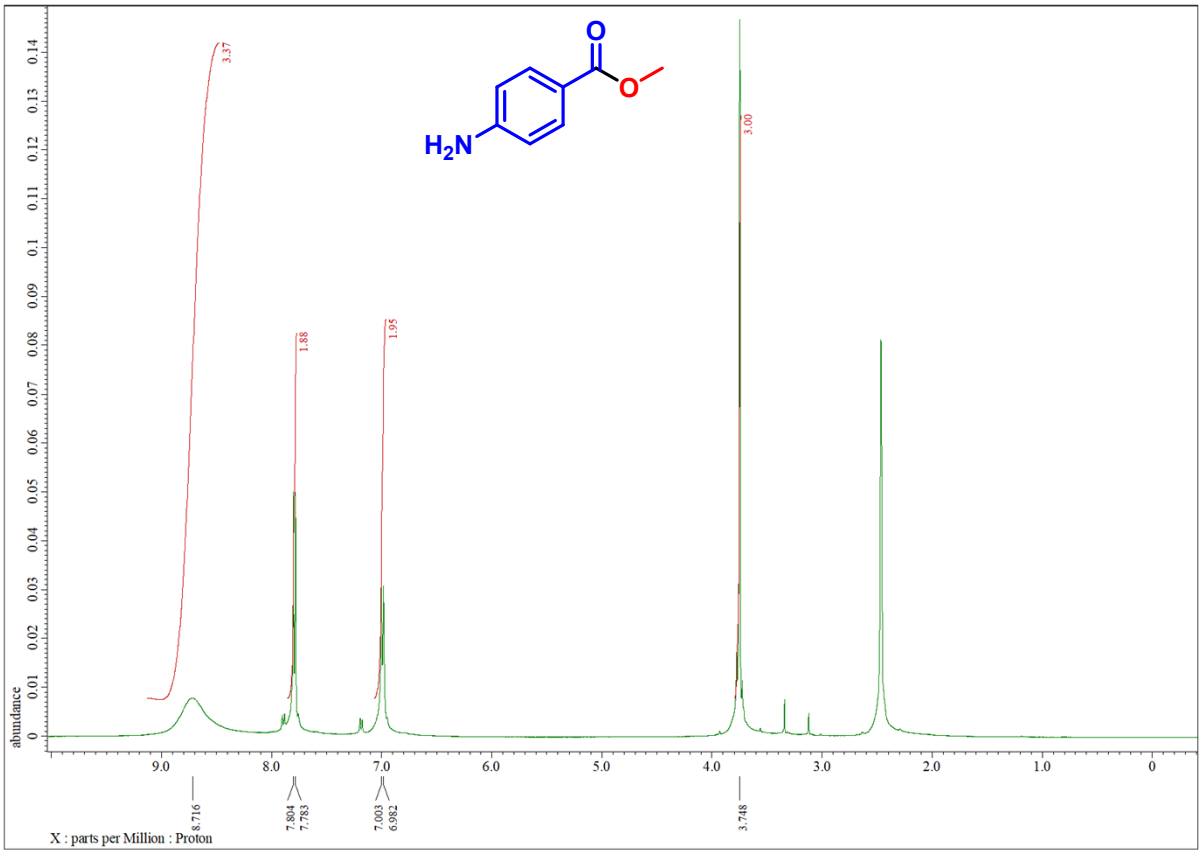


Figure S9. ^{1}H NMR spectrum of Methyl 4-aminobenzoate **C2.**

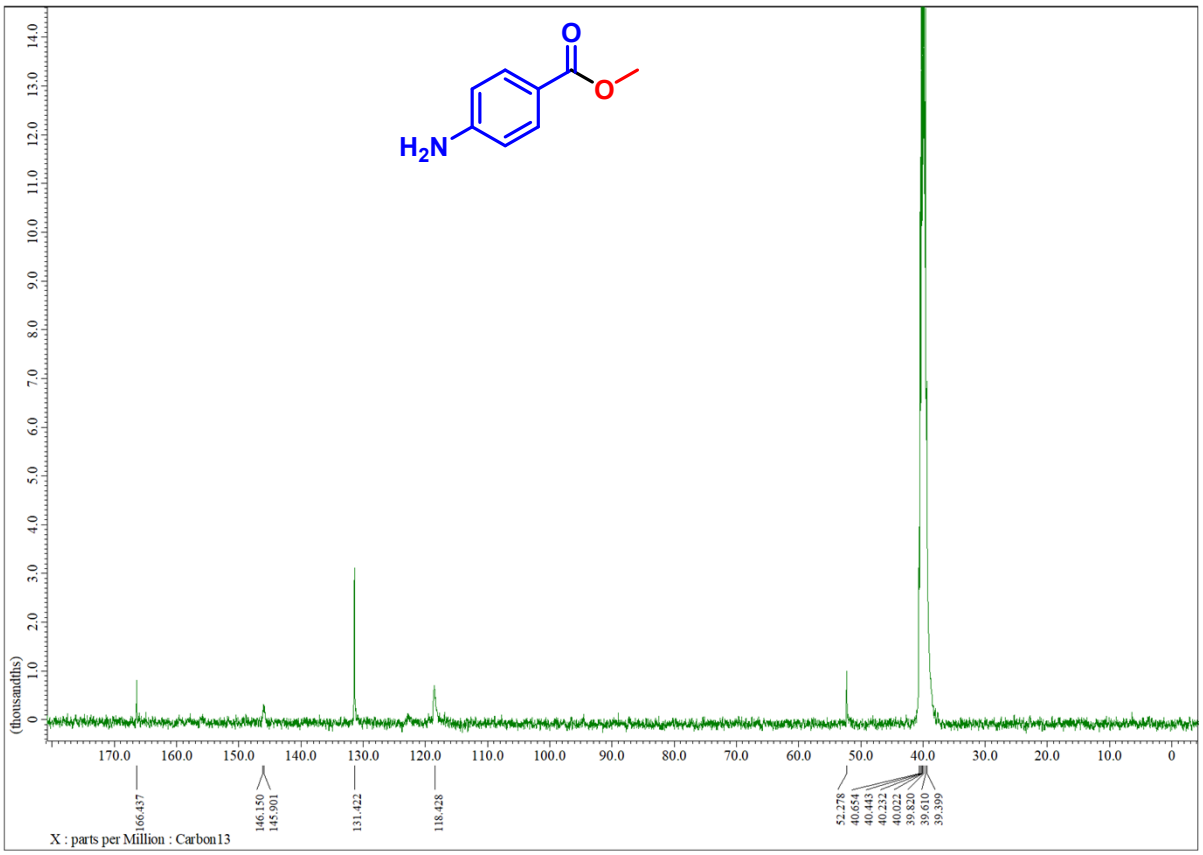


Figure S10. ^{13}C NMR spectrum of Methyl 4-aminobenzoate **C2.**

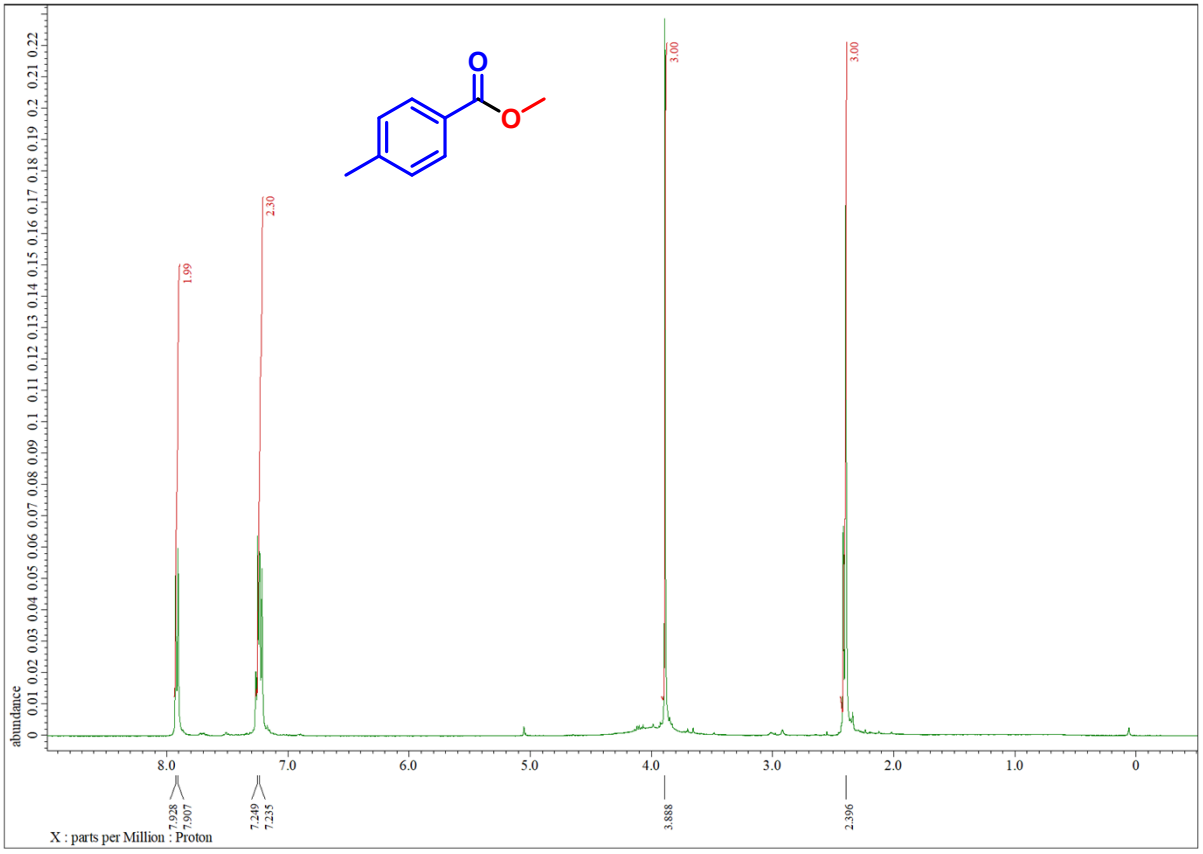


Figure S11. ^{1}H NMR spectrum of Methyl 4-methylbenzoate **C3.**

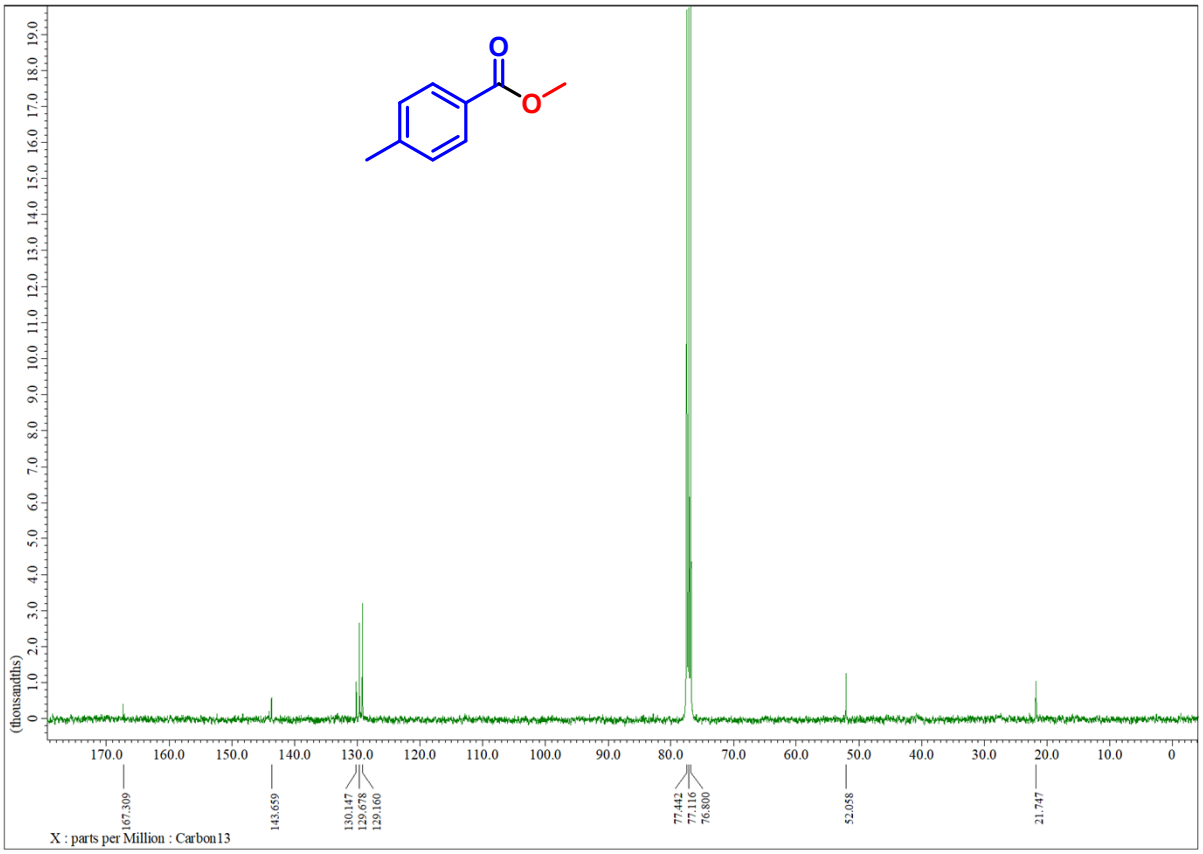


Figure S12. ^{13}C NMR spectrum of Methyl 4-methylbenzoate **C3.**

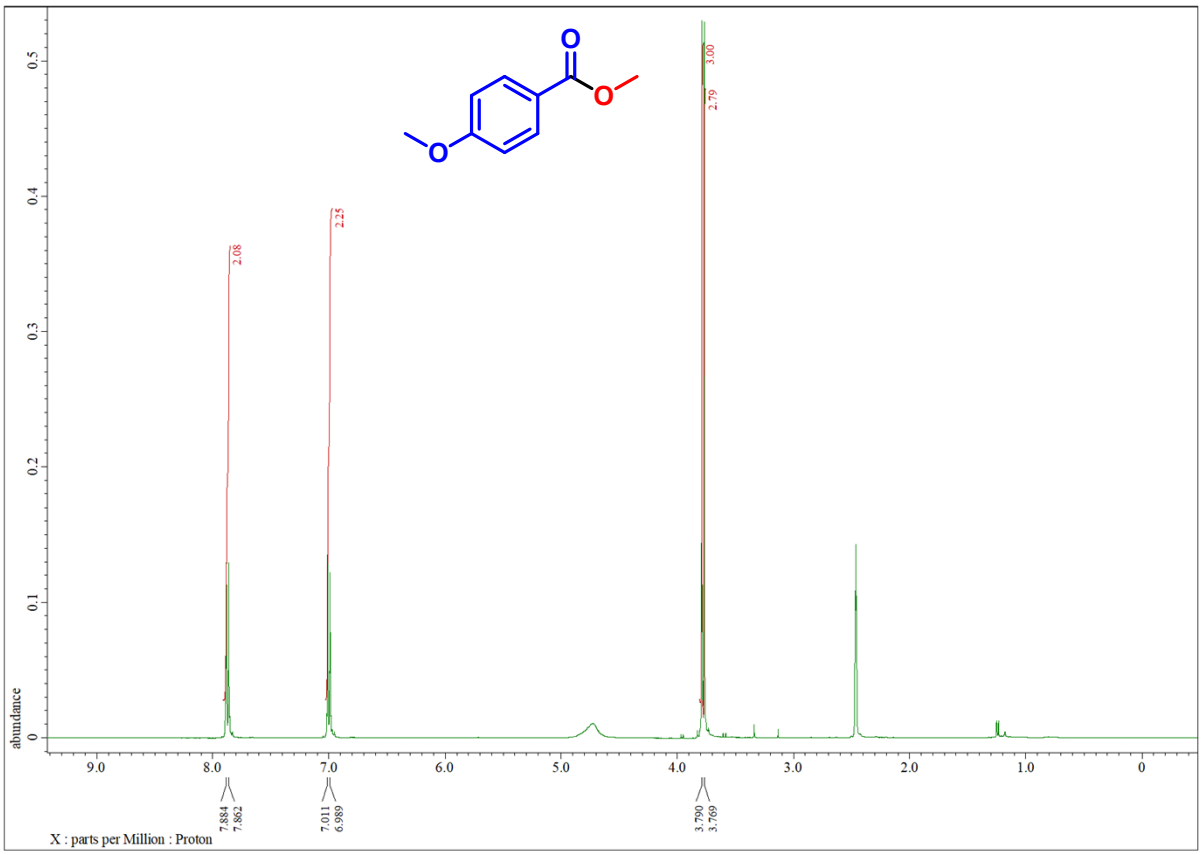


Figure S13. [1]H NMR spectrum of Methyl 4-methoxybenzoate **C4.**

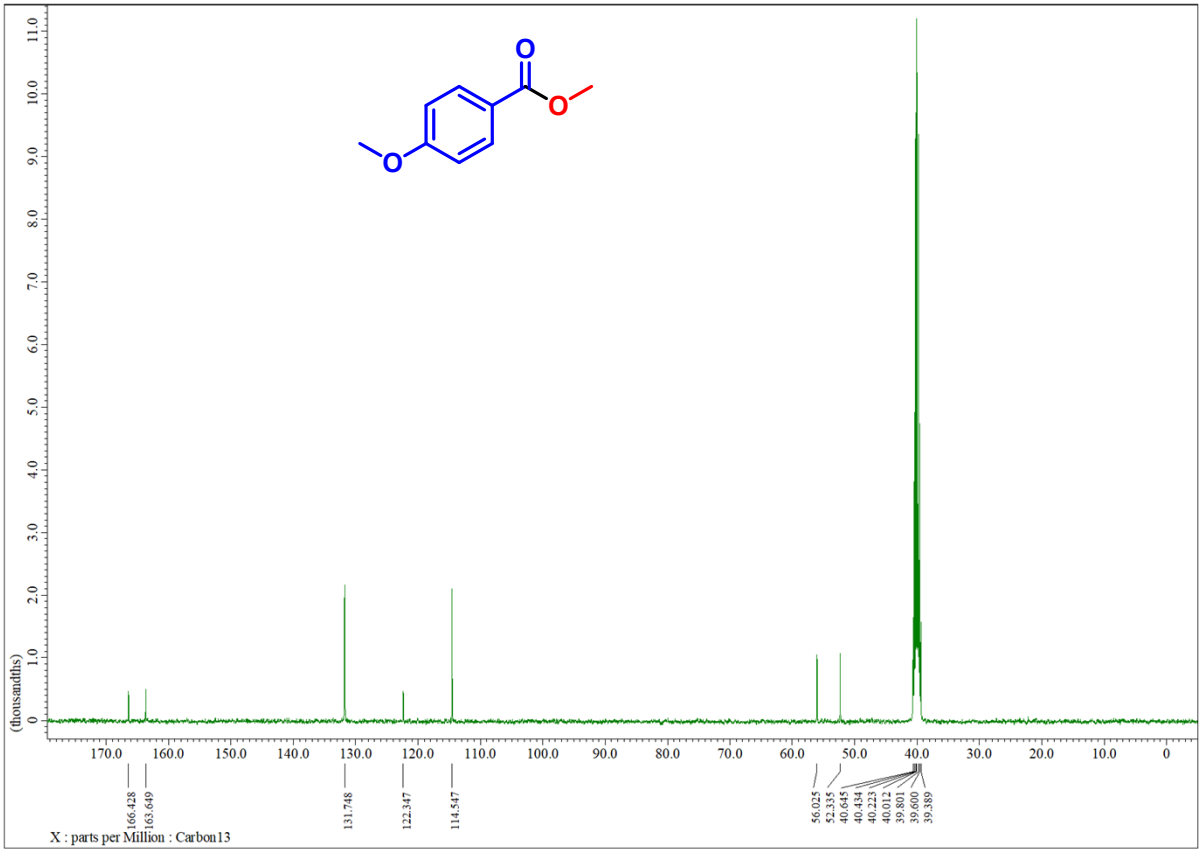


Figure S14. [13]C NMR spectrum of Methyl 4-methoxybenzoate **C4.**

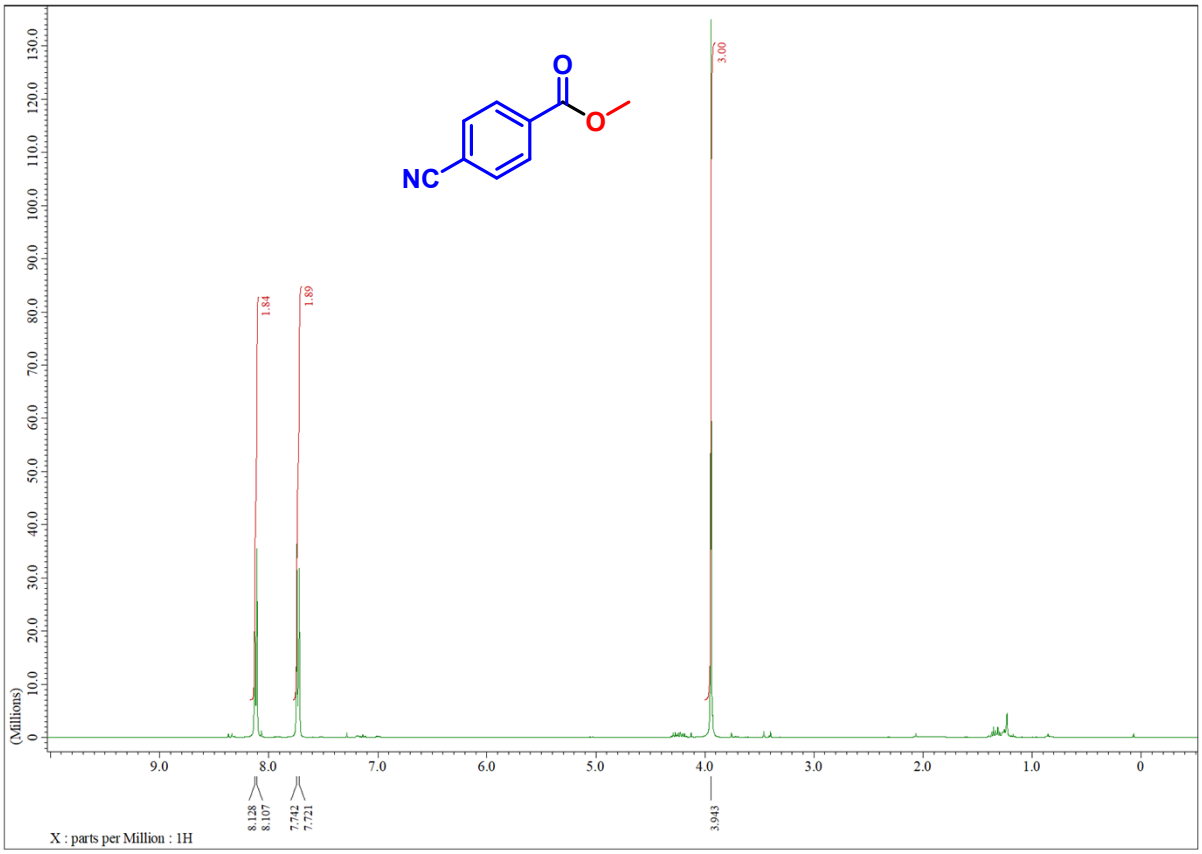


Figure S15. ^{1}H NMR spectrum of Methyl 4-cyanobenzoate **C5.**

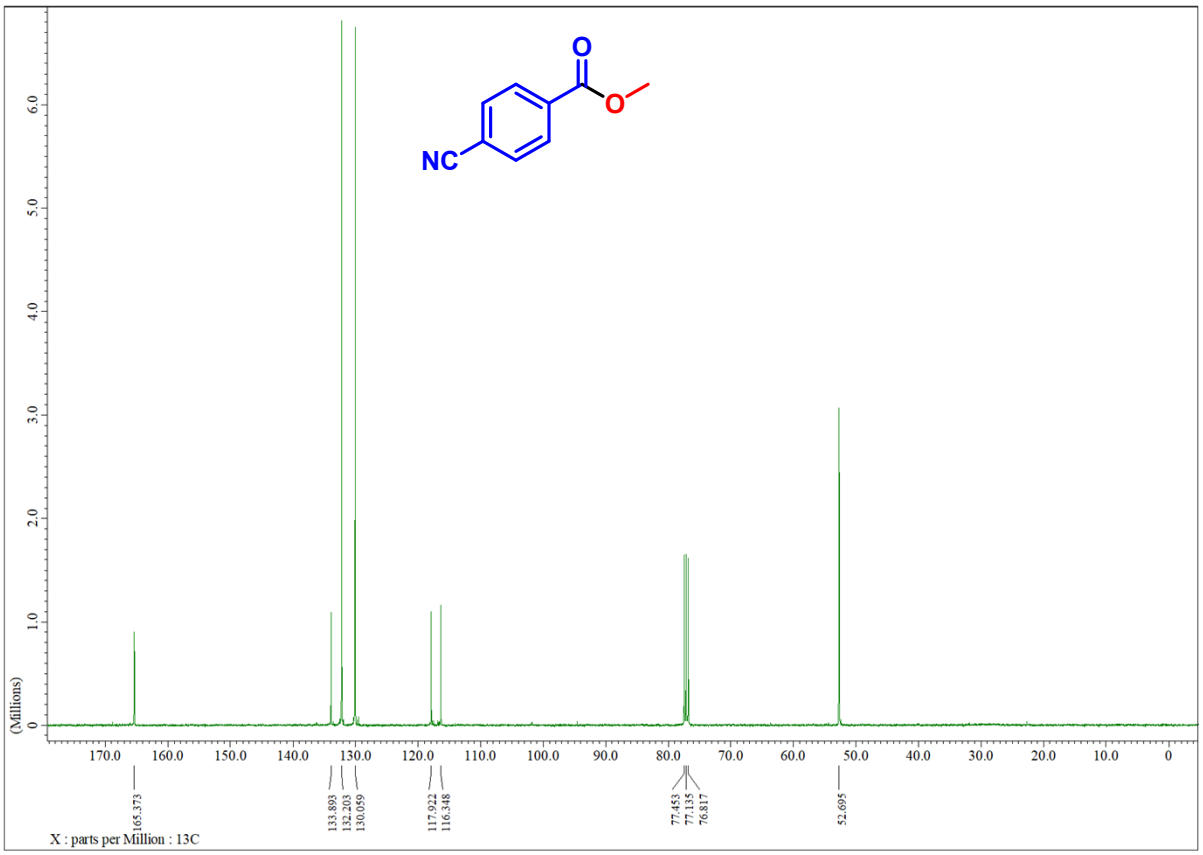


Figure S16. ^{13}C NMR spectrum of Methyl 4-cyanobenzoate **C5.**

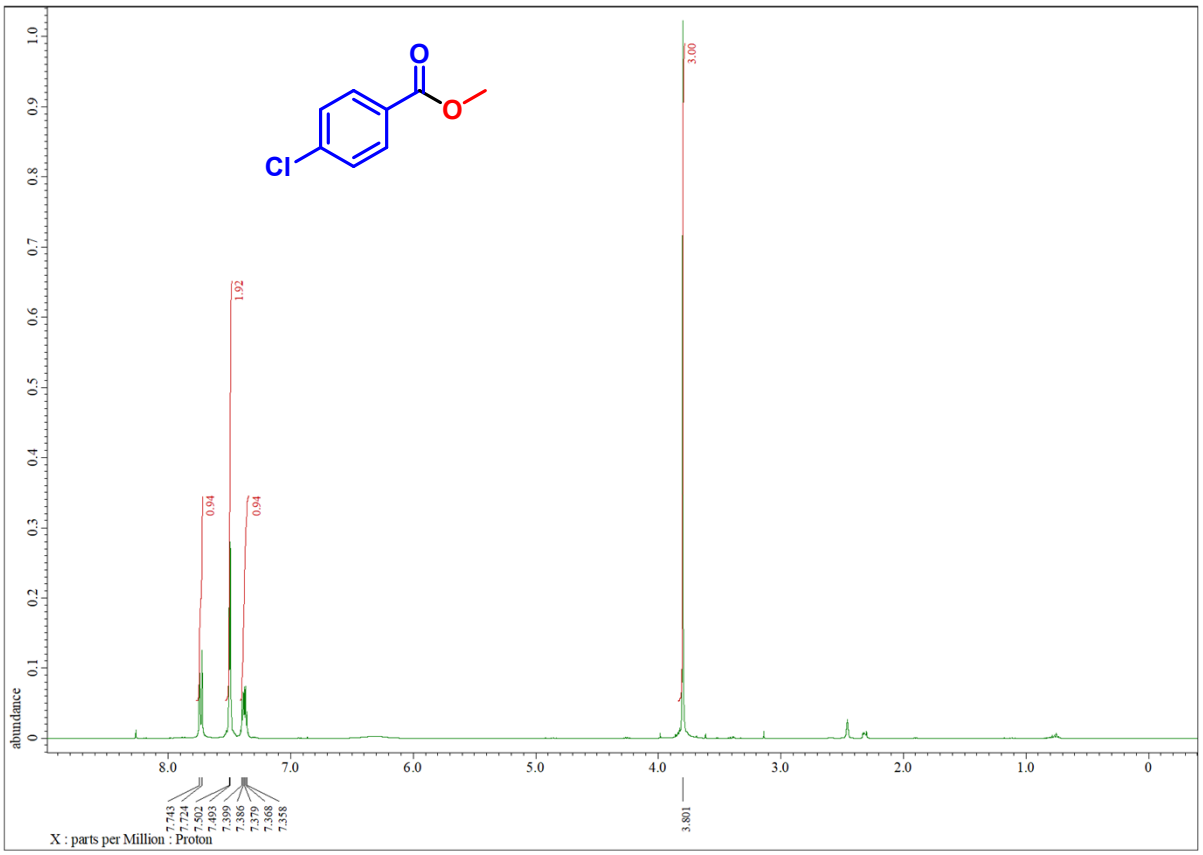


Figure S17. ^{1}H NMR spectrum of Methyl 4-chlorobenzoate **C6.**

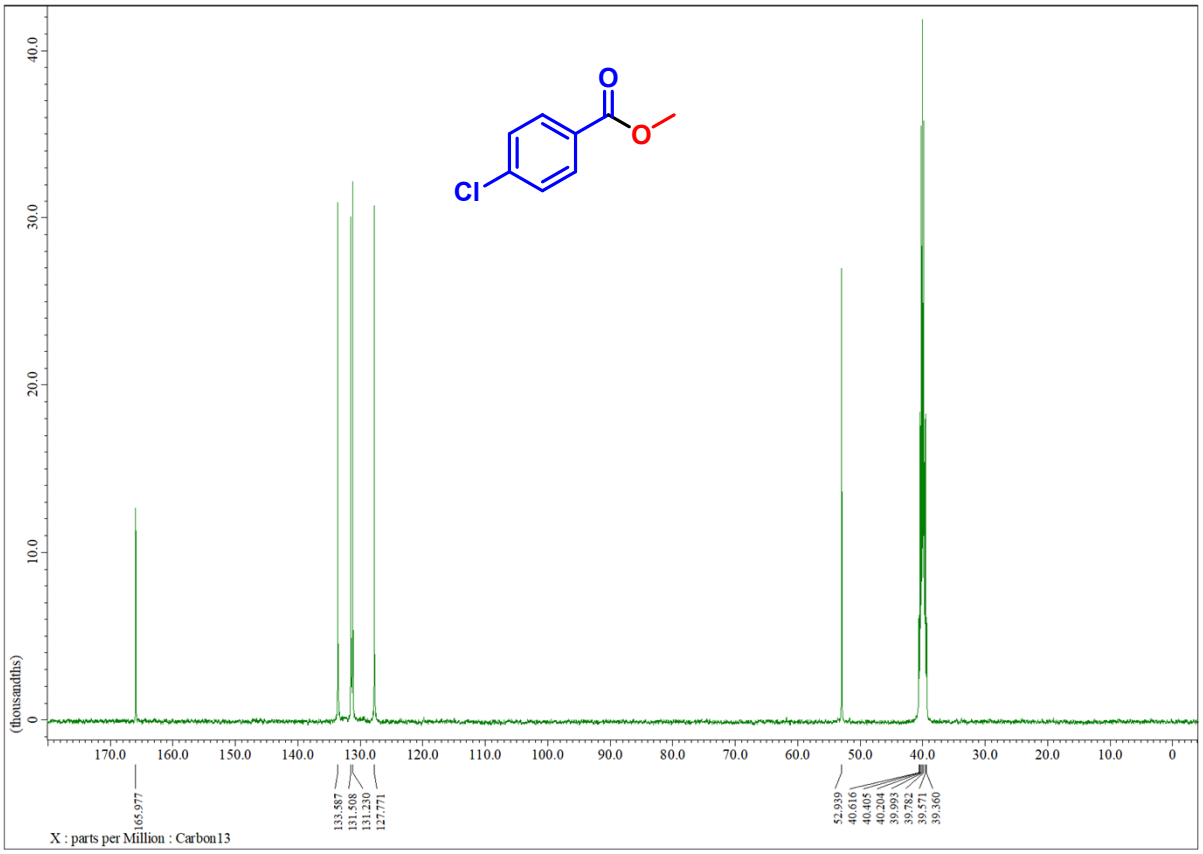


Figure S18. ^{13}C NMR spectrum of Methyl 4-chlorobenzoate **C6.**

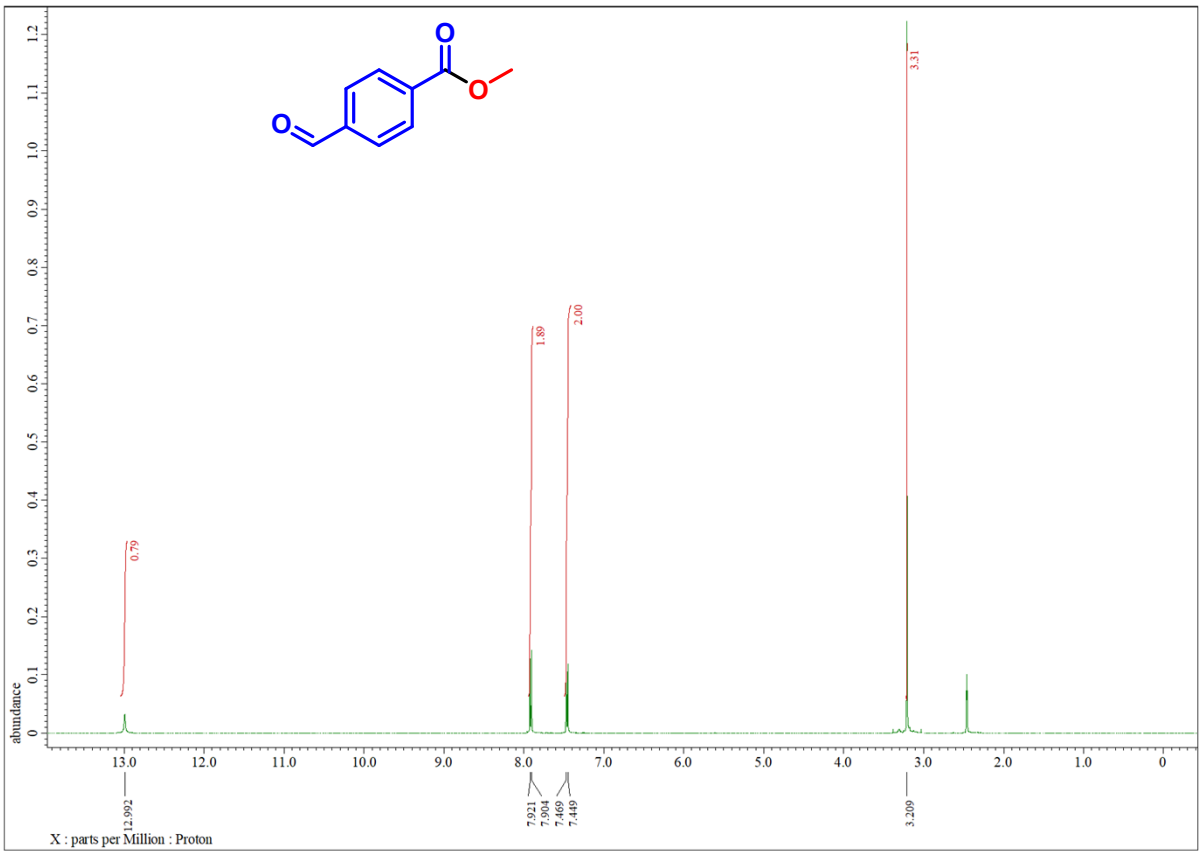


Figure S19. [1]H NMR spectrum of Methyl 4-formylbenzoate **C7.**

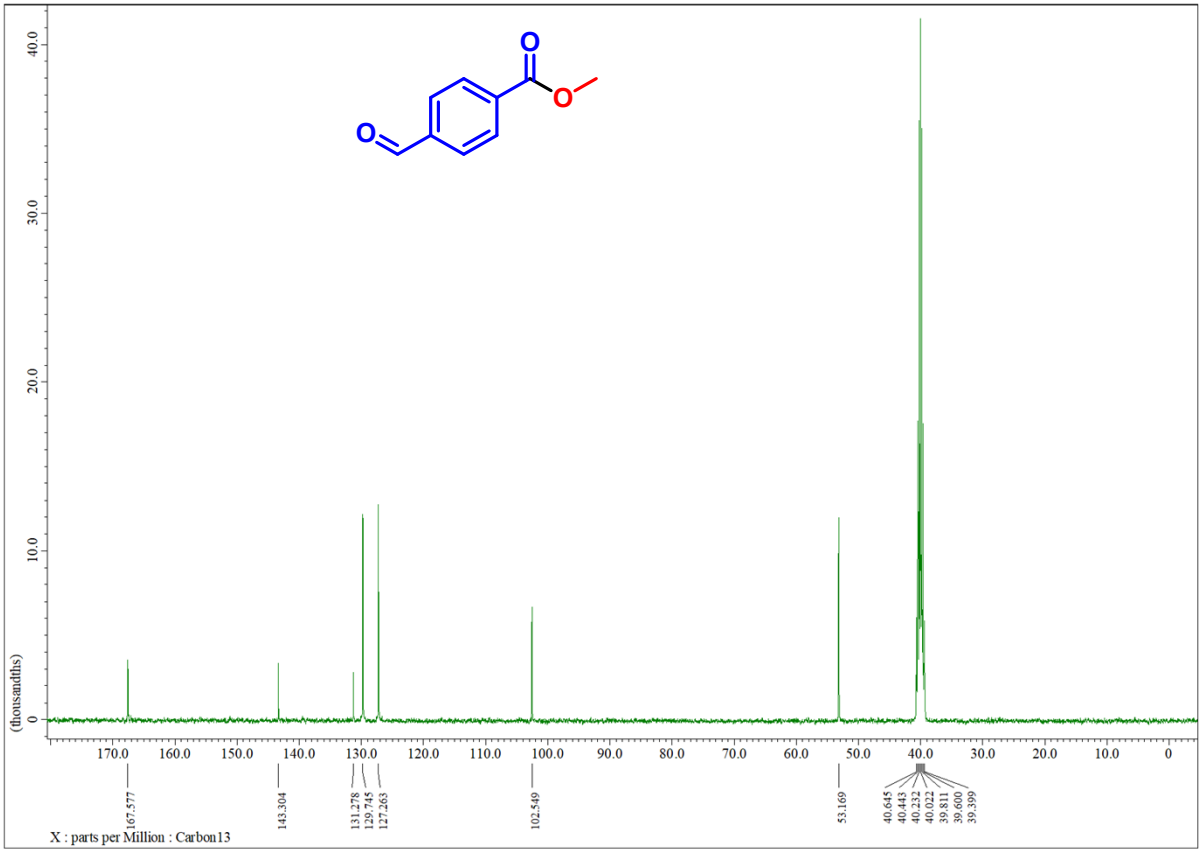


Figure S20. [13]C NMR spectrum of Methyl 4-formylbenzoate **C7.**

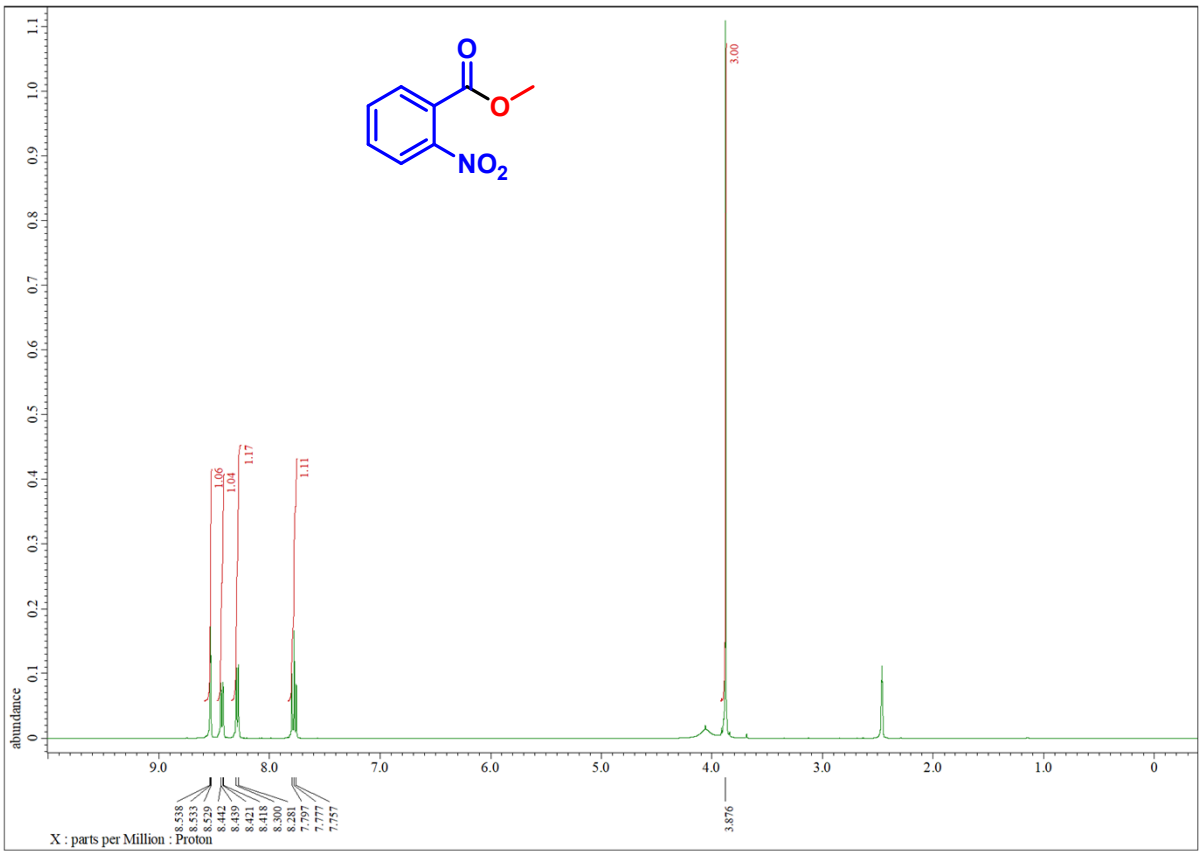


Figure S21. ^{1}H NMR spectrum of Methyl 2-nitrobenzoate **C8.**

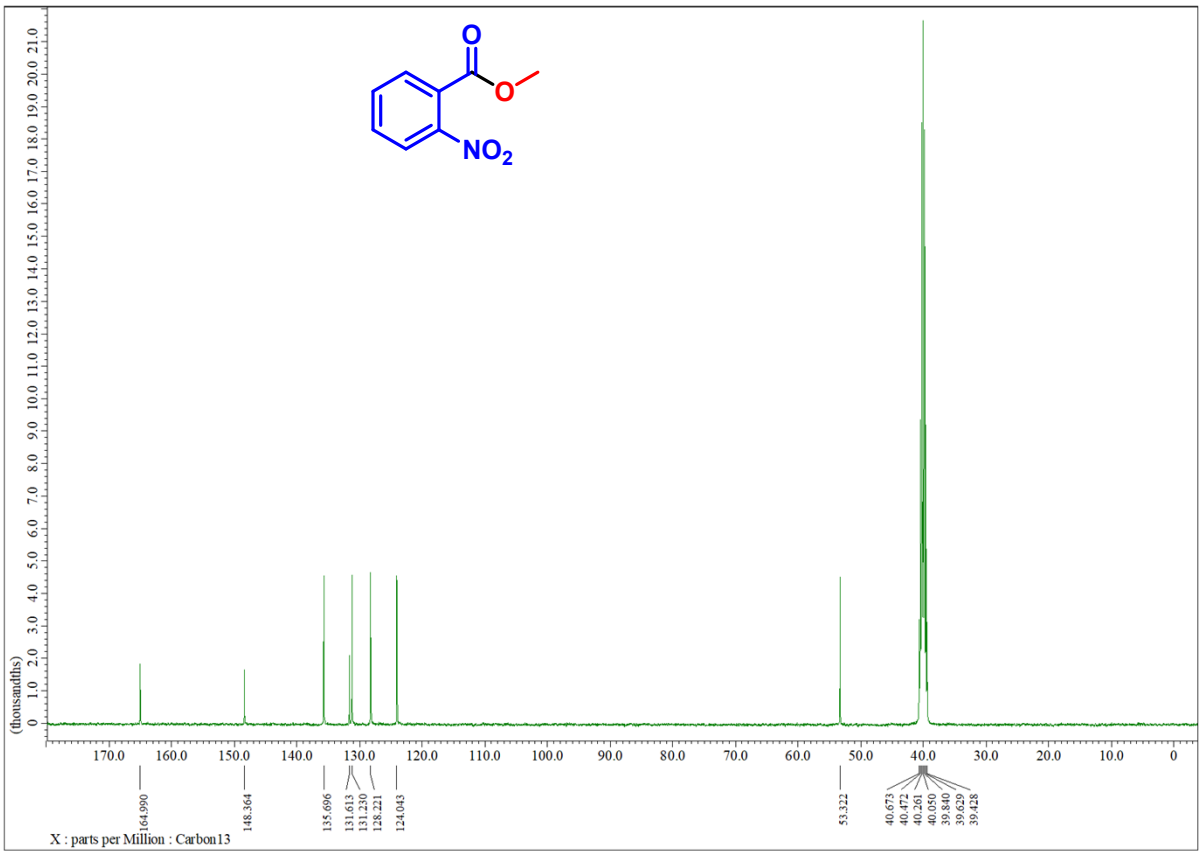


Figure S22. ^{13}C NMR spectrum of Methyl 2-nitrobenzoate **C8.**

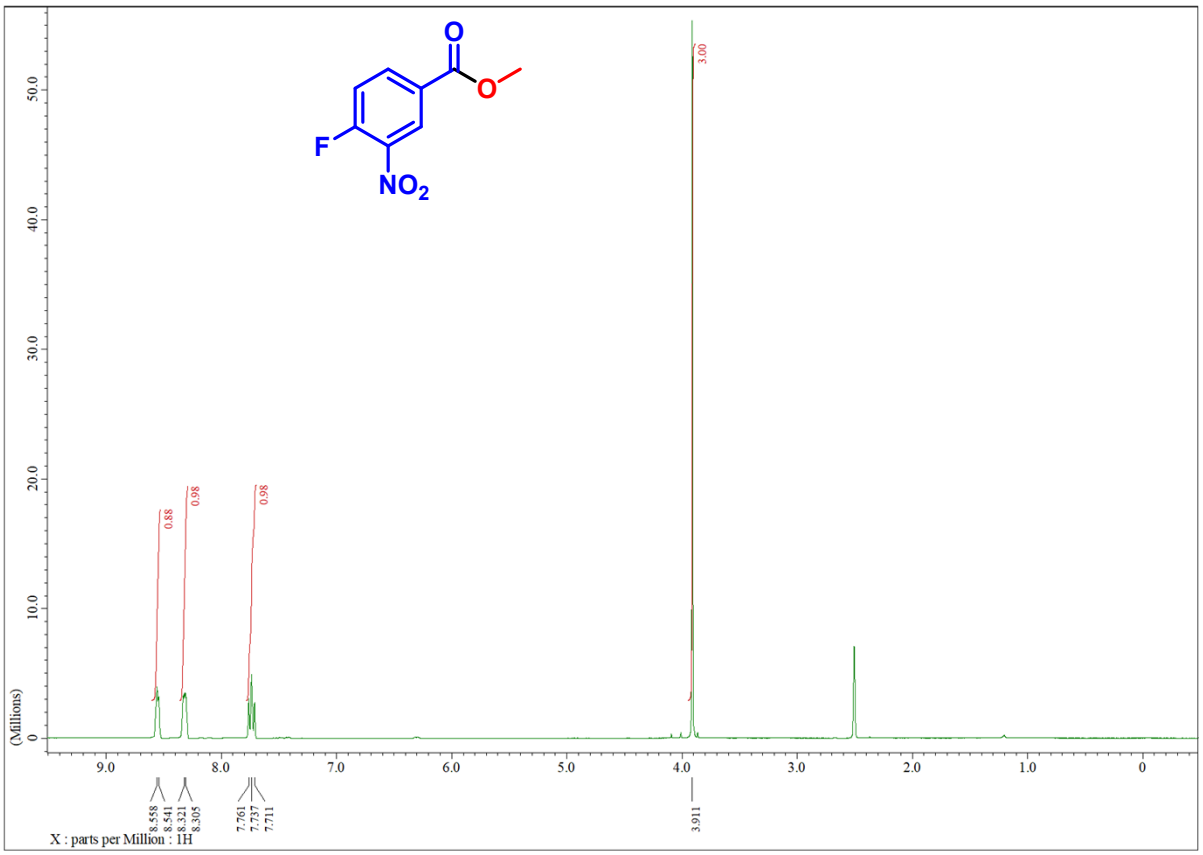


Figure S23. ^{1}H NMR spectrum of Methyl 4-fluoro-3-nitrobenzoate **C9.**

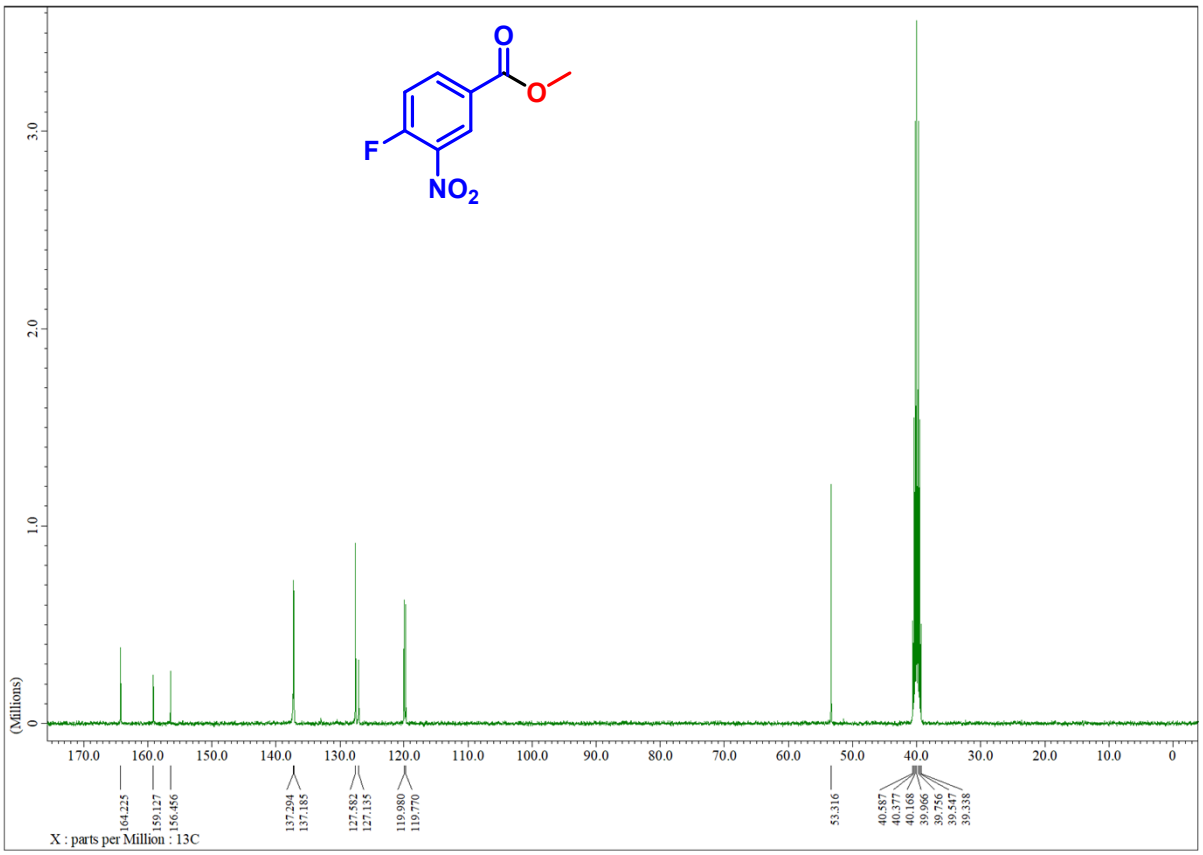


Figure S24. ^{13}C NMR spectrum of Methyl 4-fluoro-3-nitrobenzoate **C9.**

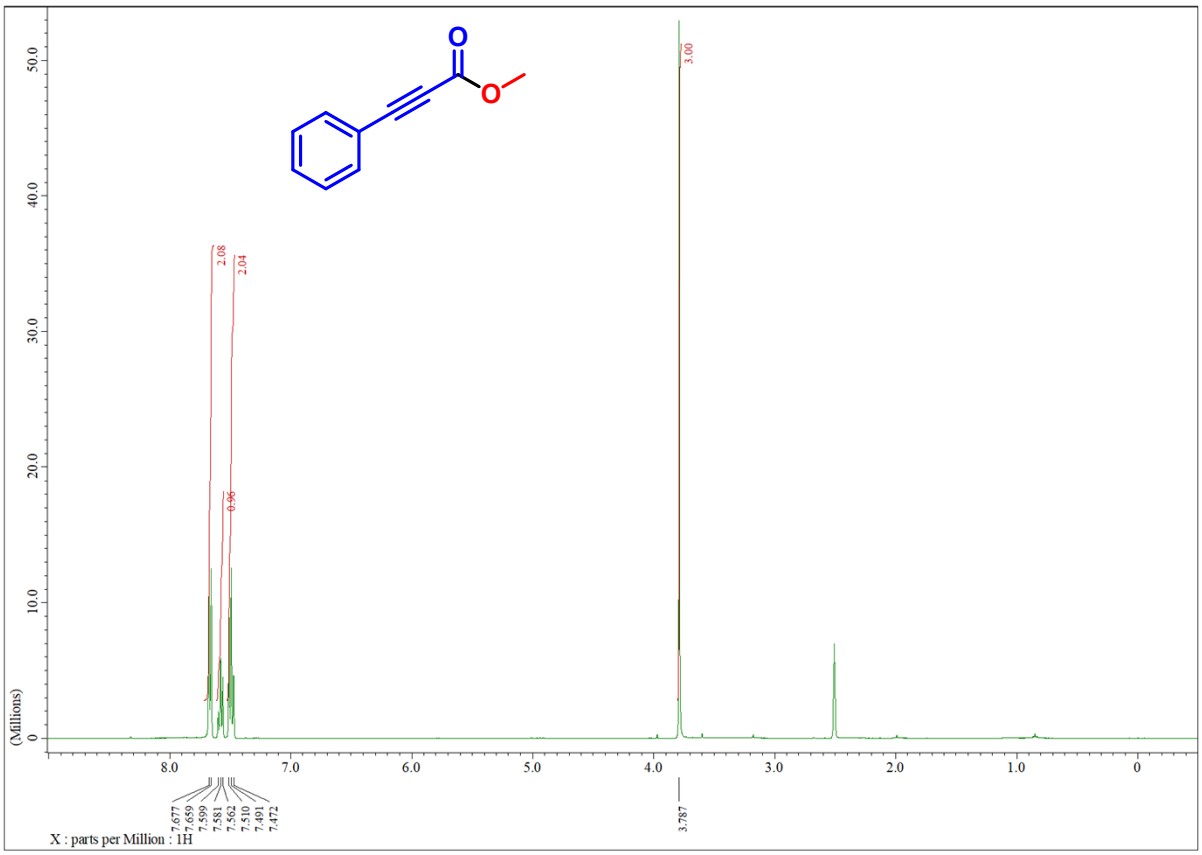


Figure S25. ^{1}H NMR spectrum of Methyl 3-phenylpropiolate **C10.**

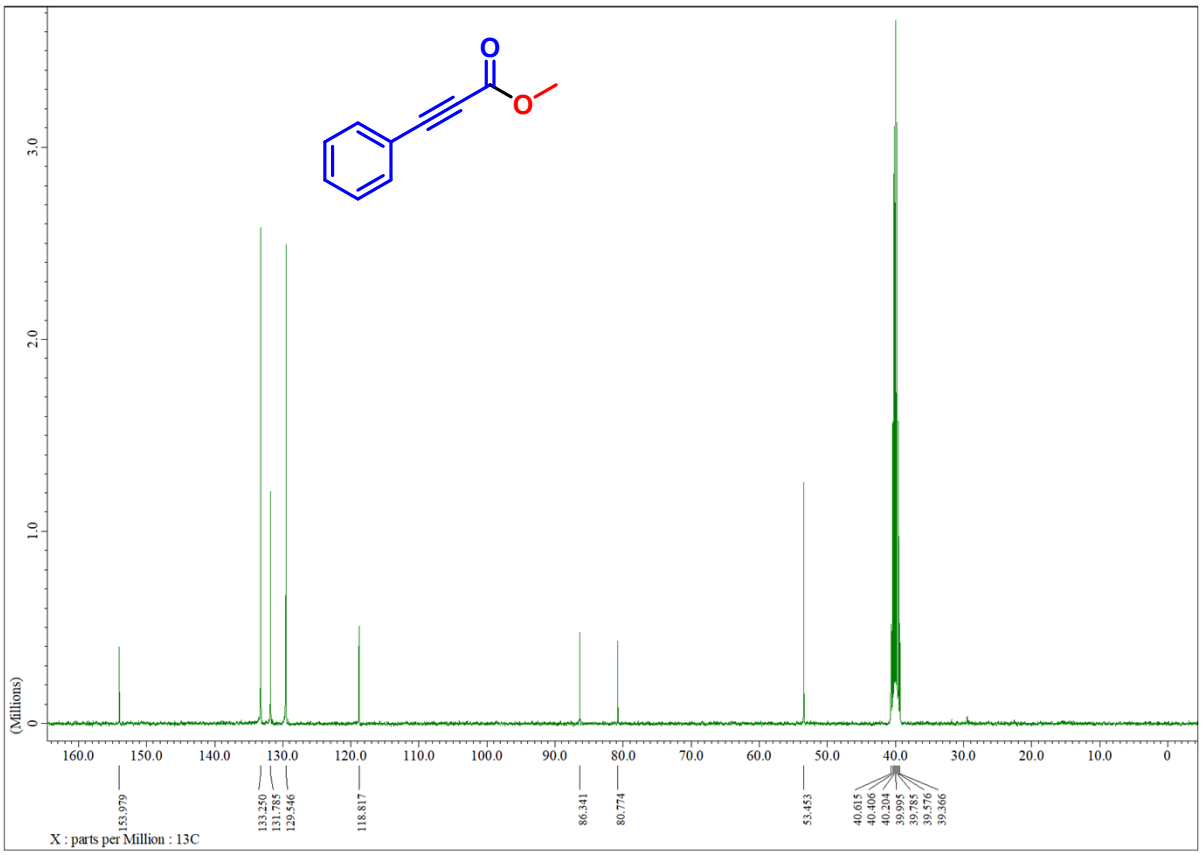


Figure S26. ^{13}C NMR spectrum of Methyl 3-phenylpropiolate **C10.**

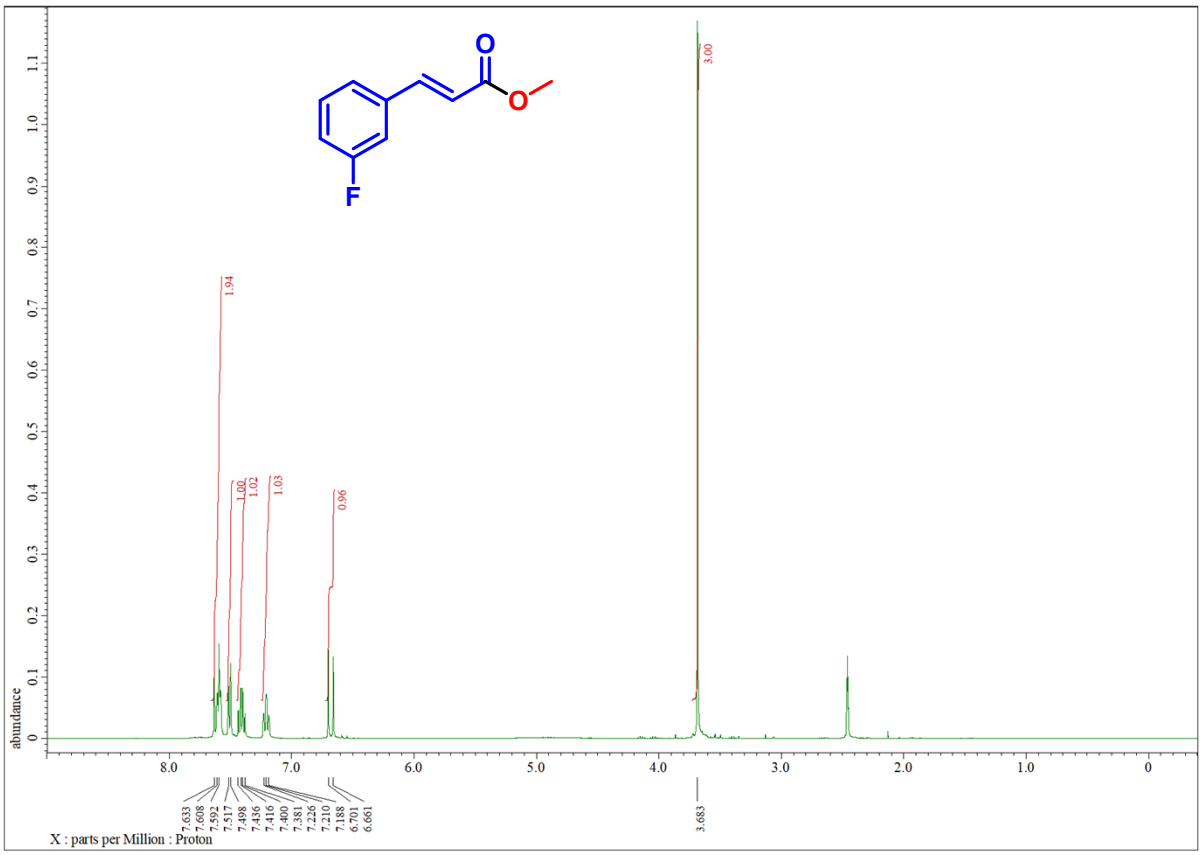


Figure S27. ^{1}H NMR spectrum of Methyl (E)-3-(3-fluorophenyl)acrylate **C11.**

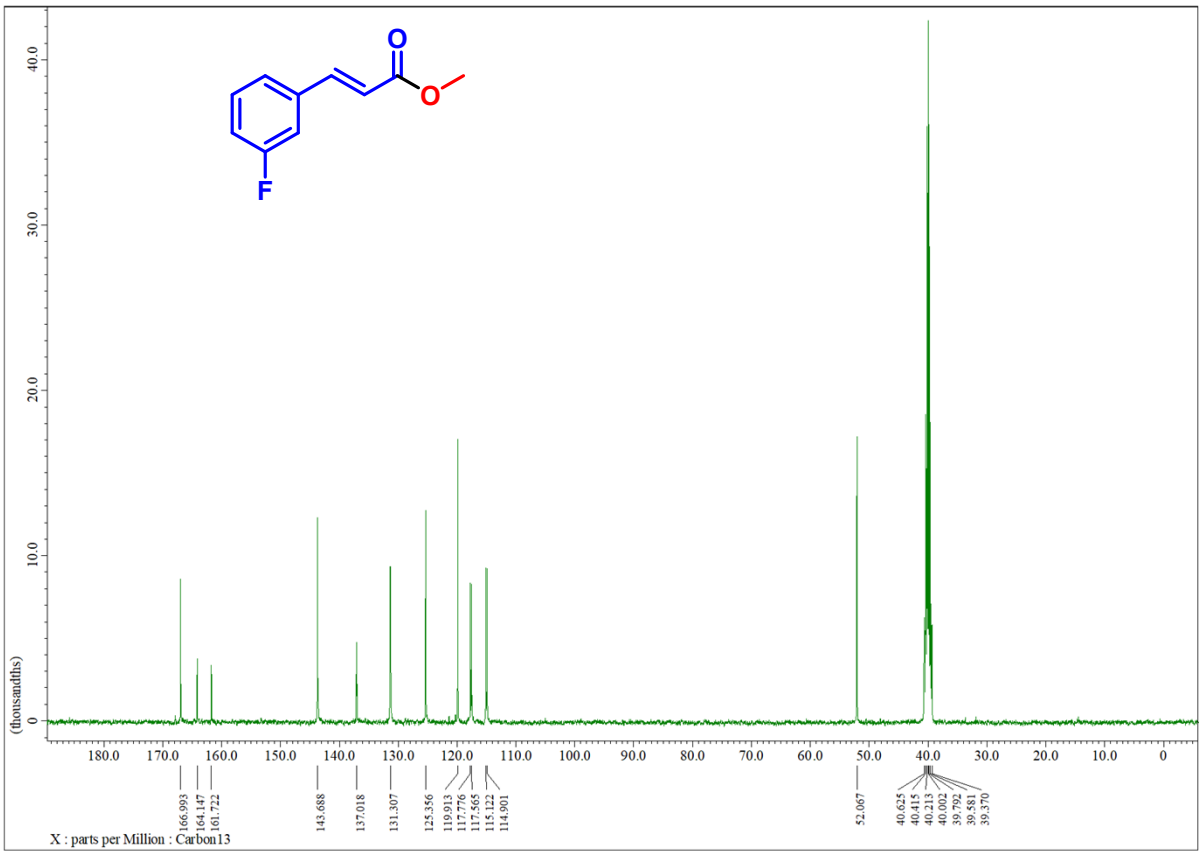


Figure S28. ^{13}C NMR spectrum of Methyl (E)-3-(3-fluorophenyl)acrylate **C11.**

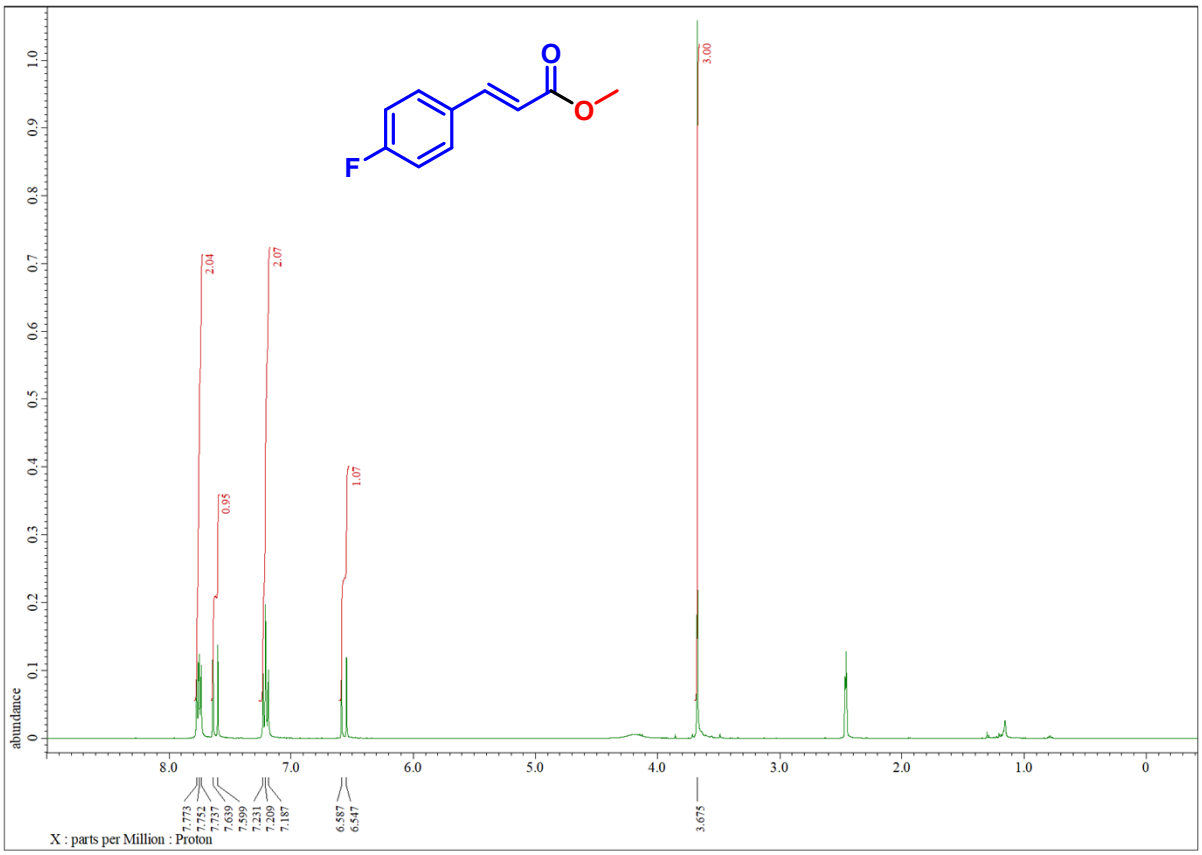


Figure S29. ^{1}H NMR spectrum of Methyl (E)-3-(4-fluorophenyl)acrylate **C12.**

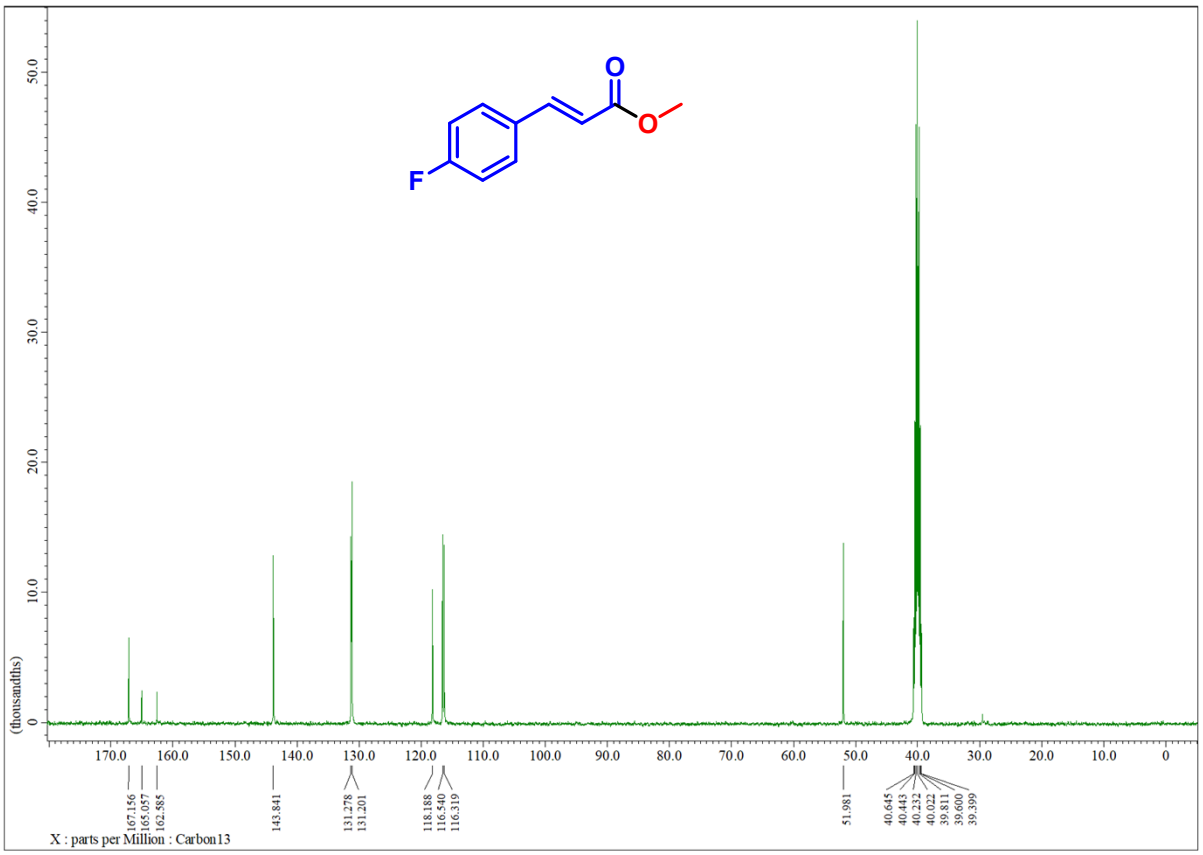


Figure S30. ^{13}C NMR spectrum of Methyl (E)-3-(4-fluorophenyl)acrylate **C12.**

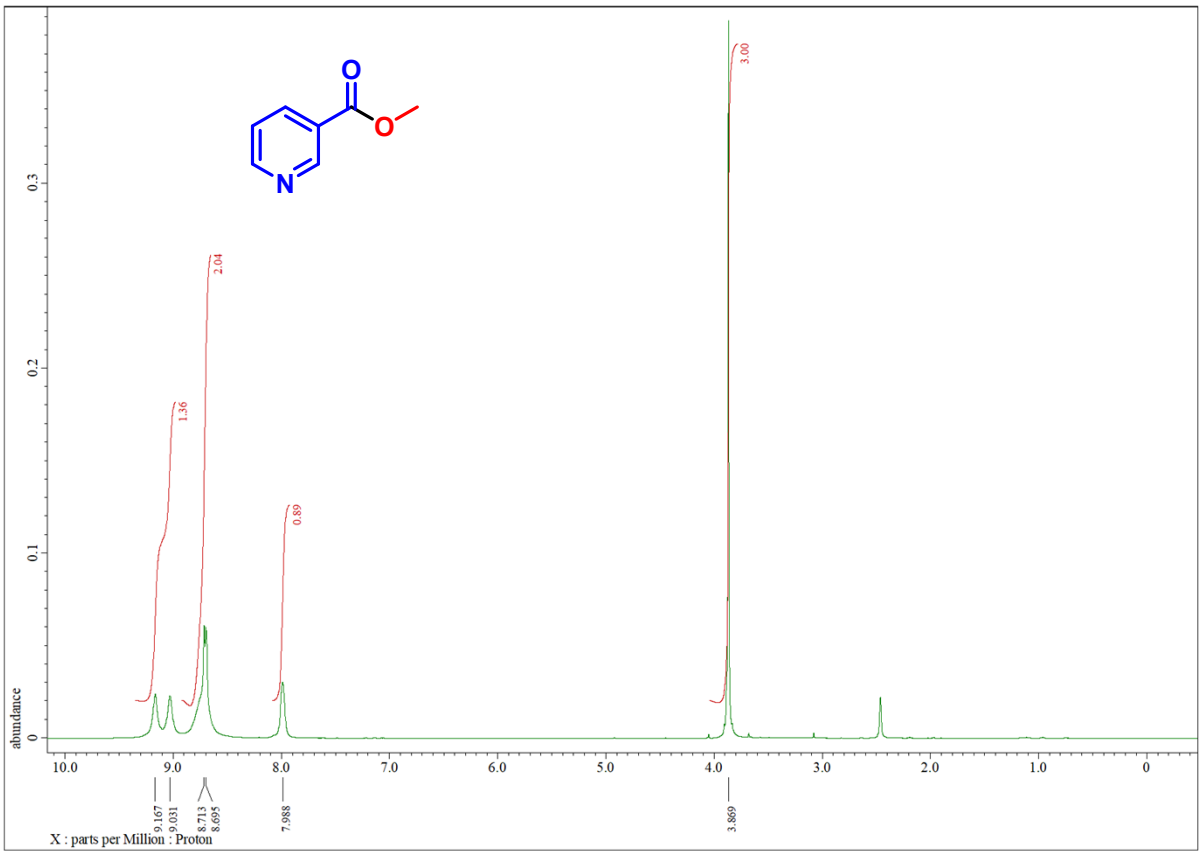


Figure S31. ^{1}H NMR spectrum of Methyl nicotinate **C13.**

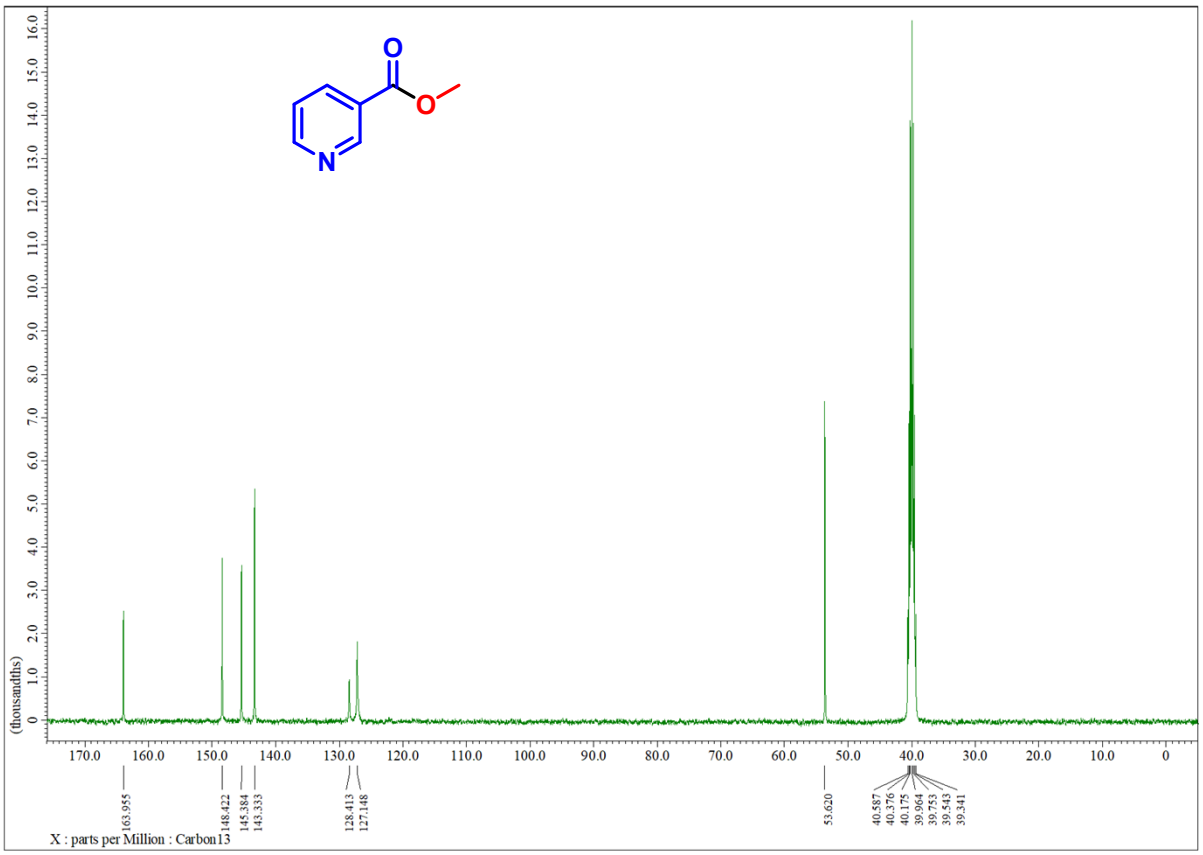


Figure S32. ^{13}C NMR spectrum of Methyl nicotinate **C13.**

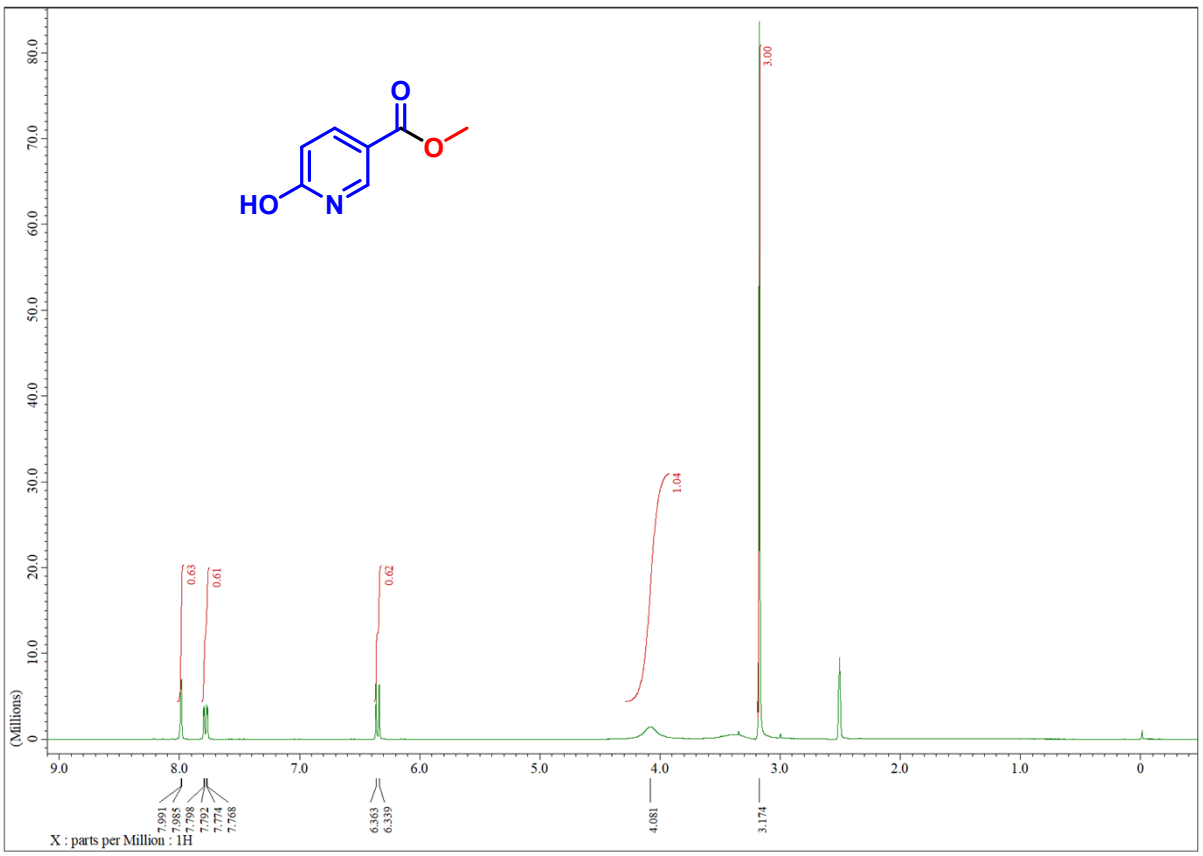


Figure S33. [1]H NMR spectrum of Methyl 6-hydroxynicotinate **C14.**

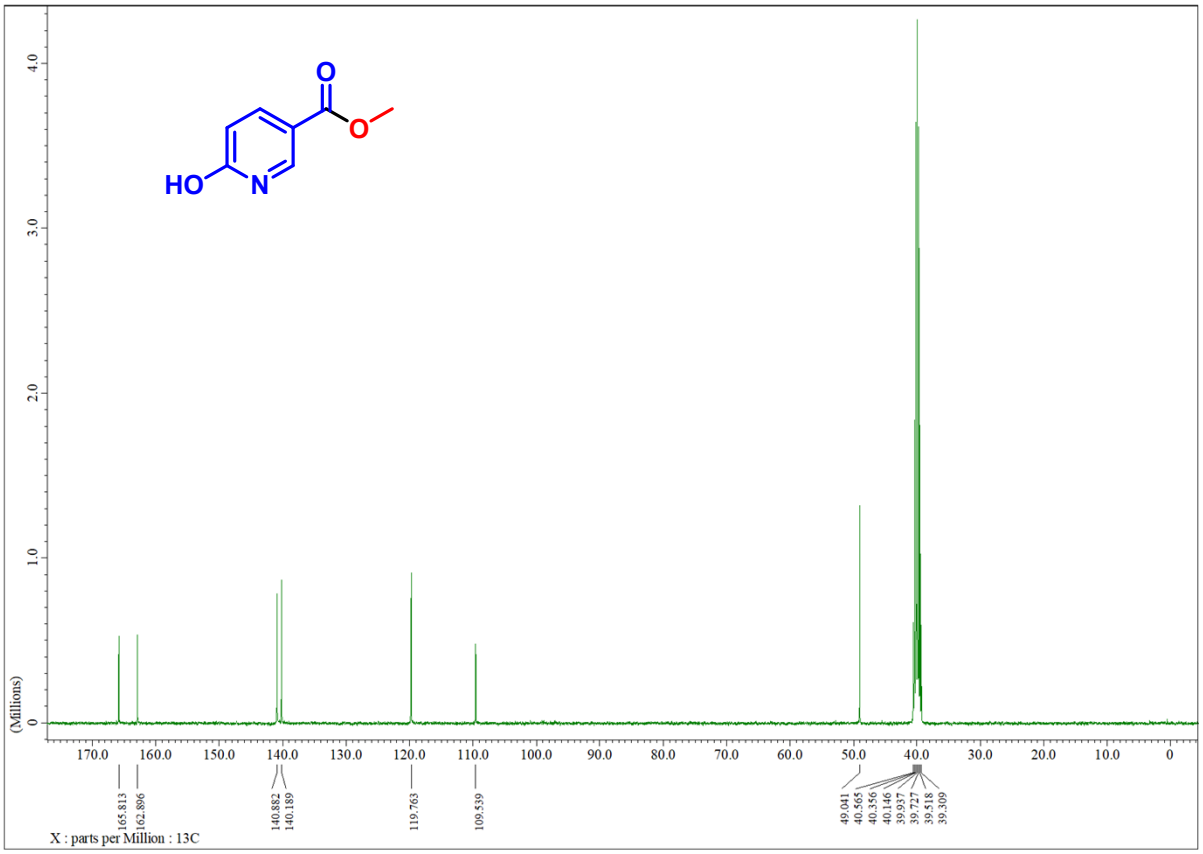


Figure S34. [13]C NMR spectrum of Methyl 6-hydroxynicotinate **C14.**

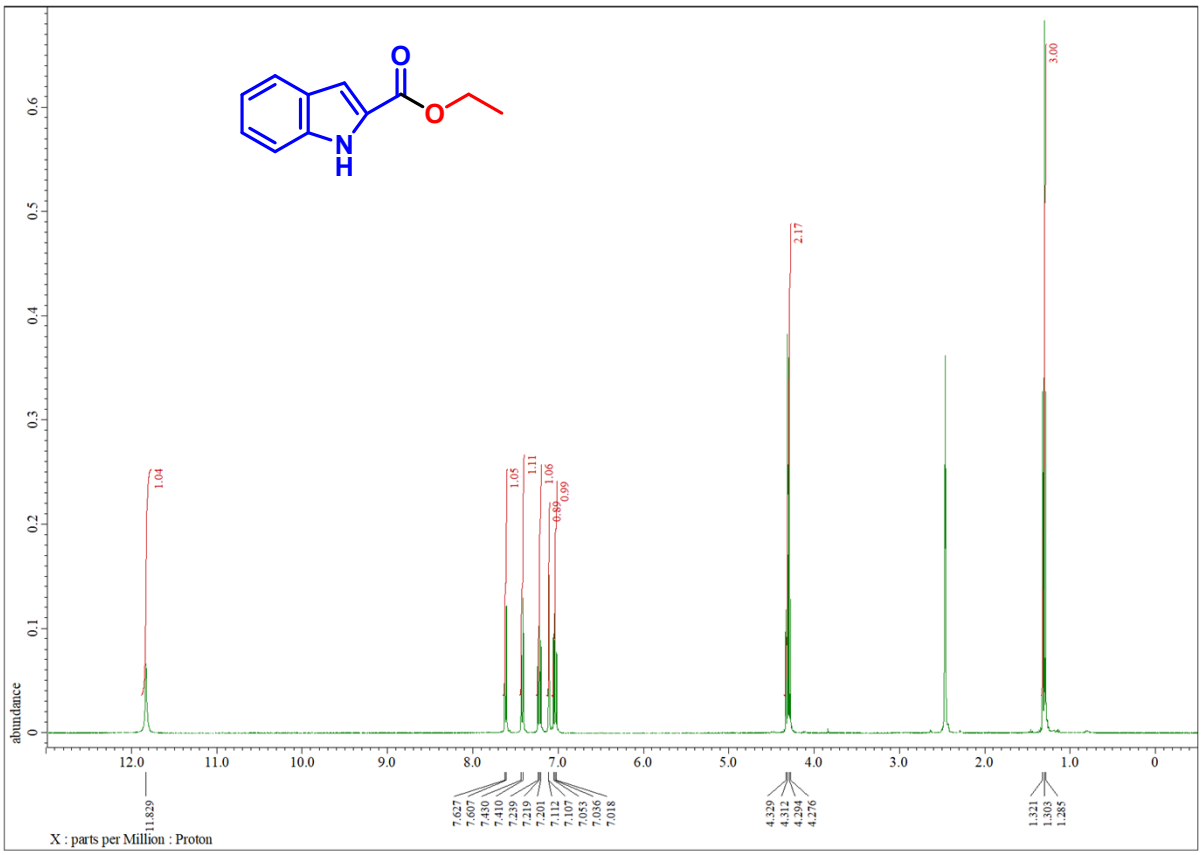


Figure S35. ^{1}H NMR spectrum of Ethyl 1H-indole-2-carboxylate **C15.**

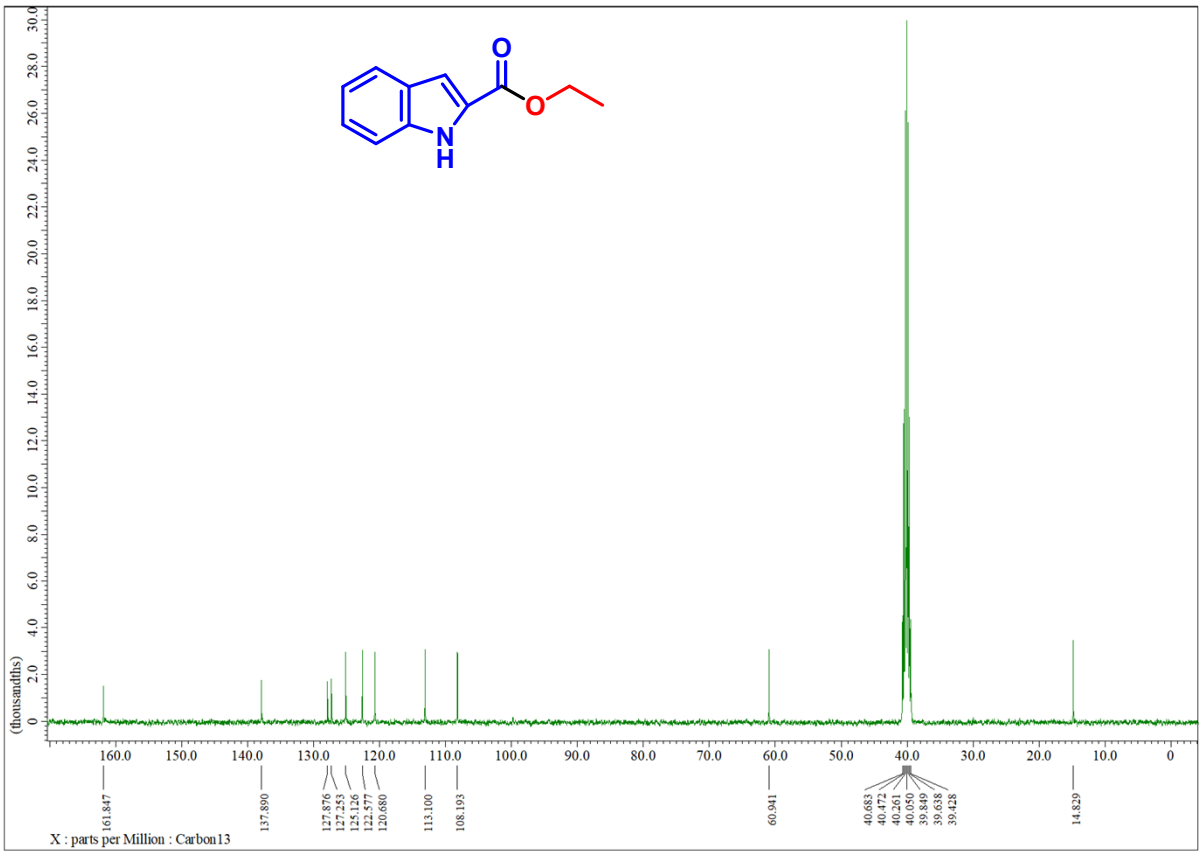


Figure S36. ^{13}C NMR spectrum of Ethyl 1H-indole-2-carboxylate **C15.**

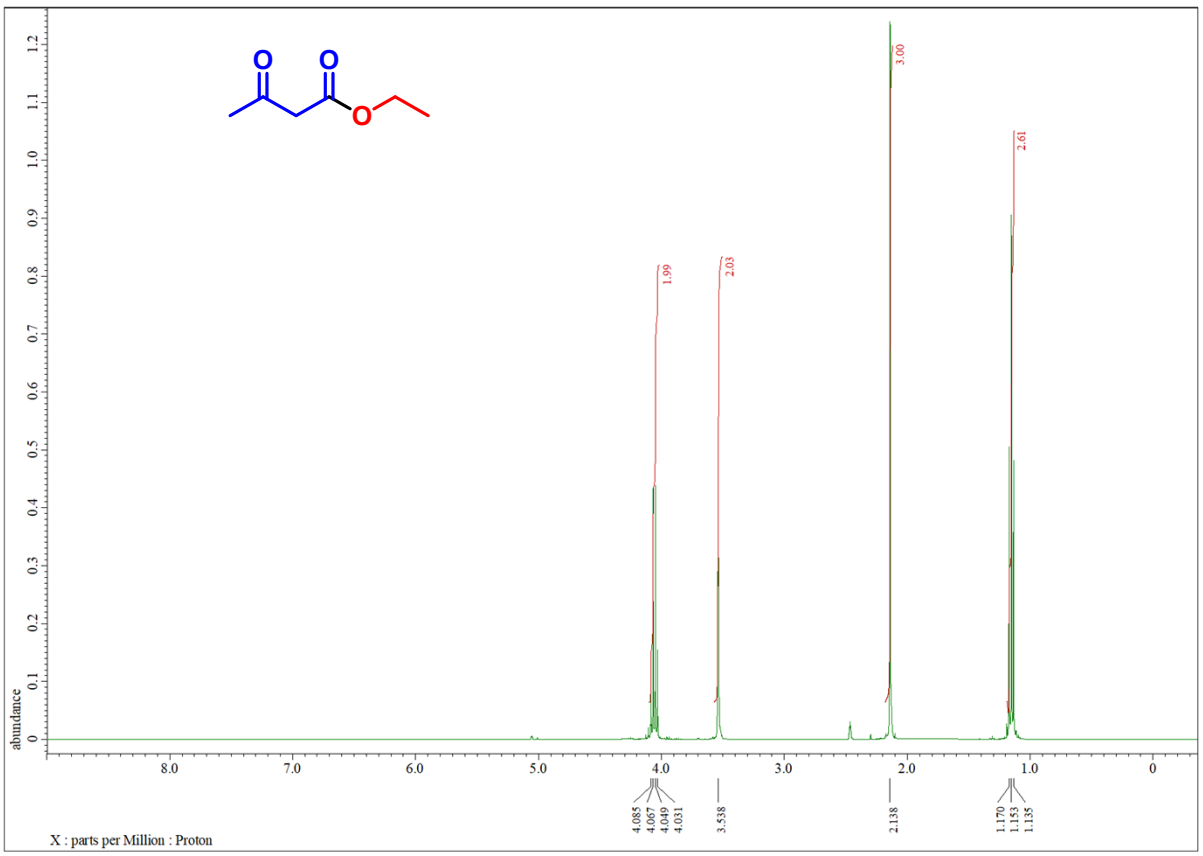


Figure S37. ^{1}H NMR spectrum of Ethyl 3-oxobutanoate **C16.**

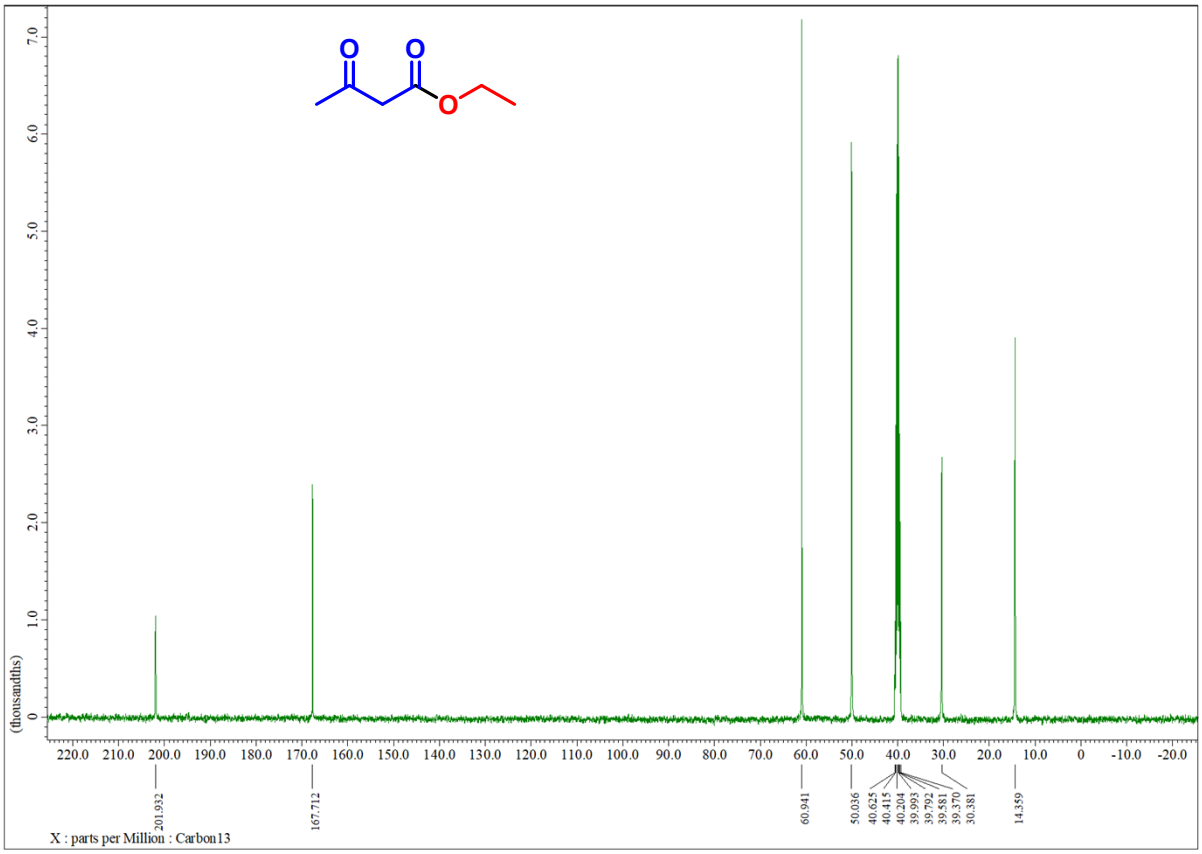


Figure S38. ^{13}C NMR spectrum of Ethyl 3-oxobutanoate **C16.**

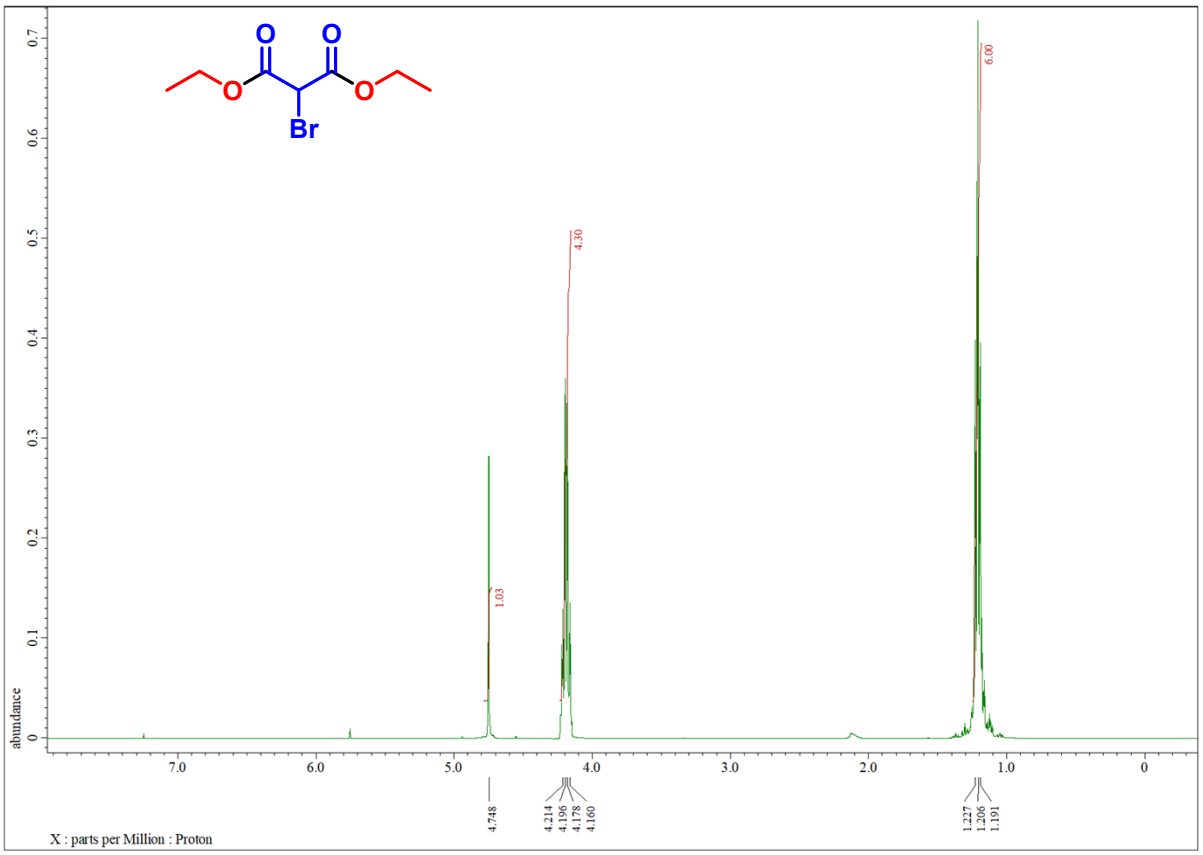


Figure S39. ^{1}H NMR spectrum of Diethyl 2-bromomalonate **C17.**

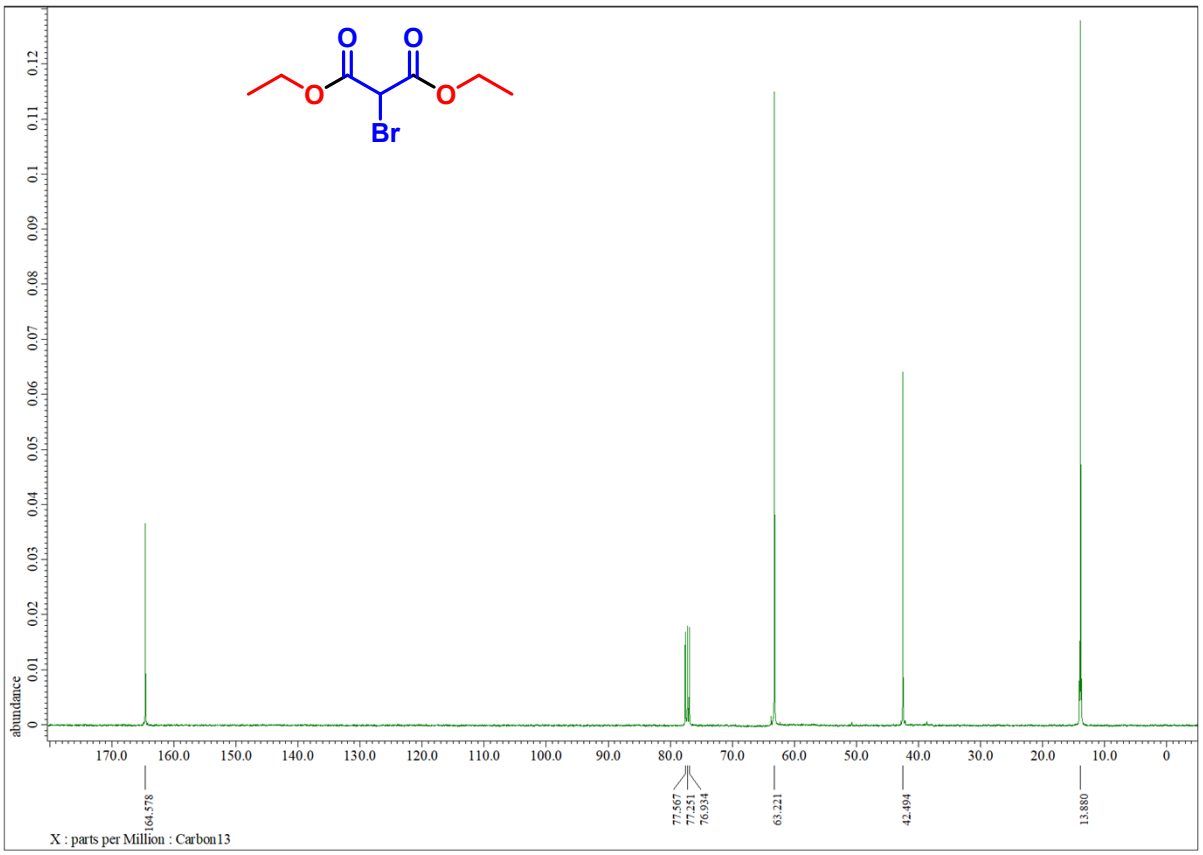


Figure S40. ^{13}C NMR spectrum of Diethyl 2-bromomalonate **C17.**

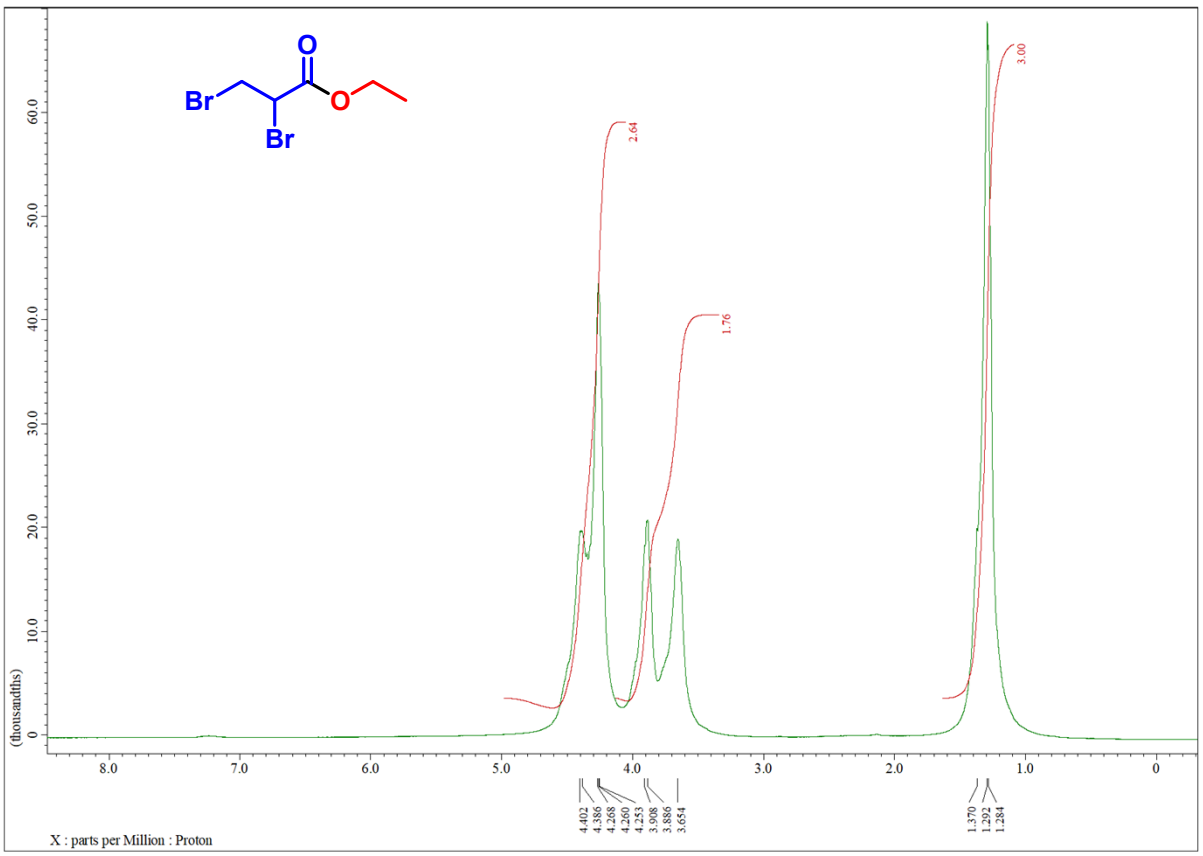


Figure S41. [1]H NMR spectrum of Ethyl 2,3-dibromopropanoate **C18.**

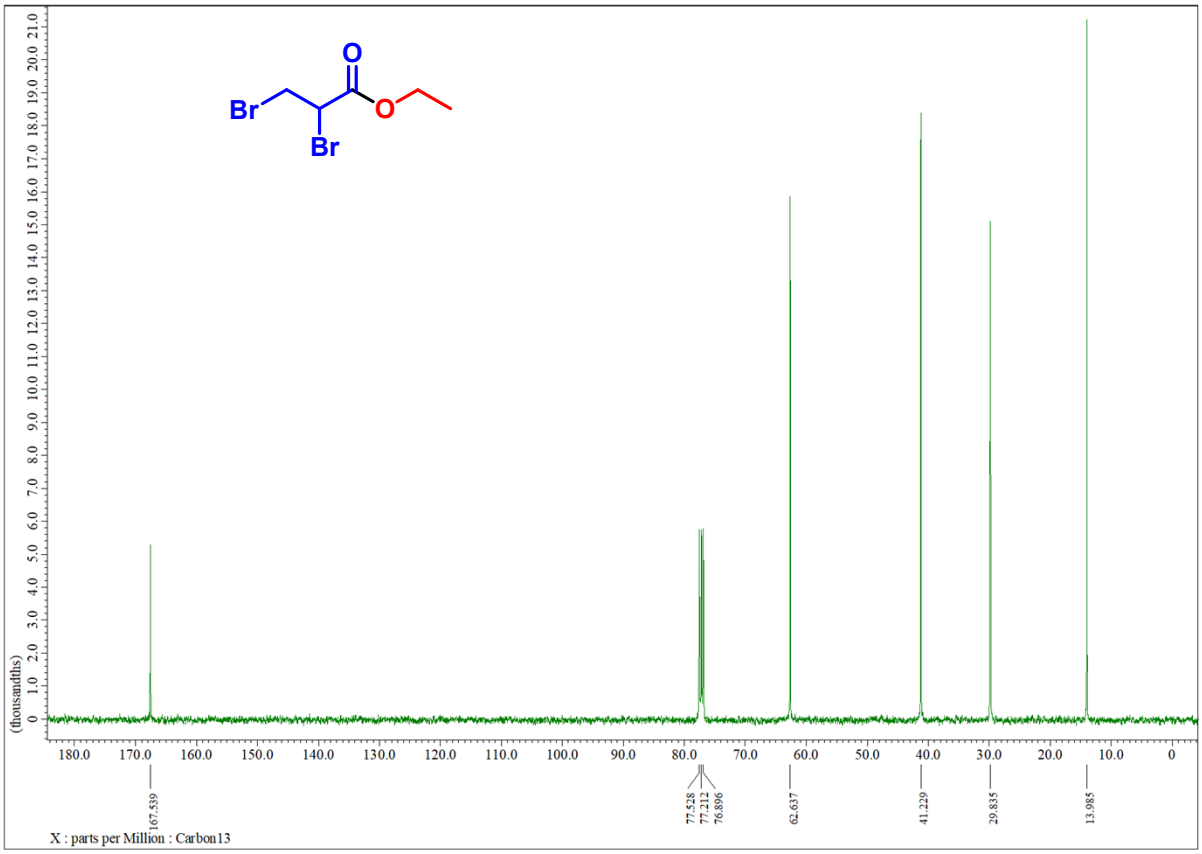


Figure S42. [13]C NMR spectrum of Ethyl 2,3-dibromopropanoate **C18.**

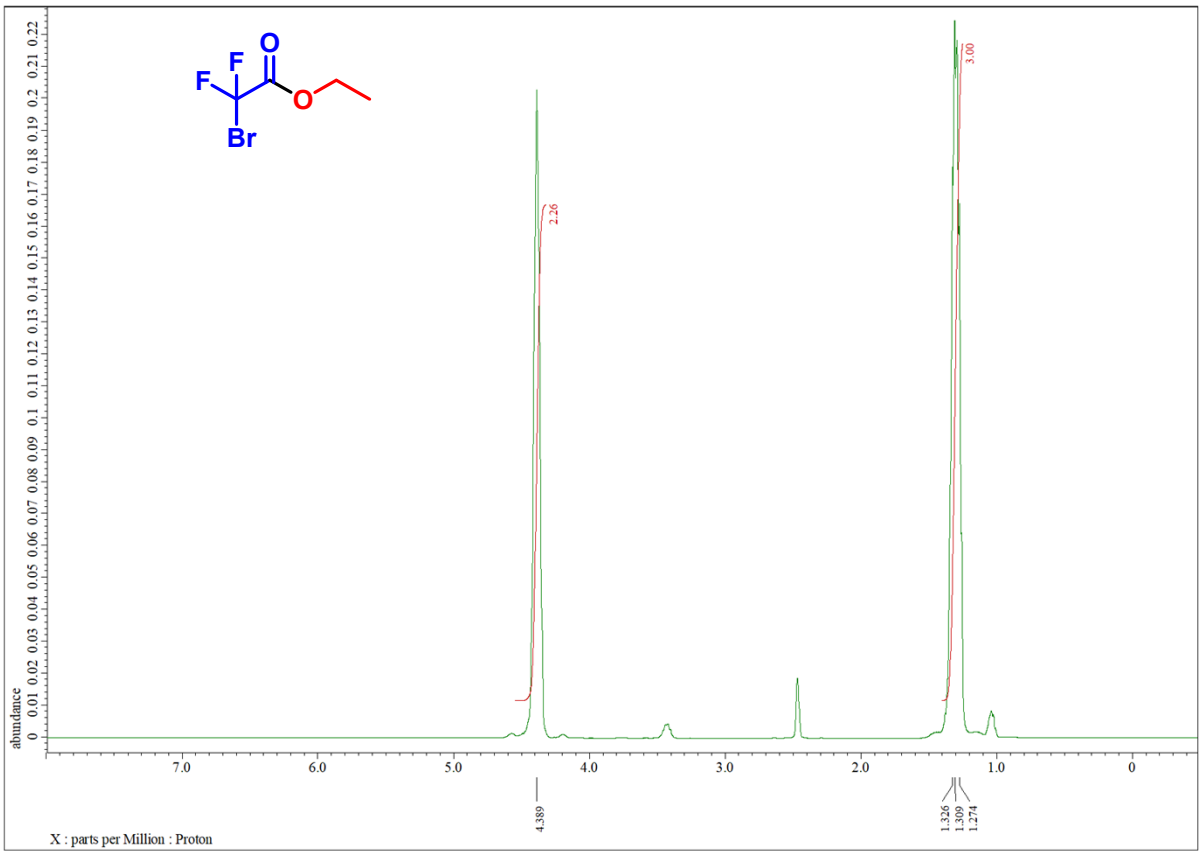


Figure S43. ^{1}H NMR spectrum of Ethyl 2-bromo-2,2-difluoroacetate **C19.**

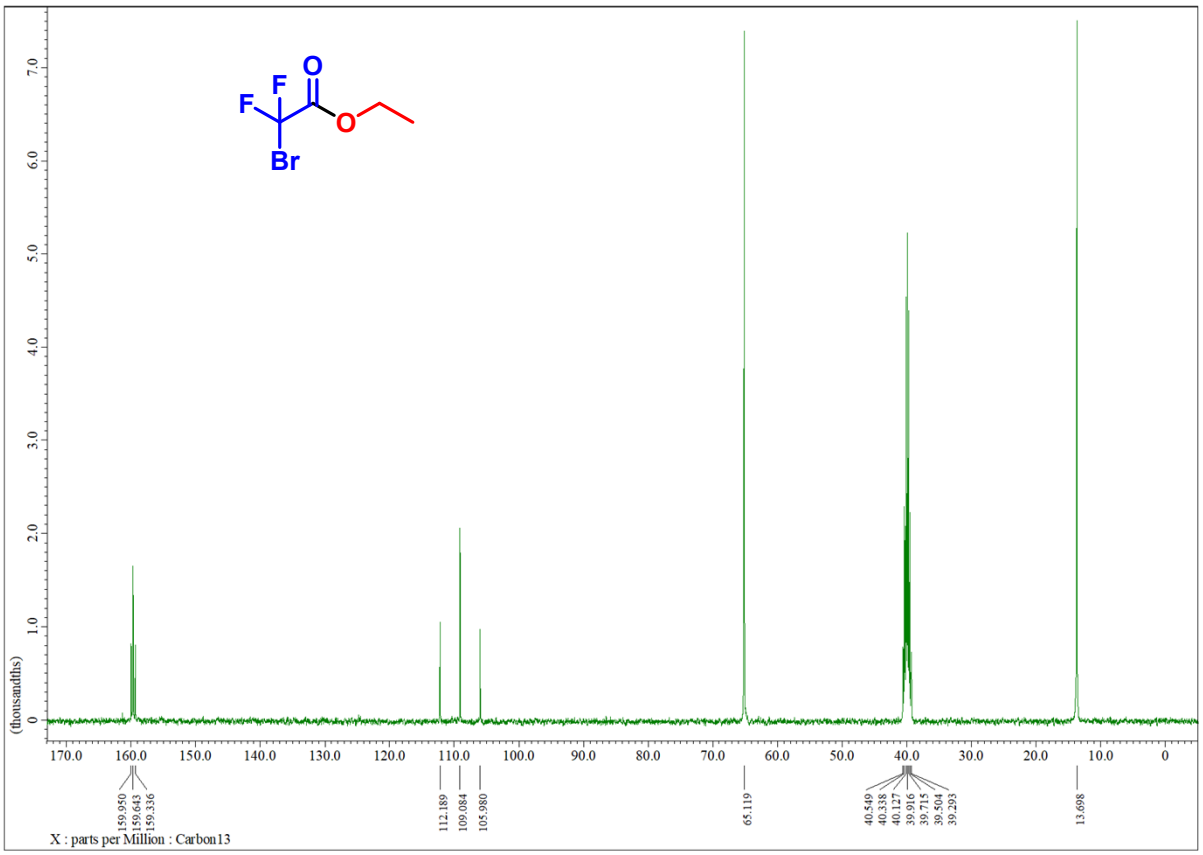


Figure S44. ^{13}C NMR spectrum of Ethyl 2-bromo-2,2-difluoroacetate **C19.**

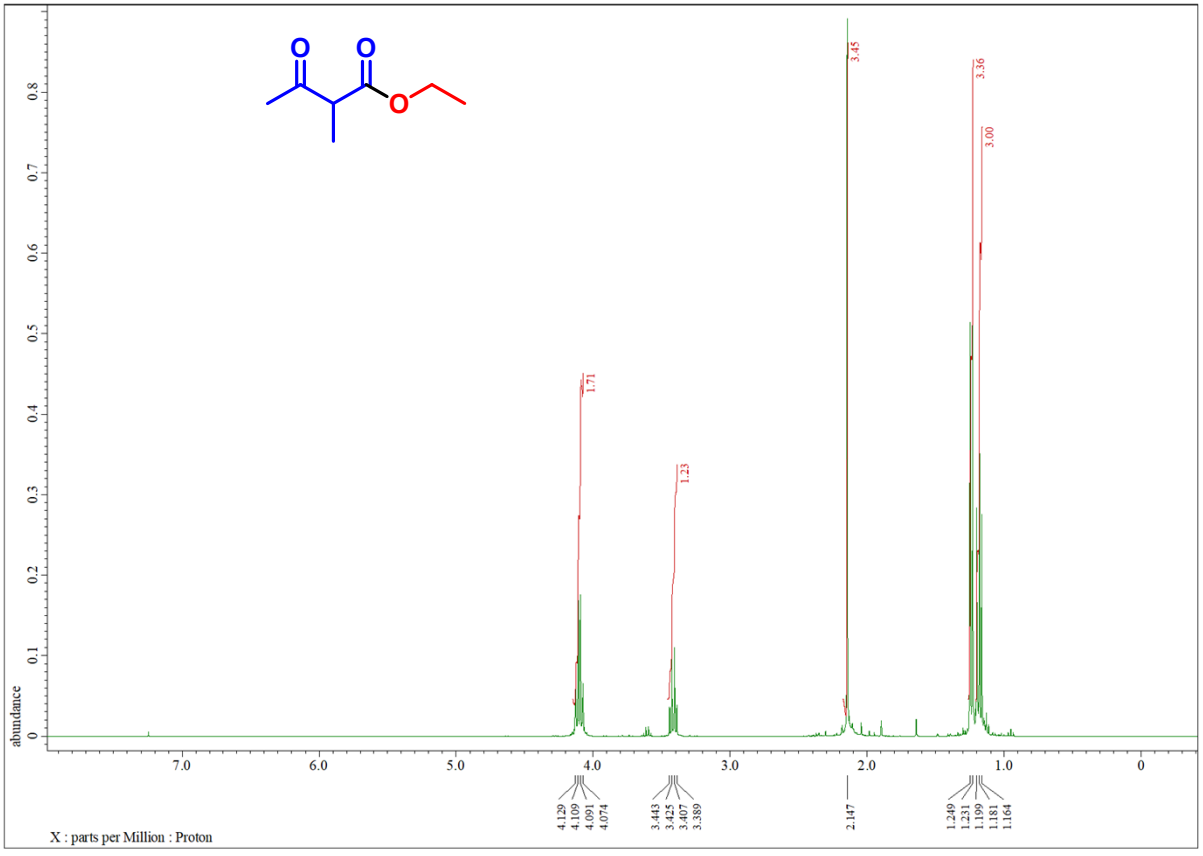


Figure S45. [1]H NMR spectrum of Ethyl 2-methyl-3-oxobutanoate **C20.**

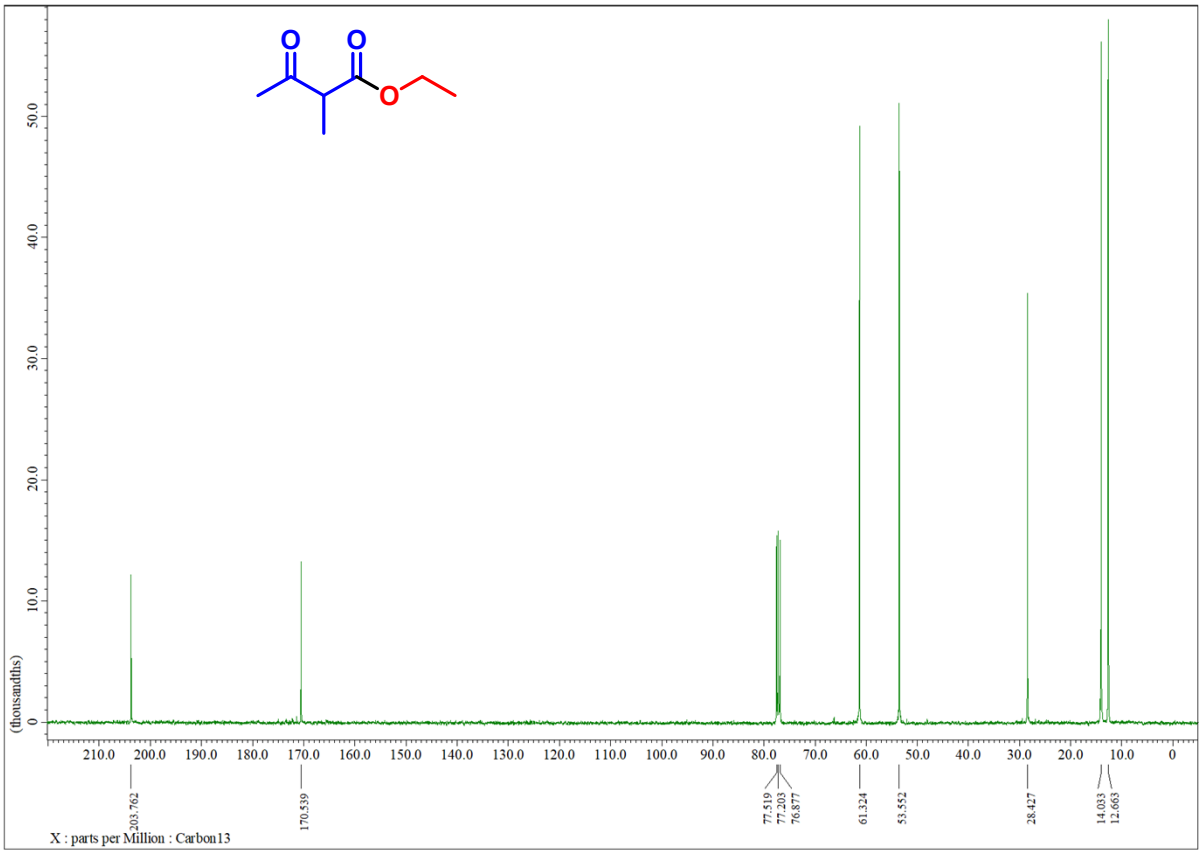


Figure S46. [13]C NMR spectrum of Ethyl 2-methyl-3-oxobutanoate **C20.**

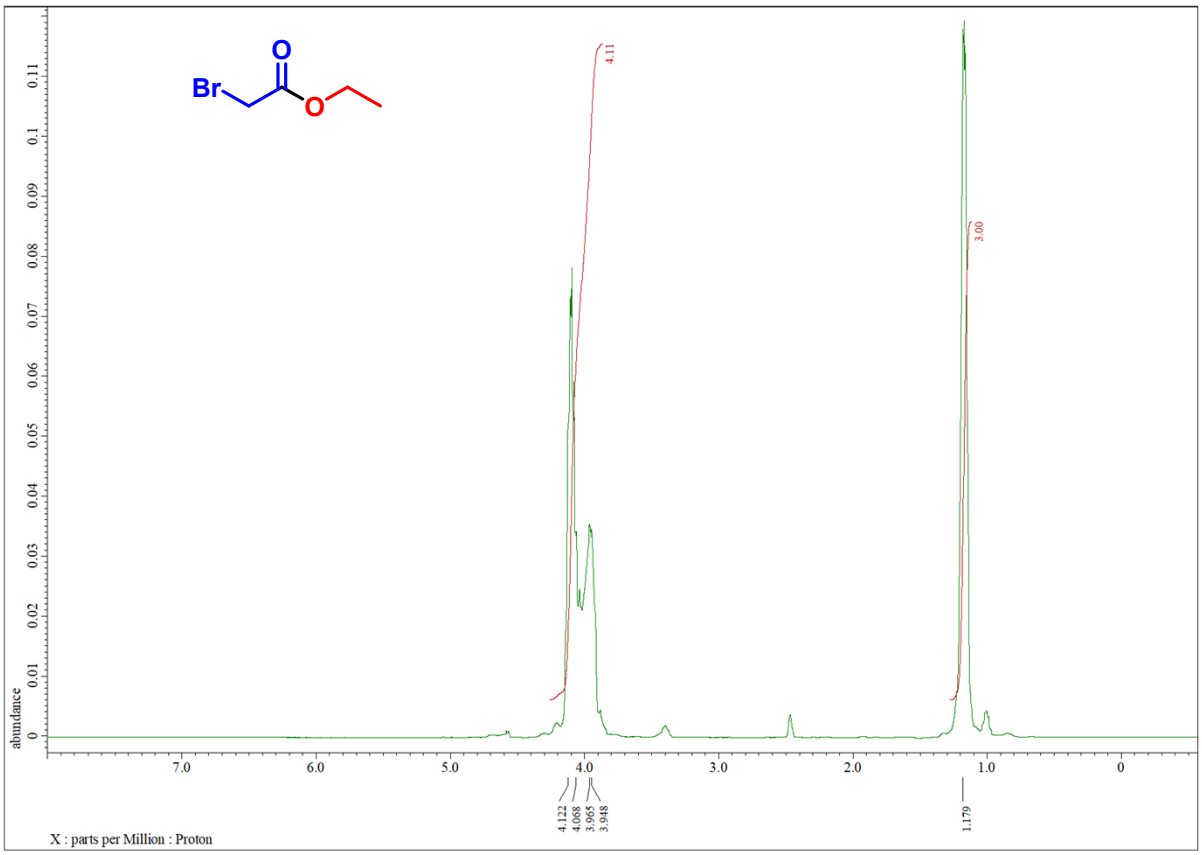


Figure S47. ^{1}H NMR spectrum of Ethyl 2-bromoacetate **C21.**

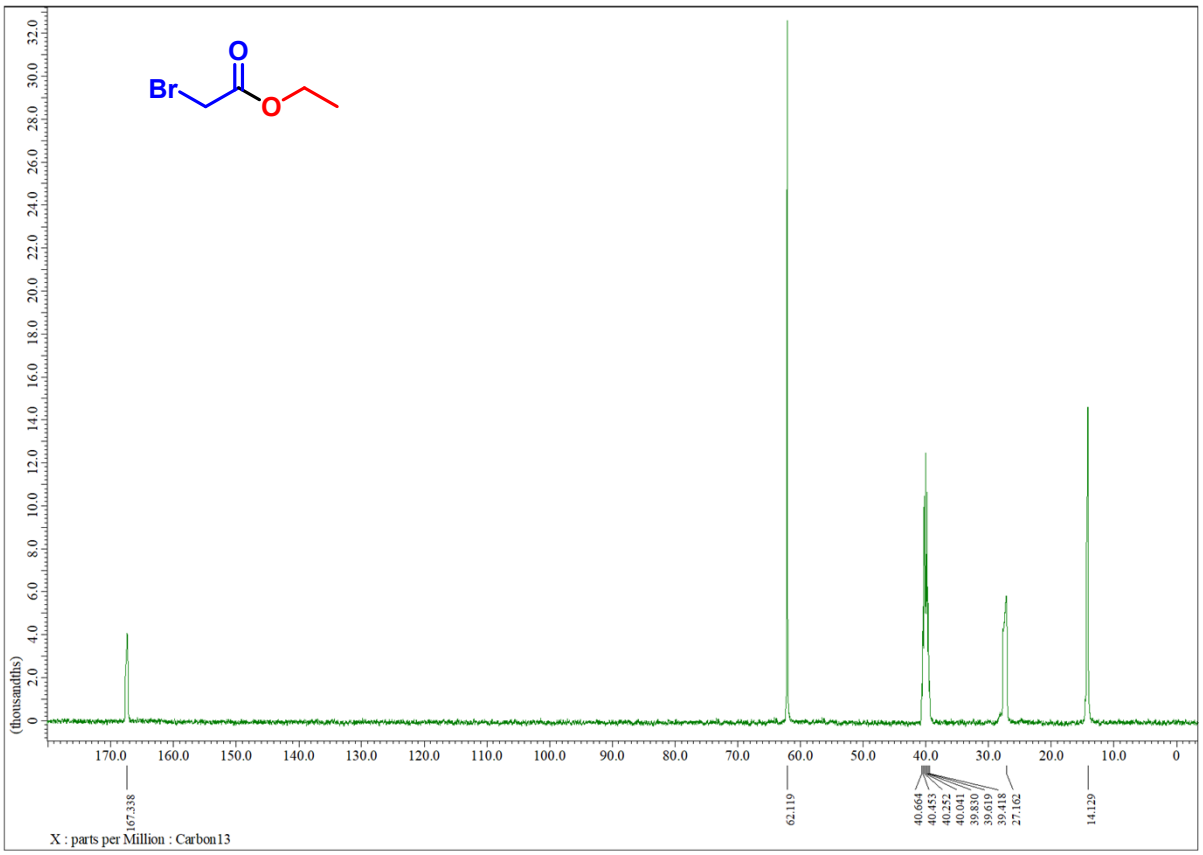


Figure S48. ^{13}C NMR spectrum of Ethyl 2-bromoacetate **C21.**

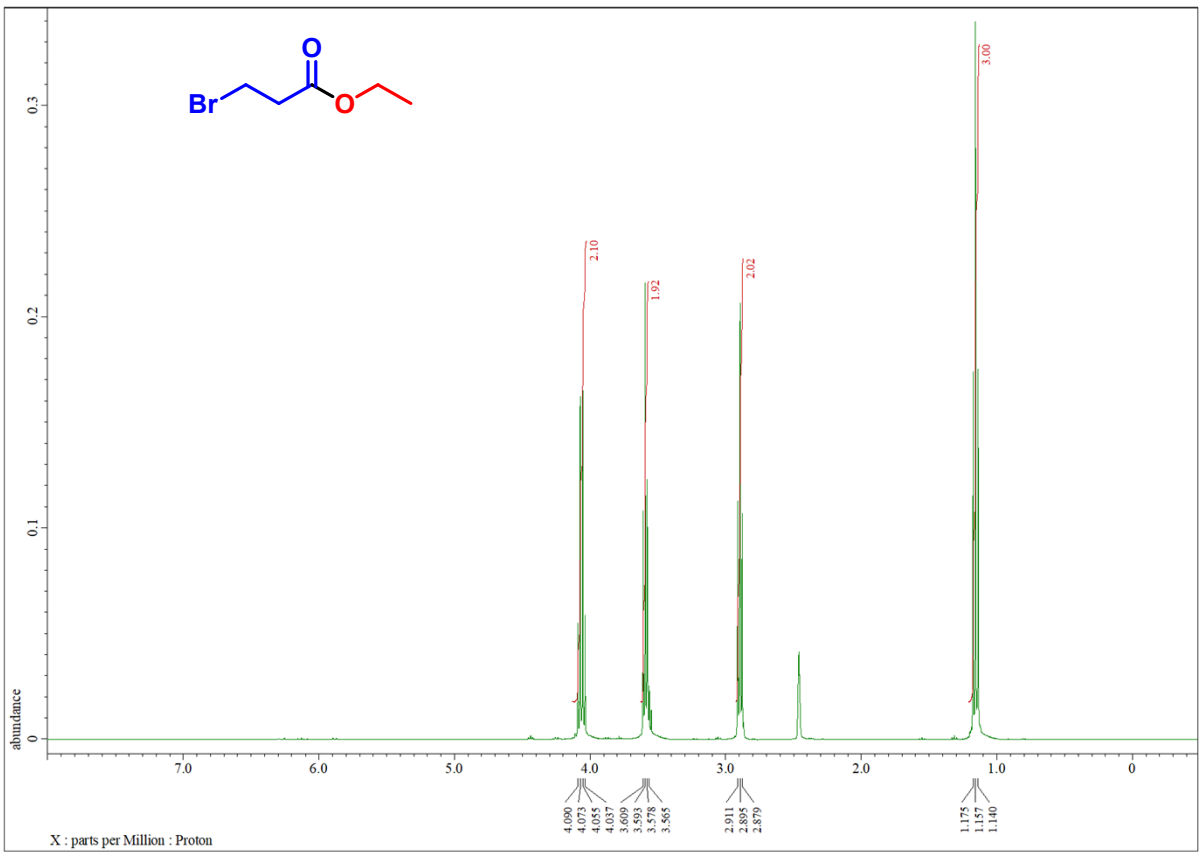


Figure S49. [1]H NMR spectrum of Ethyl 3-bromopropanoate **C22.**

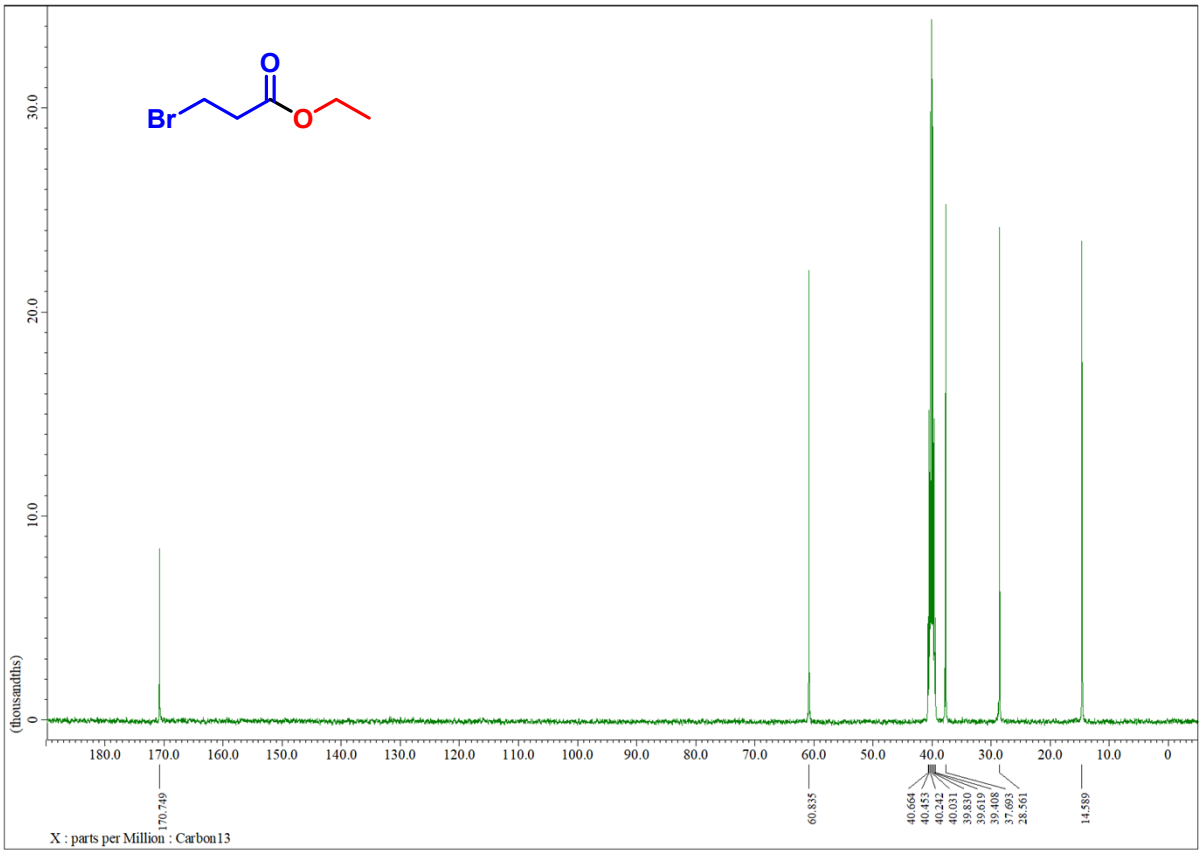


Figure S50. [13]C NMR spectrum of Ethyl 3-bromopropanoate **C22.**

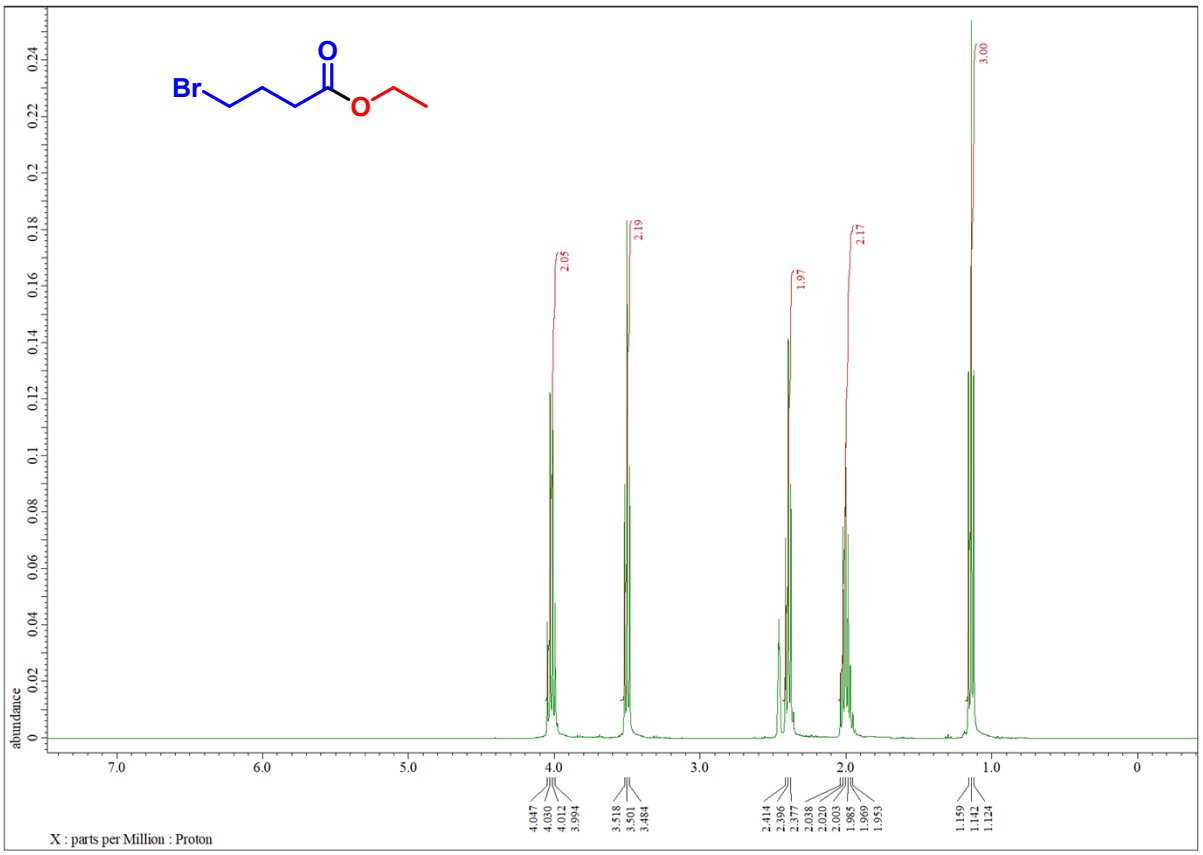


Figure S51. ^{1}H NMR spectrum of Ethyl 4-bromobutanoate **C23.**

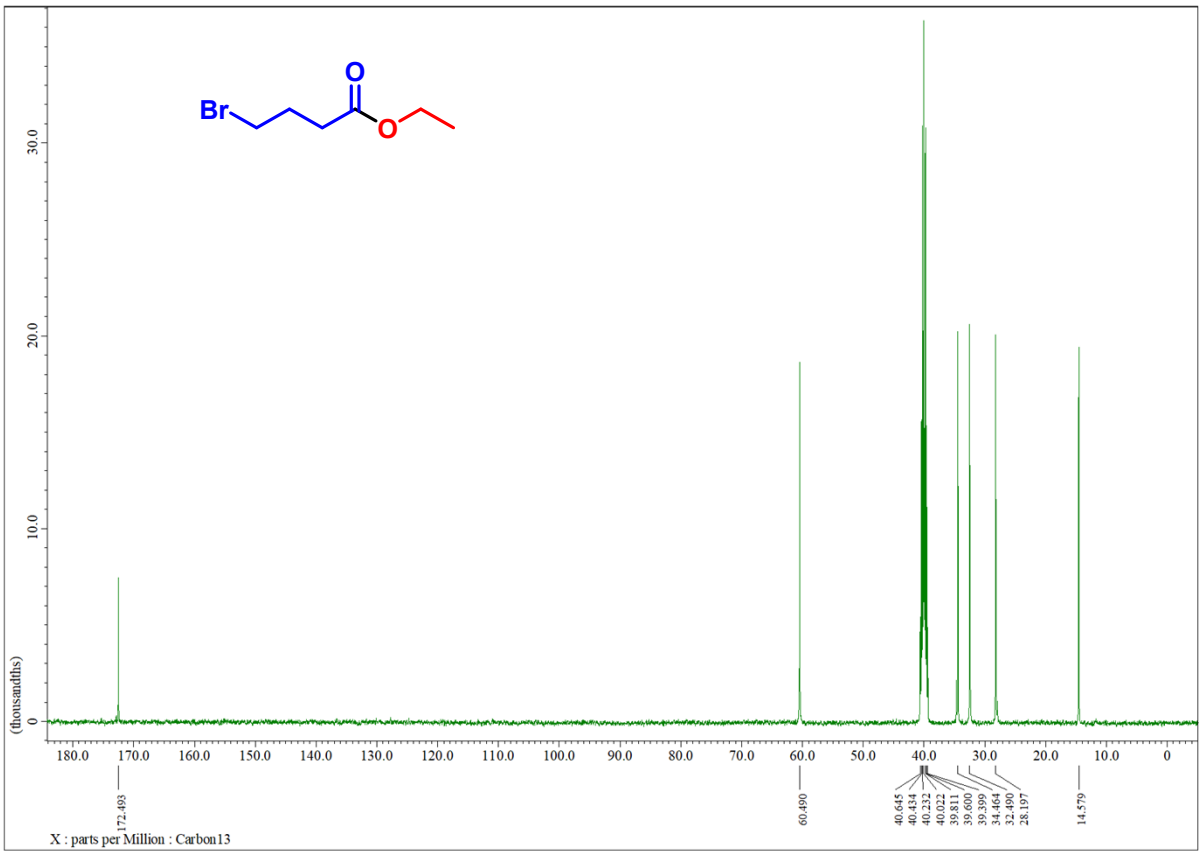


Figure S52. ^{13}C NMR spectrum of Ethyl 4-bromobutanoate **C23.**

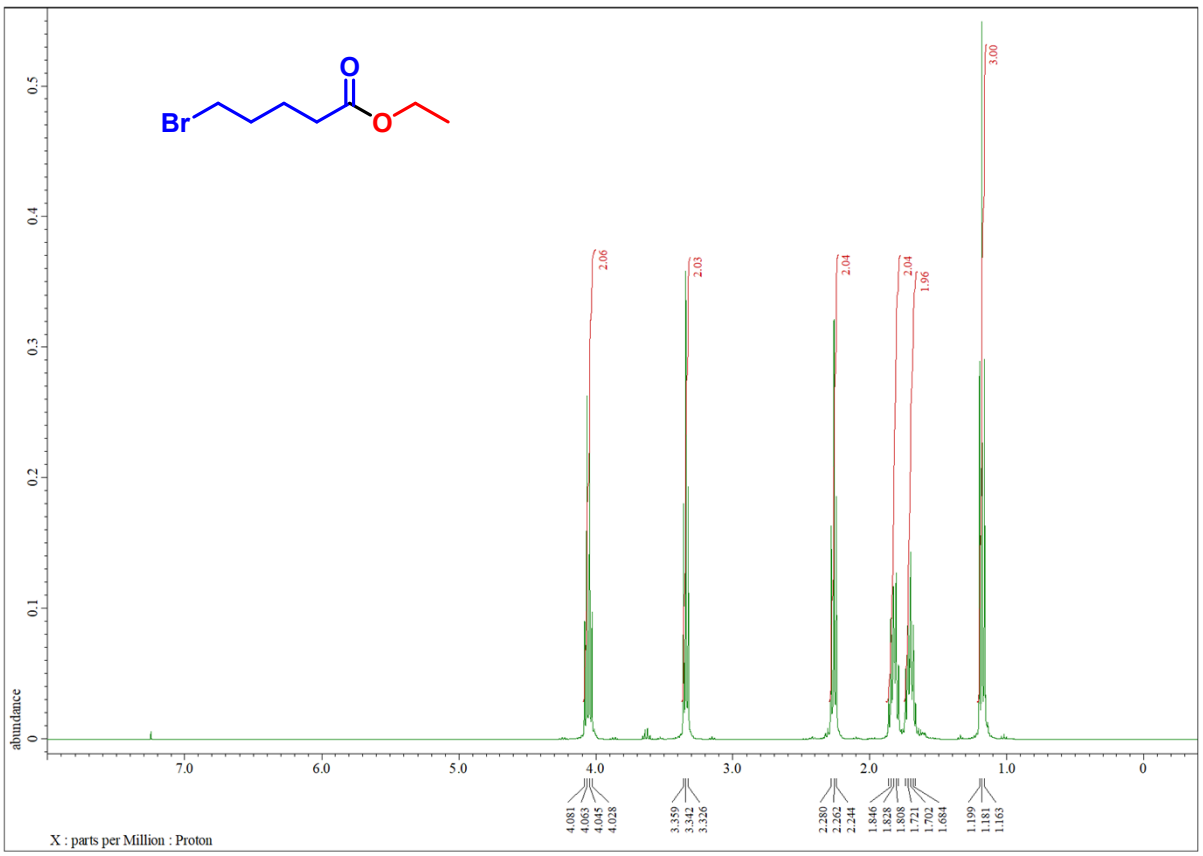


Figure S53. [1]H NMR spectrum of Ethyl 5-bromopentanoate **C24.**

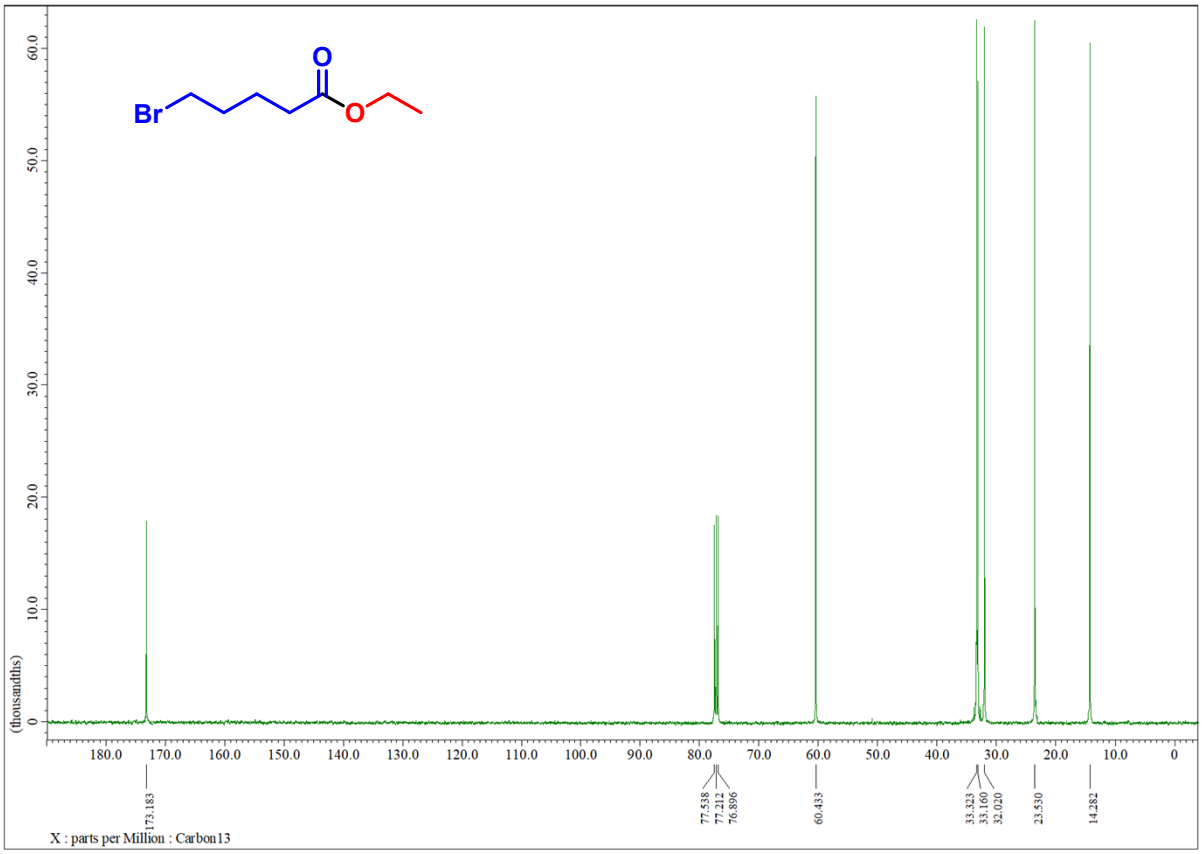


Figure S54. [13]C NMR spectrum of Ethyl 5-bromopentanoate **C24.**

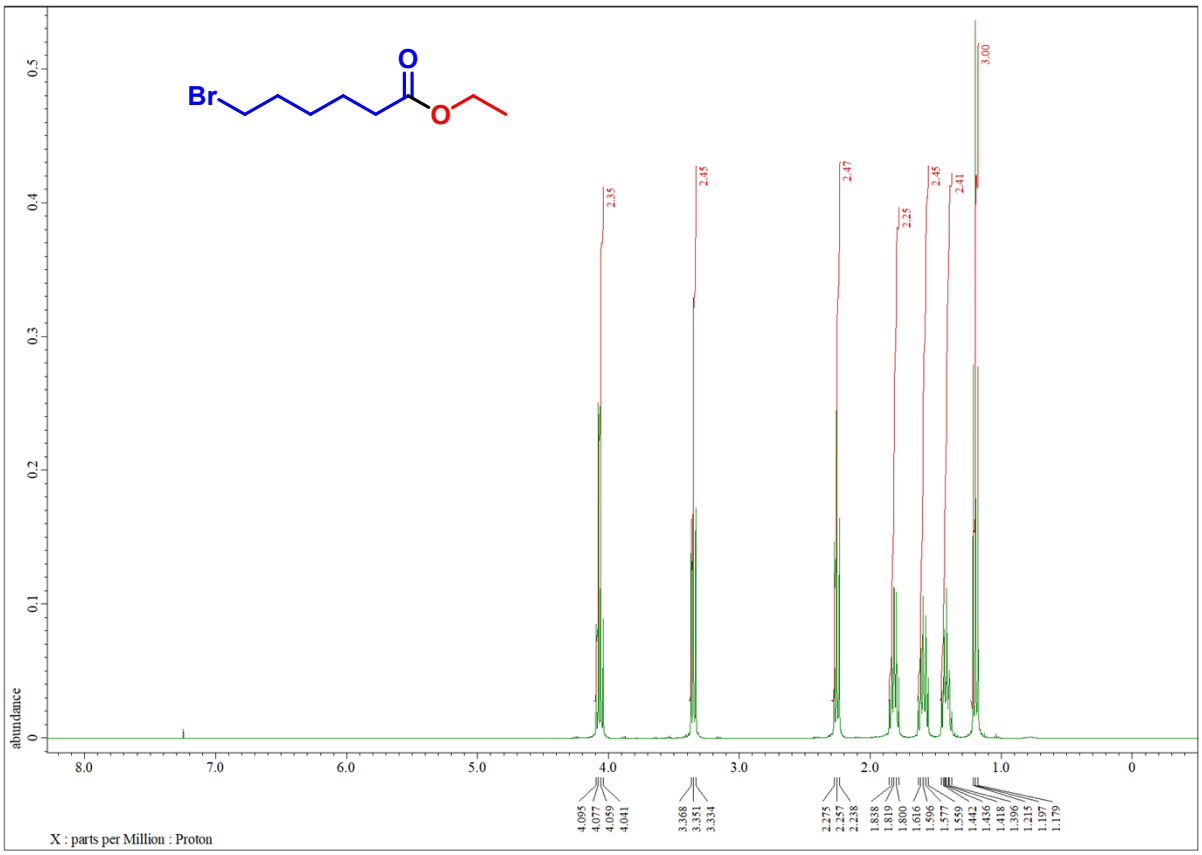


Figure S55. ^{1}H NMR spectrum of Ethyl 6-bromohexanoate **C25.**

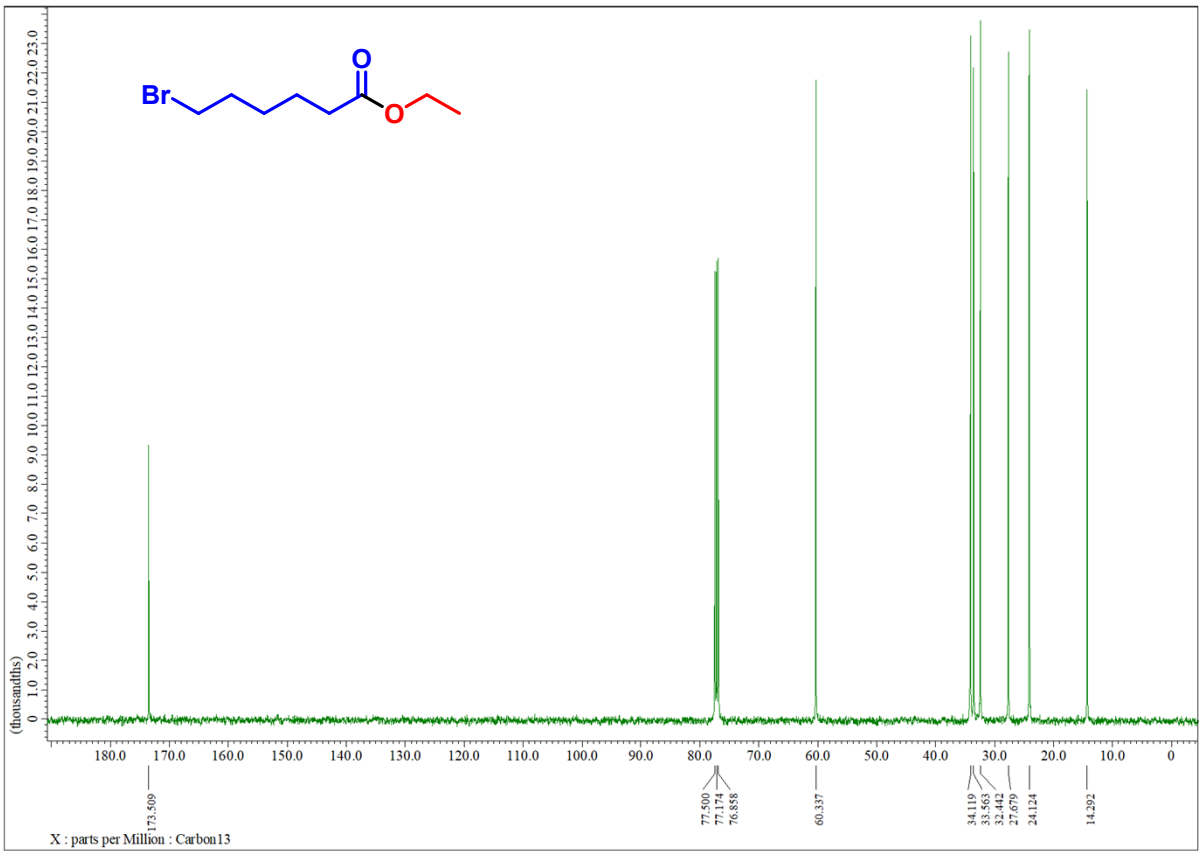


Figure S56. ^{13}C NMR spectrum of Ethyl 6-bromohexanoate **C25.**

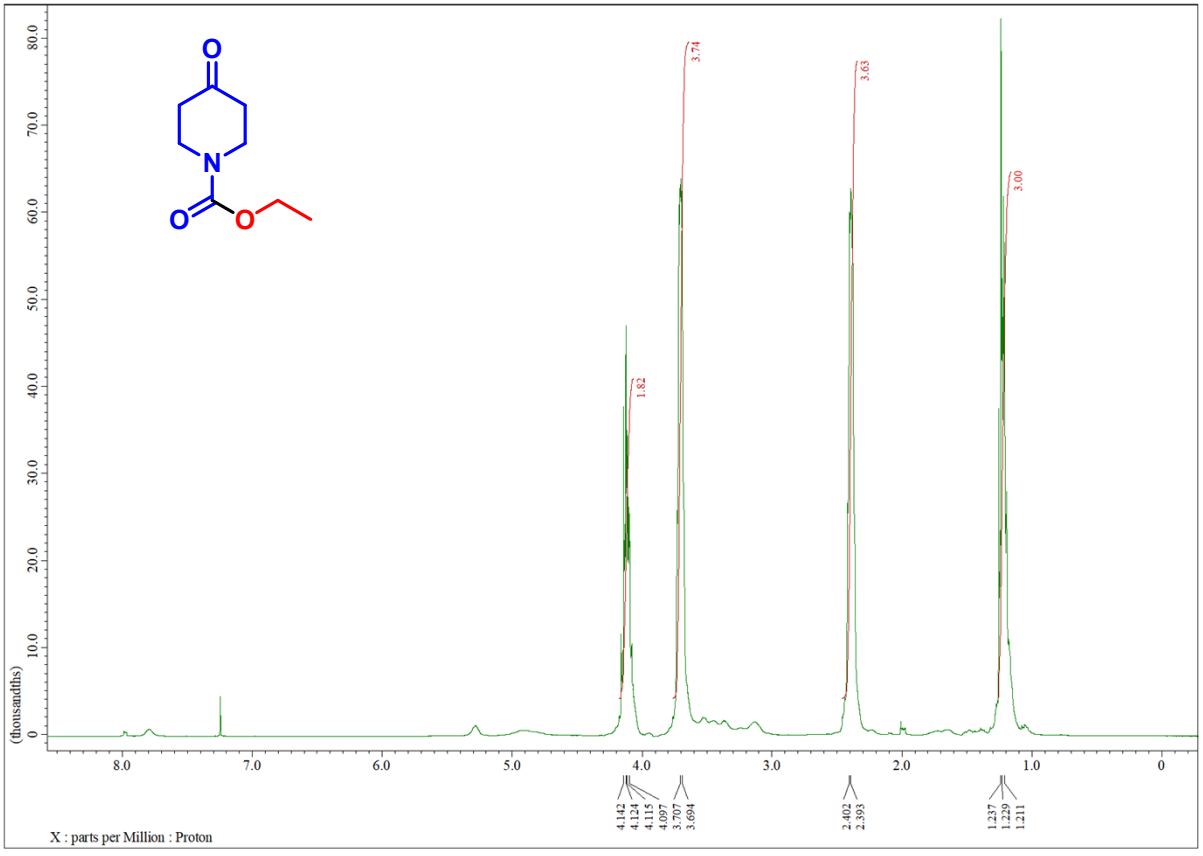


Figure S57. ^{1}H NMR spectrum of Ethyl 4-oxopiperidine-1-carboxylate **C26.**

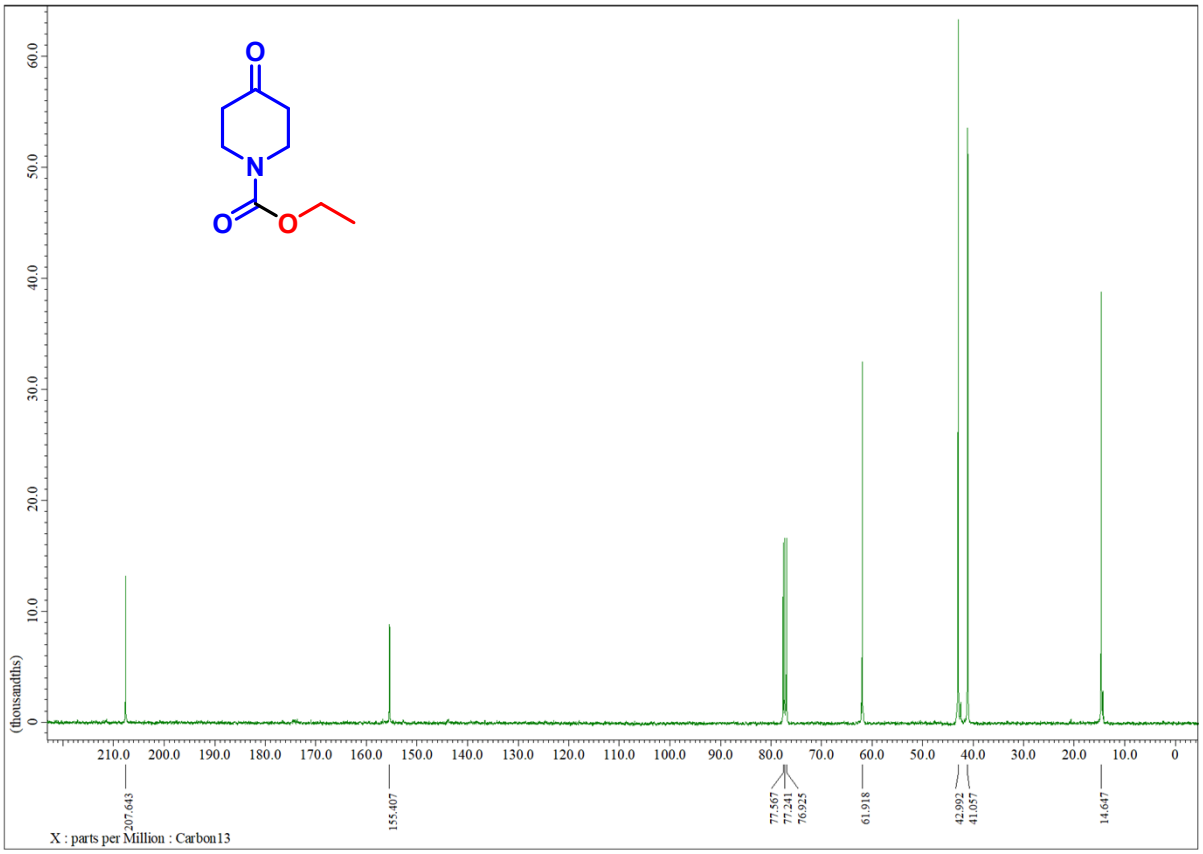


Figure S58. ^{13}C NMR spectrum of Ethyl 4-oxopiperidine-1-carboxylate **C26.**

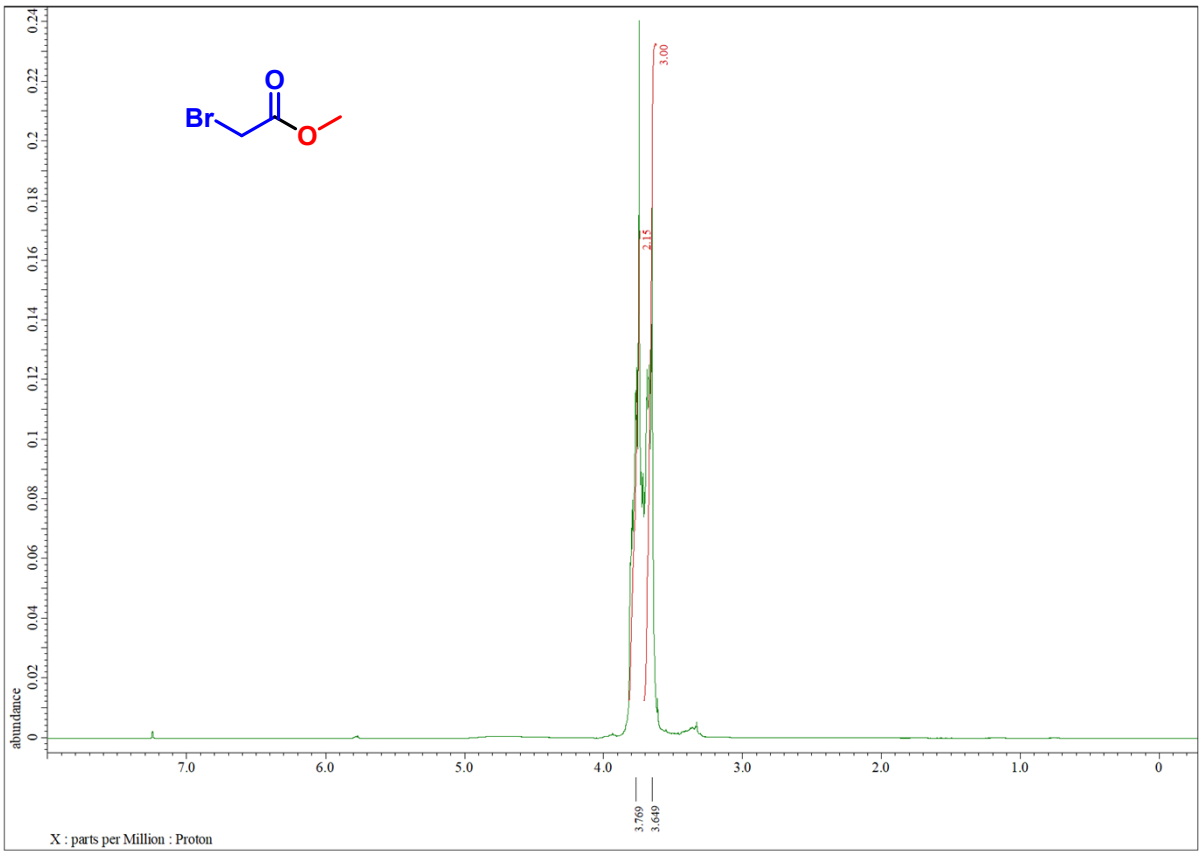


Figure S59. ^{1}H NMR spectrum of Methyl 2-bromoacetate **C27.**

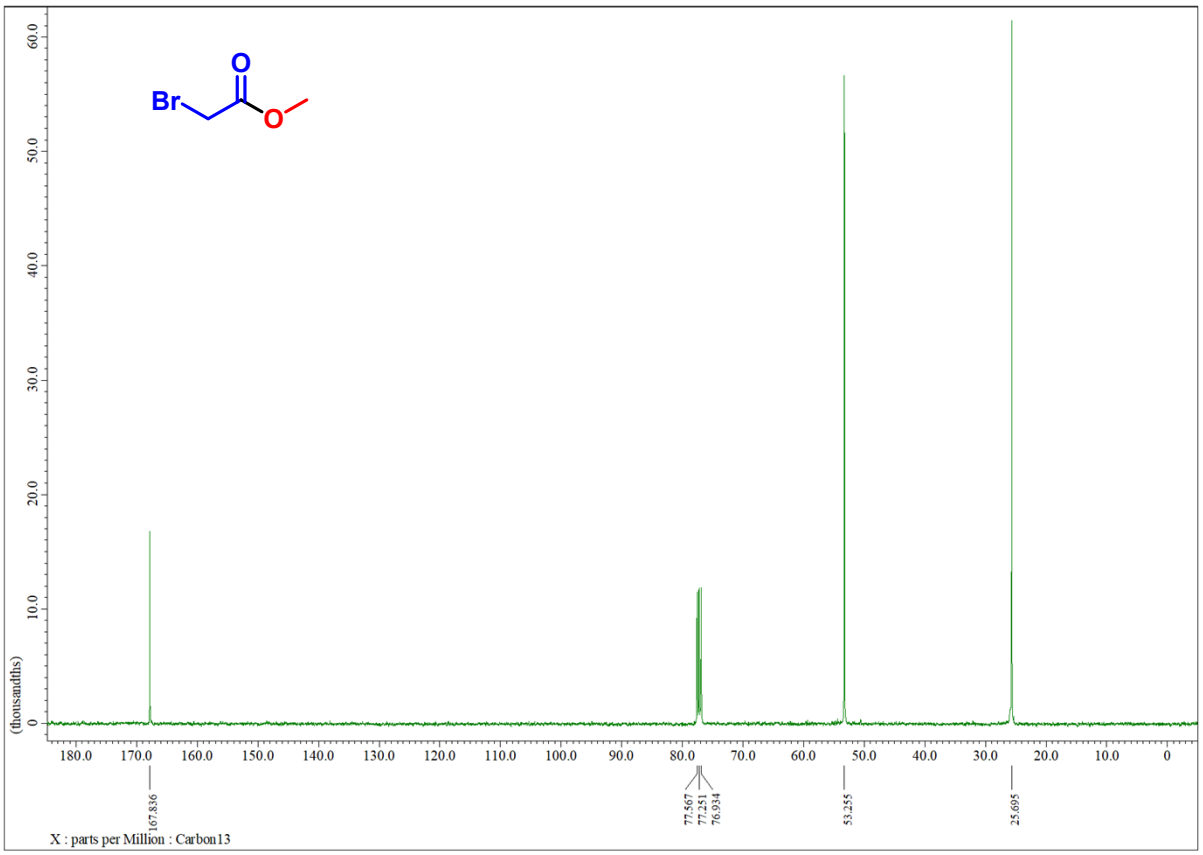


Figure S60. ^{13}C NMR spectrum of Methyl 2-bromoacetate **C27.**

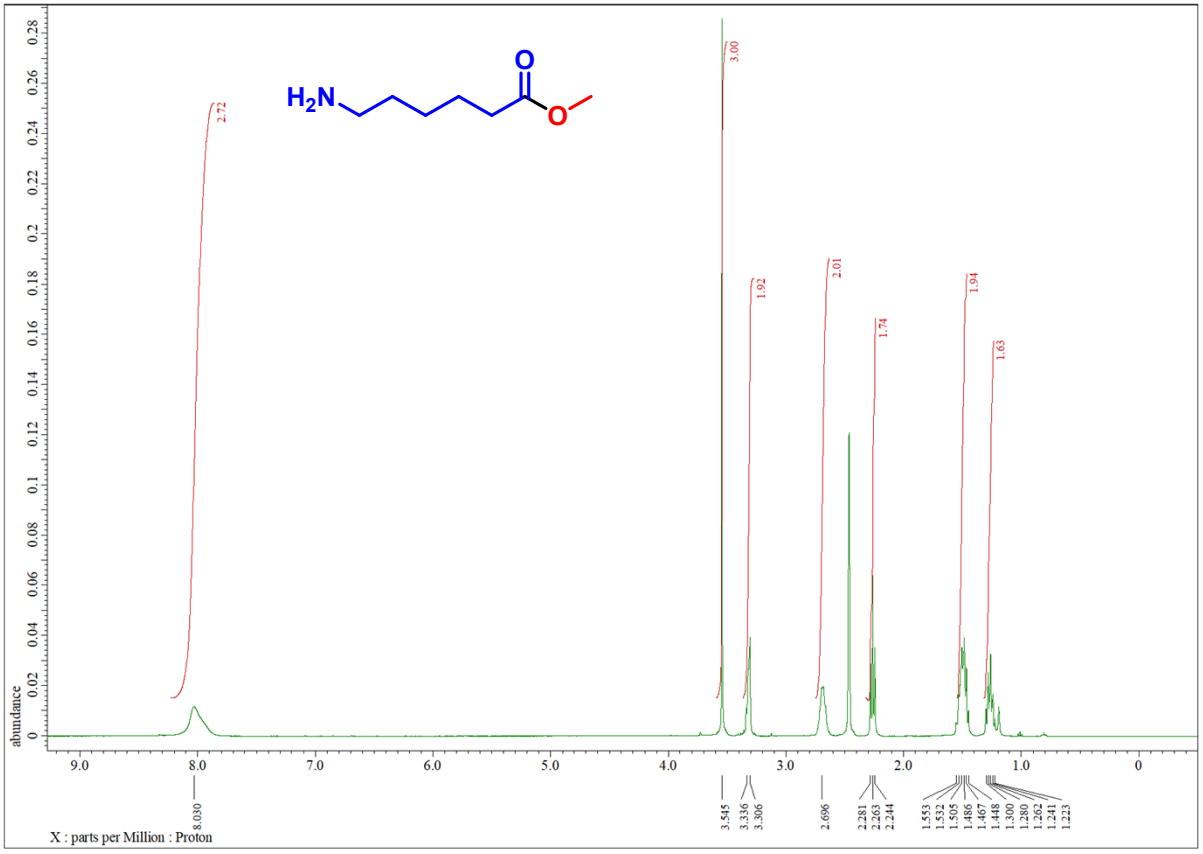


Figure S61. [1]H NMR spectrum of Methyl 6-aminohexanoate **C28.**

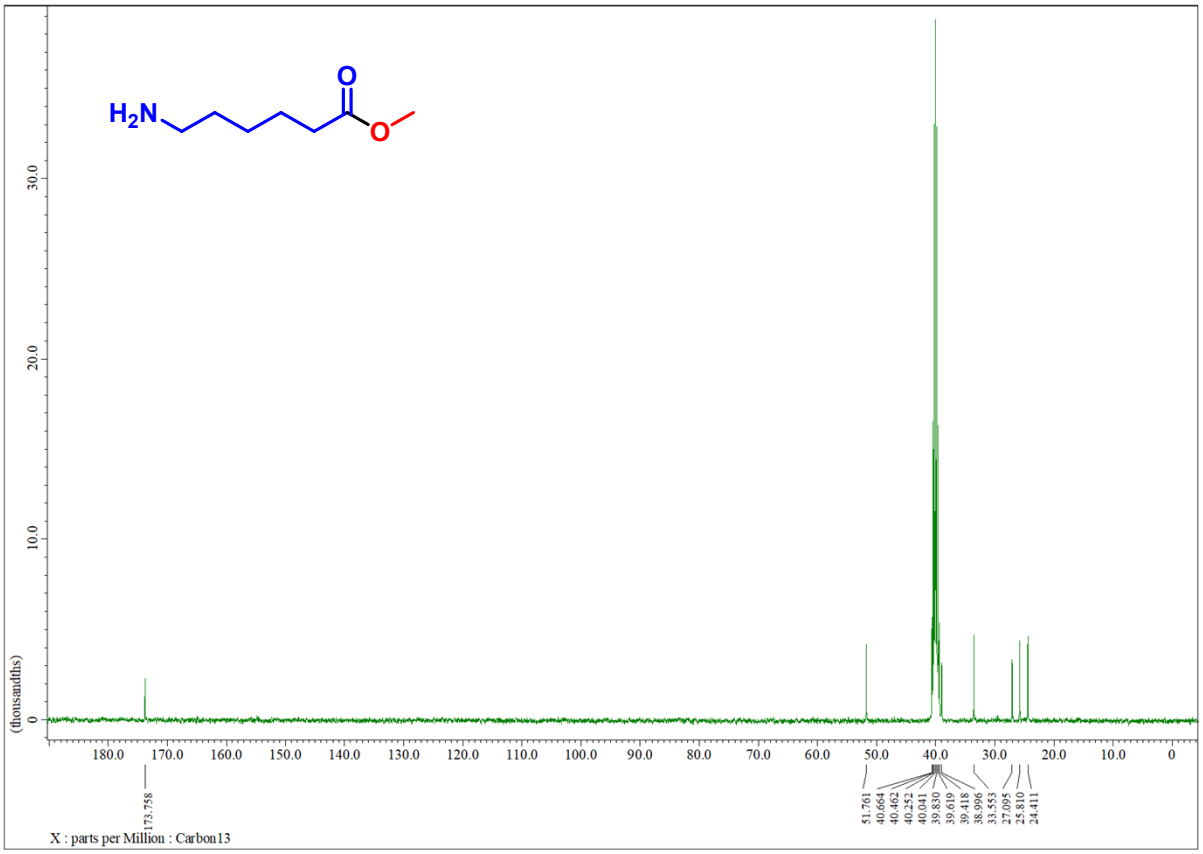


Figure S62. [13]C NMR spectrum of Methyl 6-aminohexanoate **C28.**

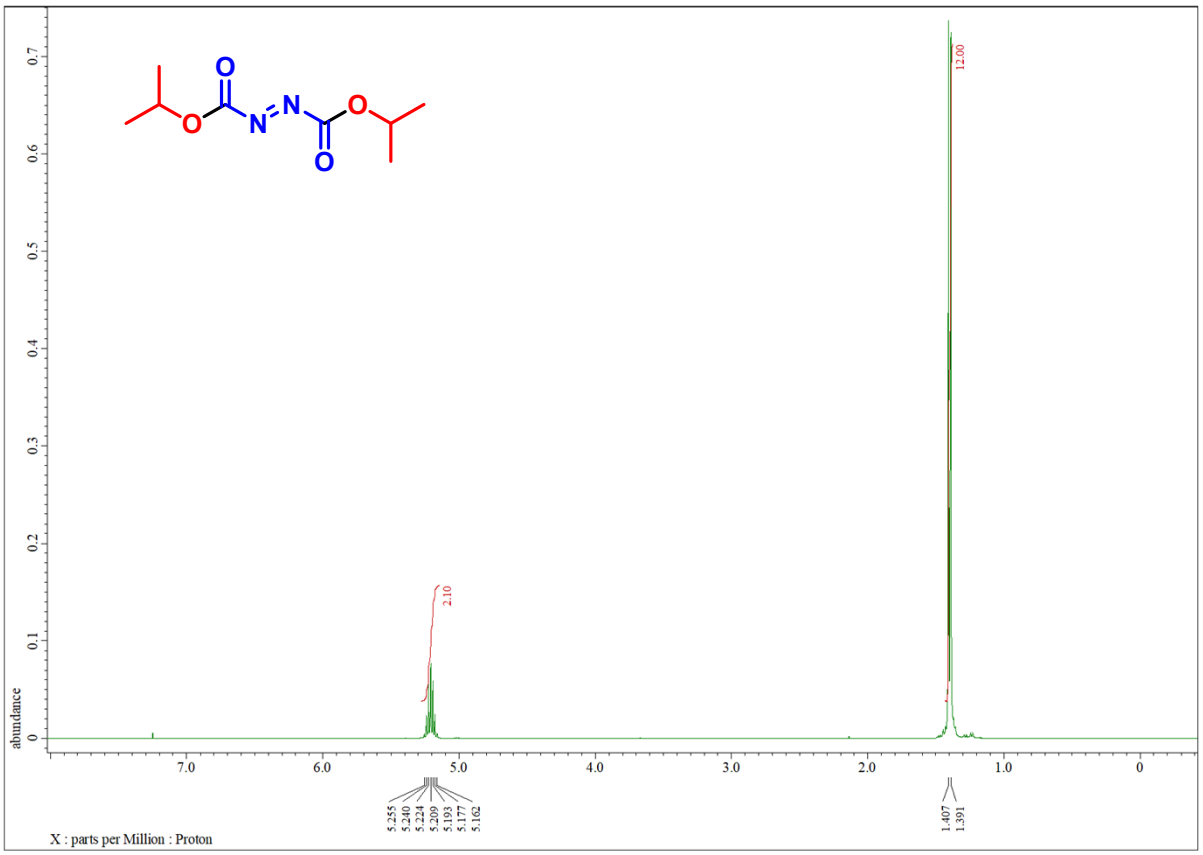


Figure S63. ^{1}H NMR spectrum of Diisopropyl (E)-diazene-1,2-dicarboxylate **C29.**

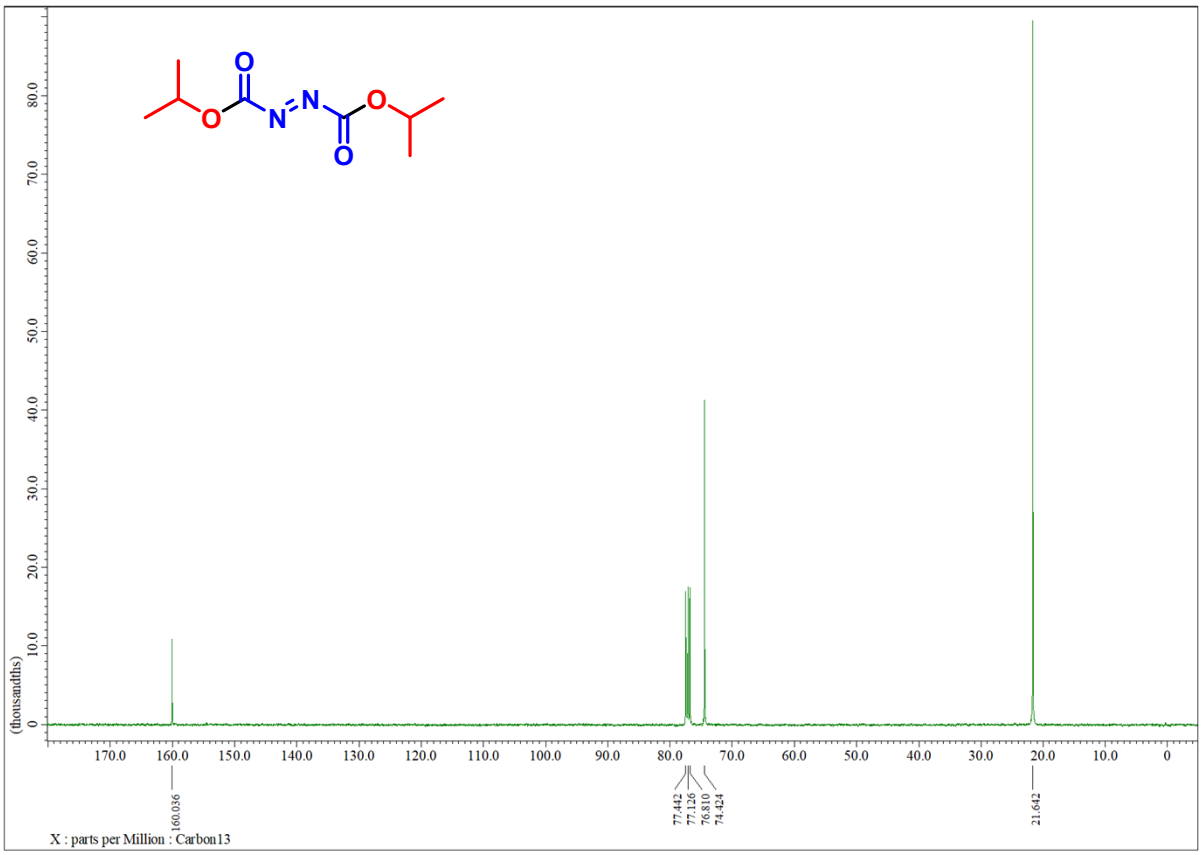


Figure S64. ^{13}C NMR spectrum of Di-isopropyl (E)-diazene-1,2-dicarboxylate **C29.**

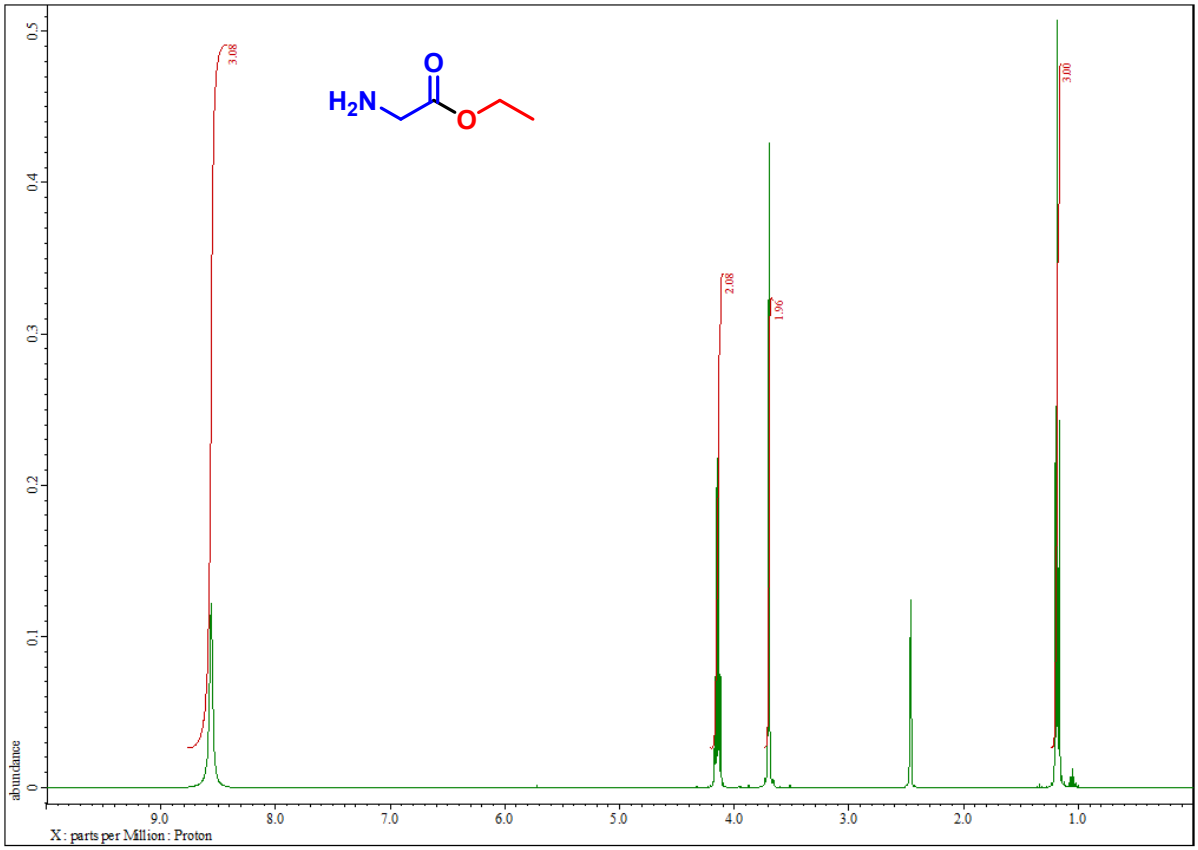


Figure S65. ^{1}H NMR spectrum of Ethyl glycinate **D1.**

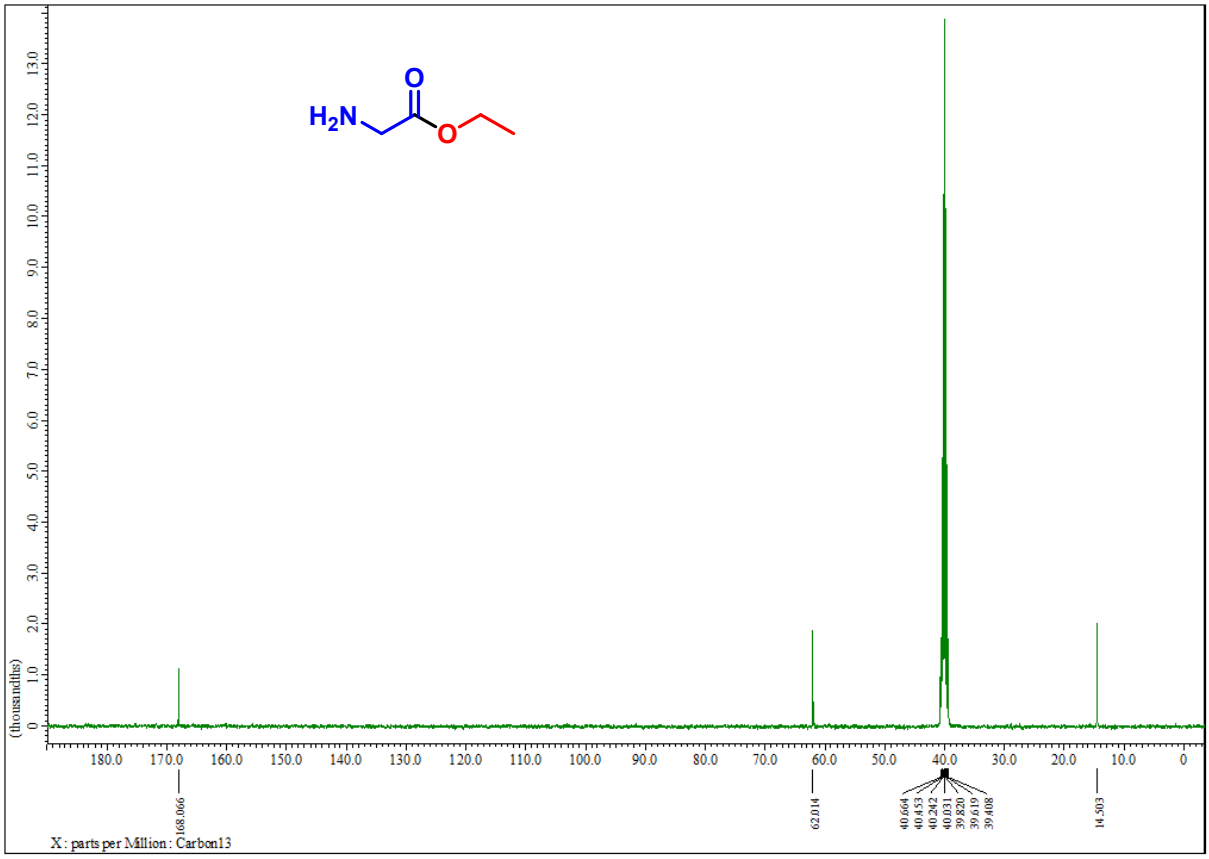


Figure S66. ^{13}C NMR spectrum of Ethyl glycinate **D1.**

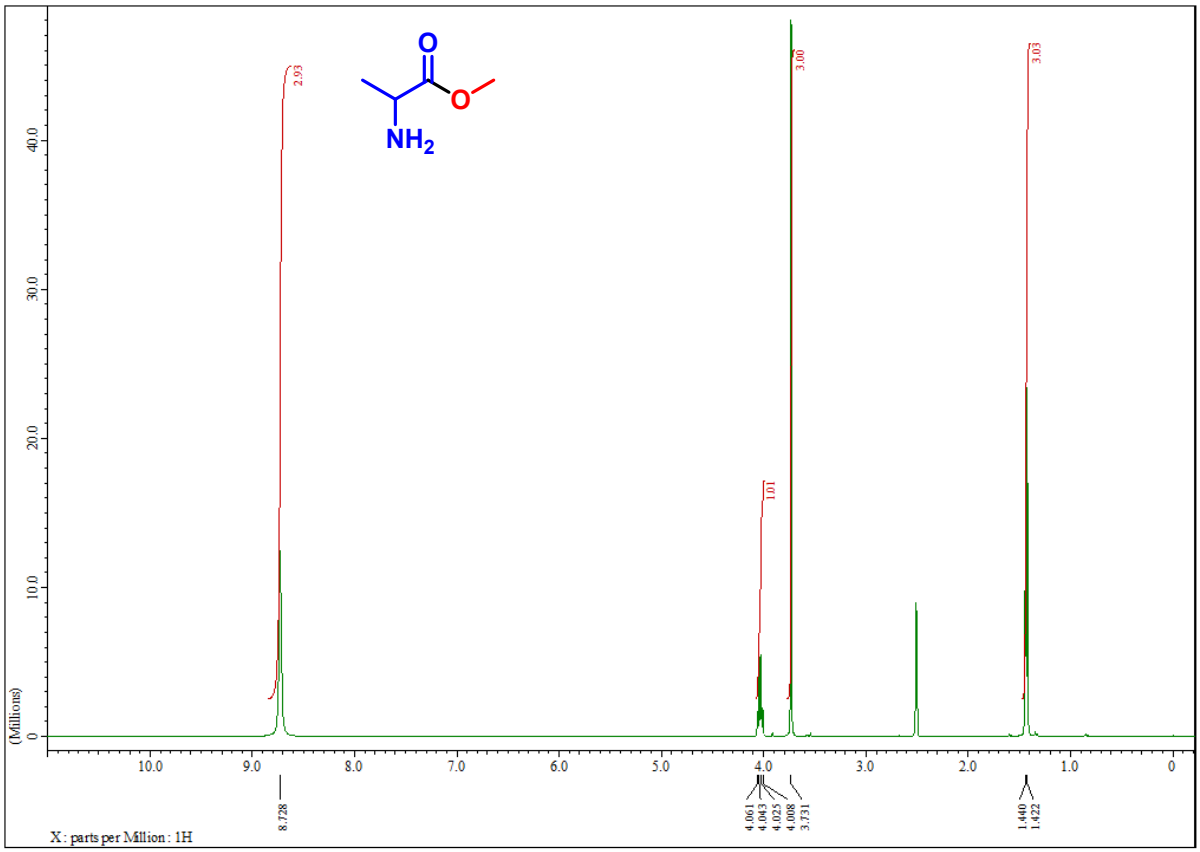


Figure S67. ^{1}H NMR spectrum of Methyl alaninate **D2.**

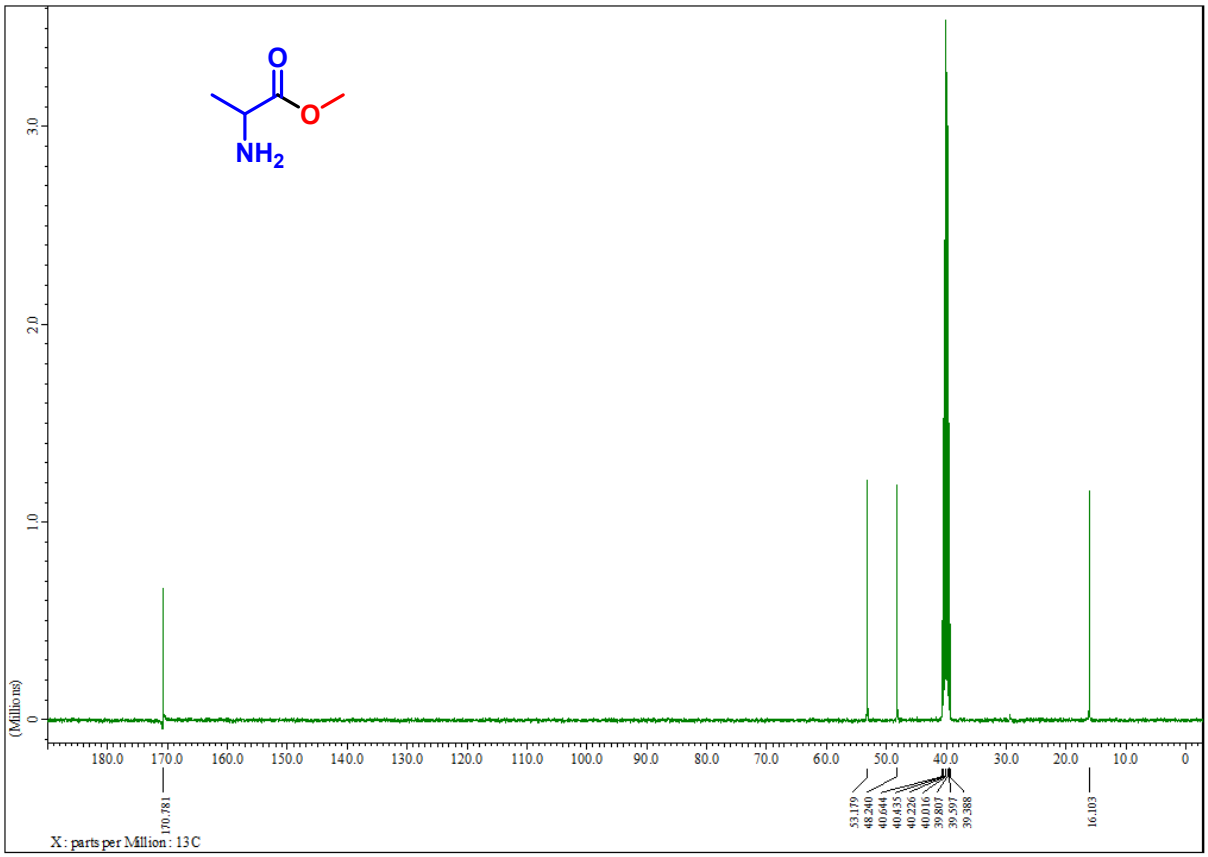


Figure S68. ^{13}C NMR spectrum of Methyl alaninate **D2.**

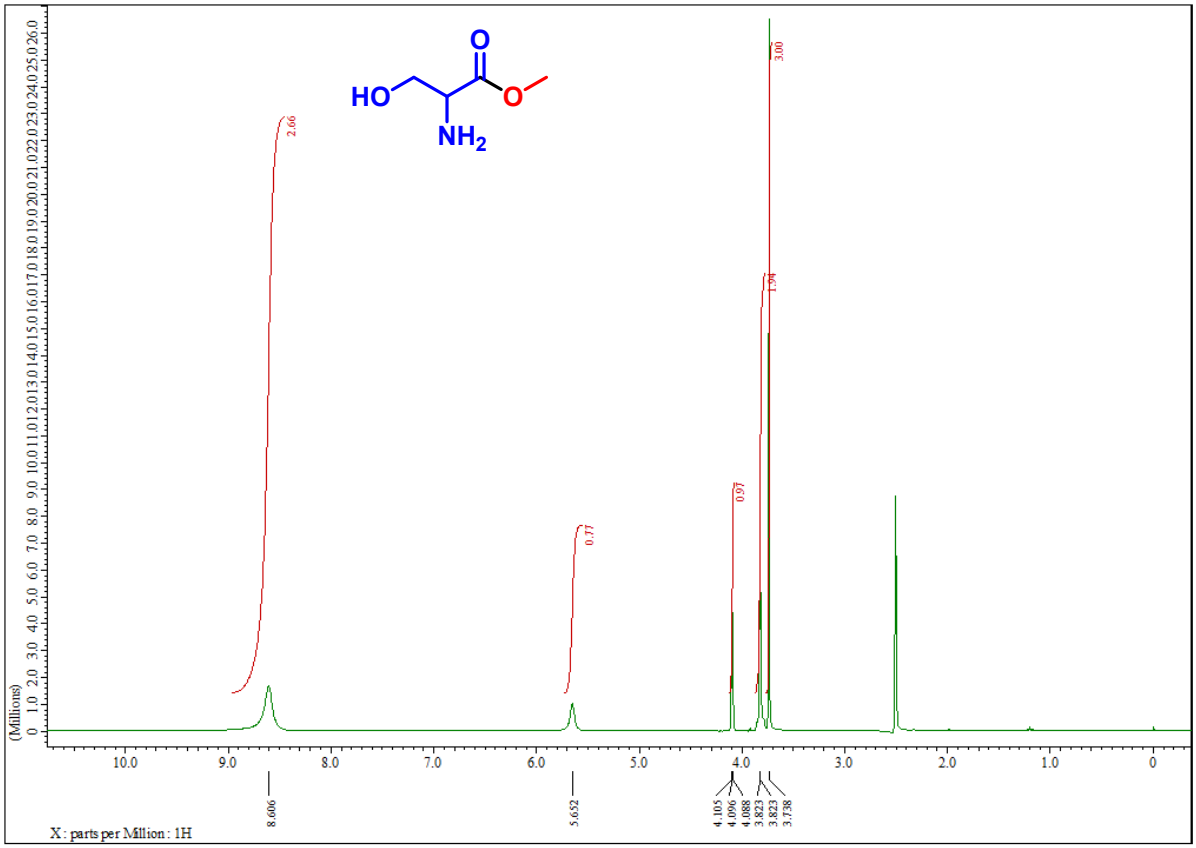


Figure S69. ^{1}H NMR spectrum of Methyl serinate **D3.**

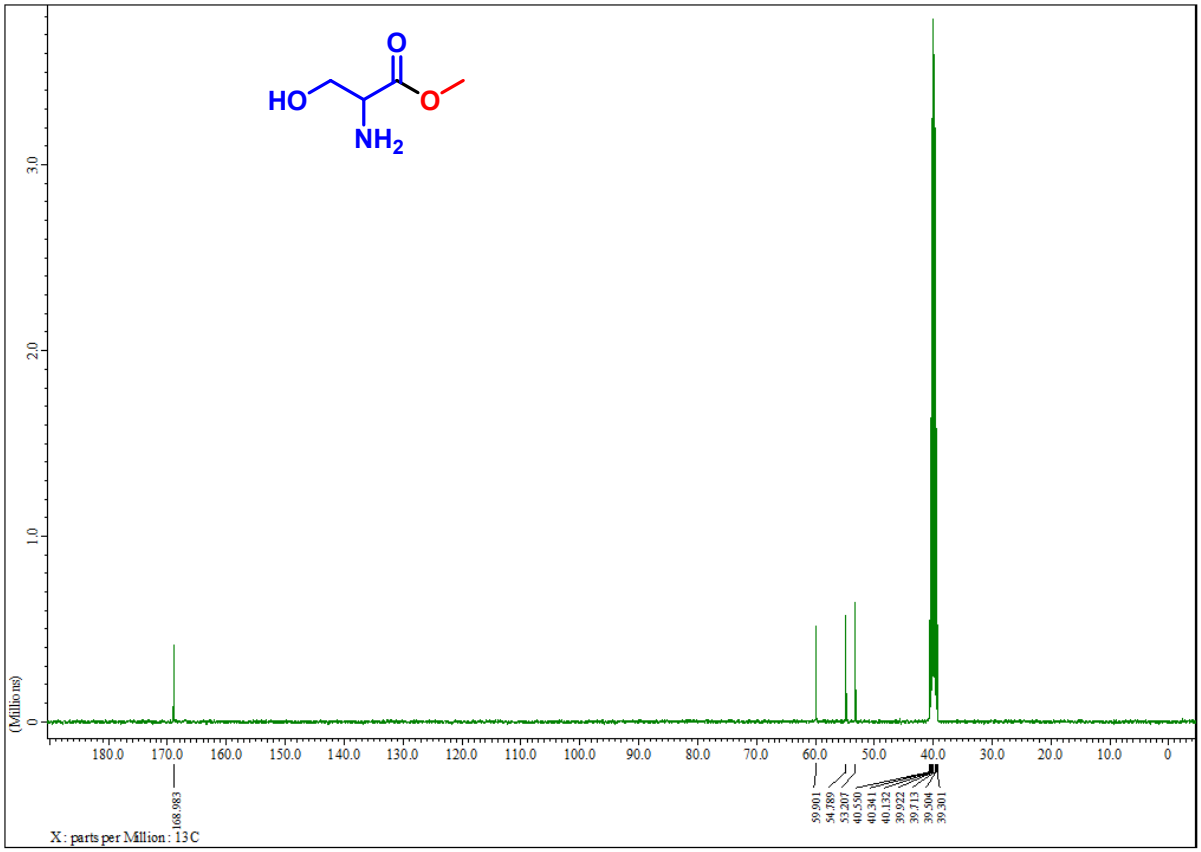


Figure S70. ^{13}C NMR spectrum of Methyl serinate **D3.**

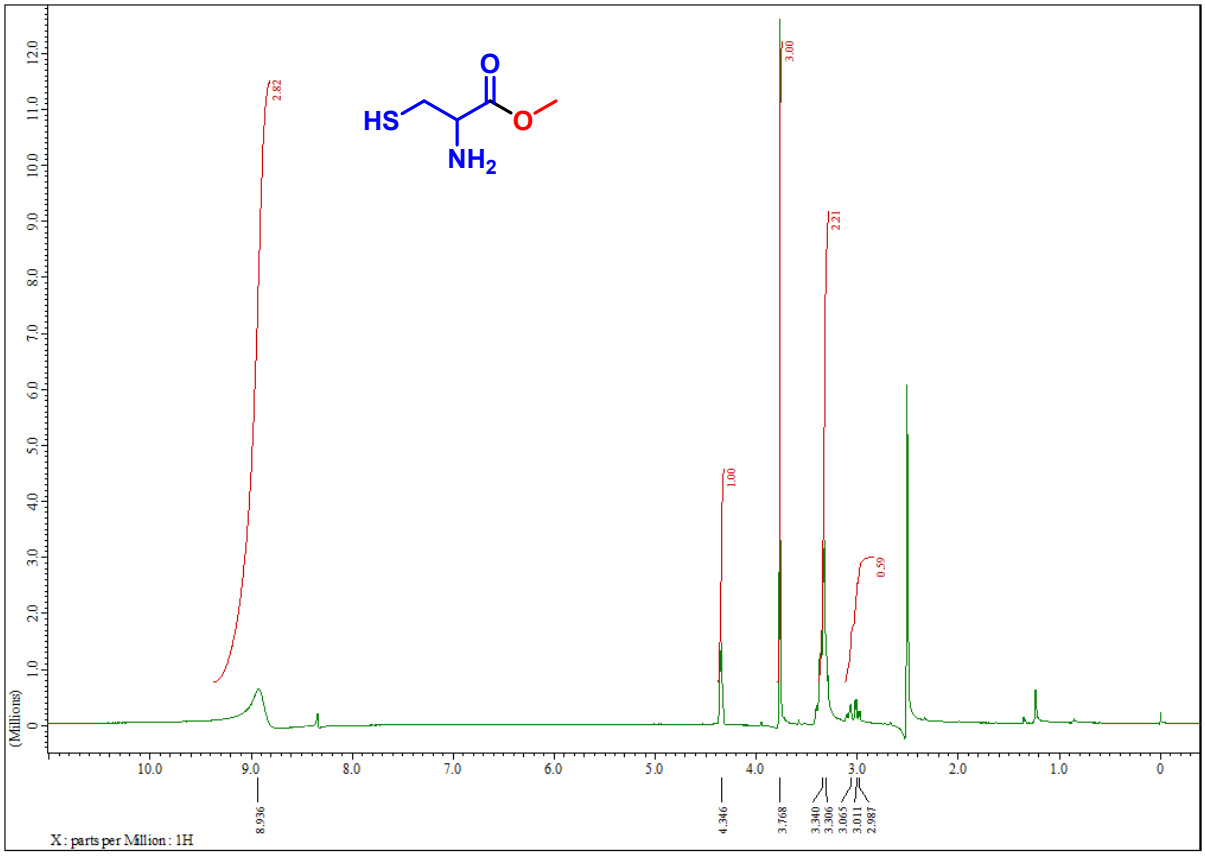


Figure S71. ^{1}H NMR spectrum of Methyl cysteinate **D4.**

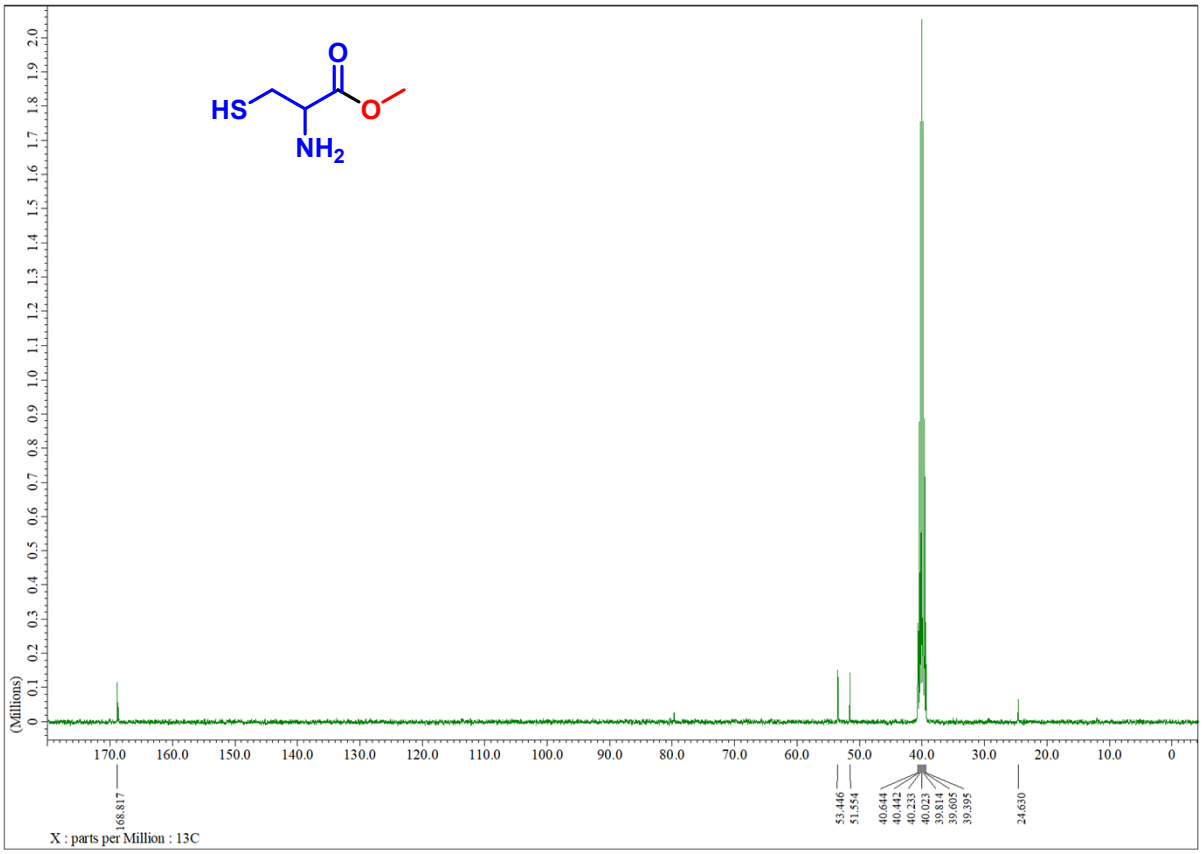


Figure S72. ^{13}C NMR spectrum of Methyl cysteinate **D4.**

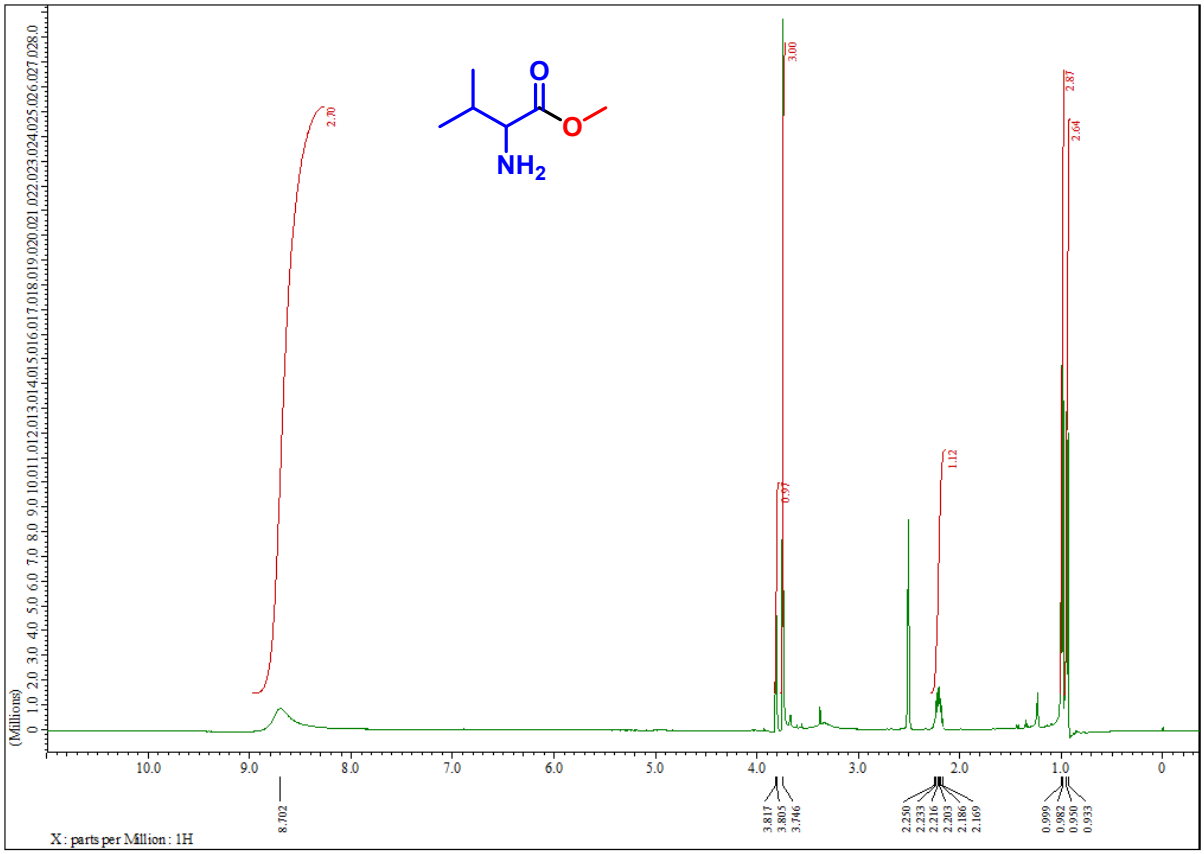


Figure S73. ^{1}H NMR spectrum of Methyl valinate **D5.**

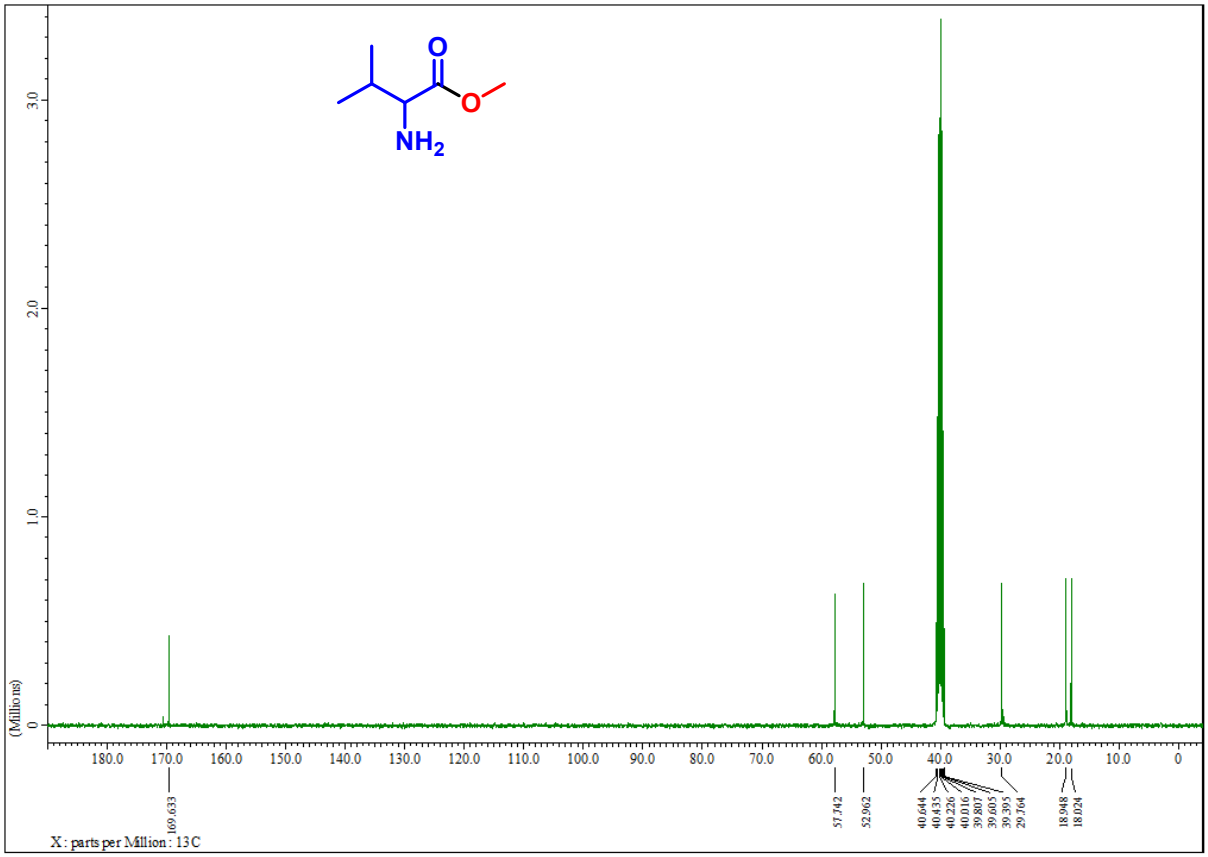


Figure S74. ^{13}C NMR spectrum of Methyl valinate **D5.**

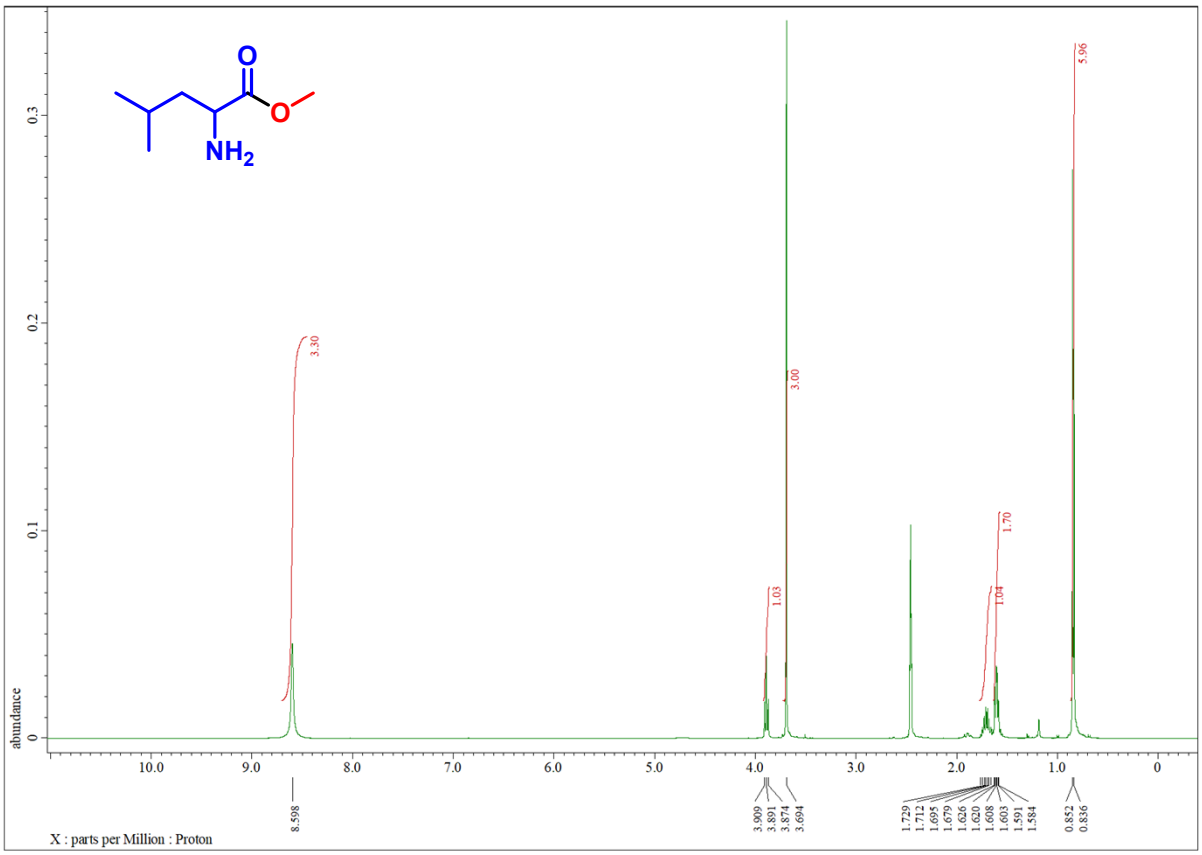


Figure S75. ^{1}H NMR spectrum of Methyl leucinate **D6.**

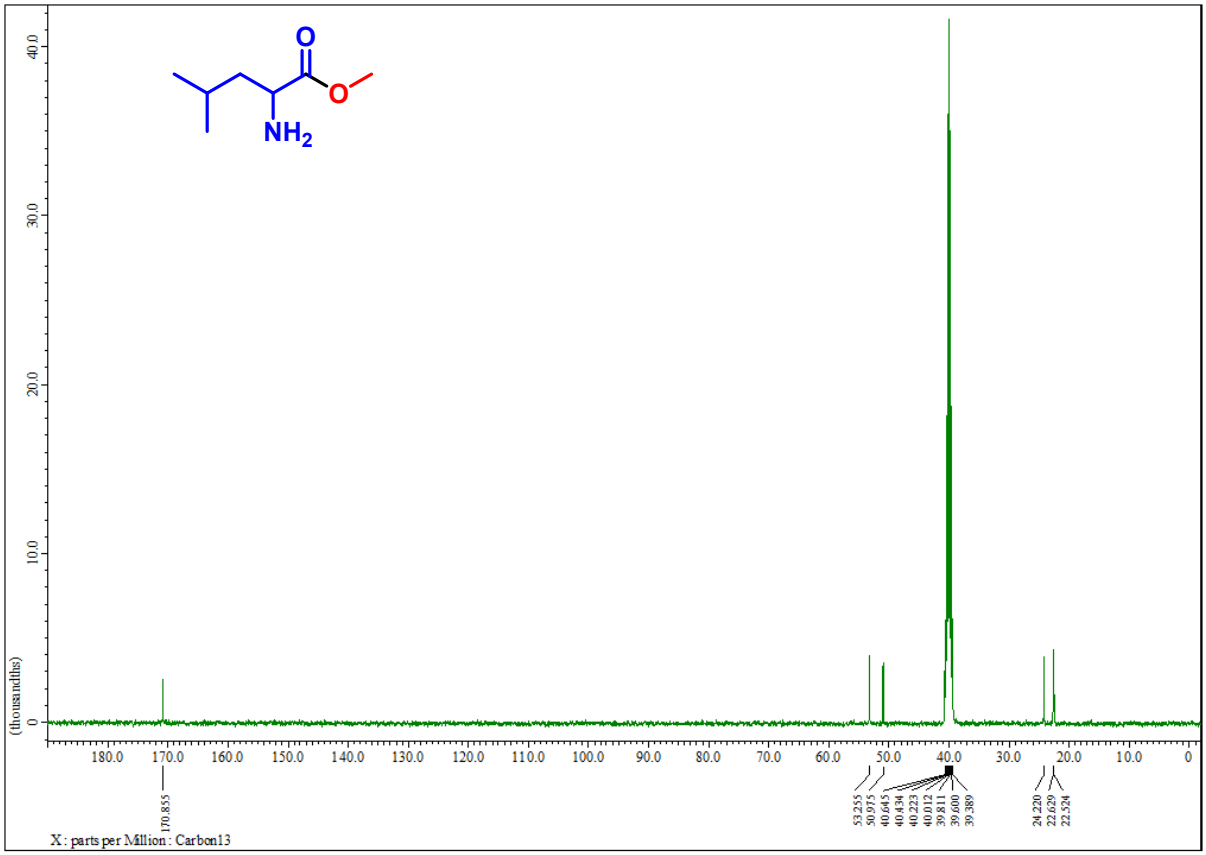


Figure S76. ^{13}C NMR spectrum of Methyl leucinate **D6.**

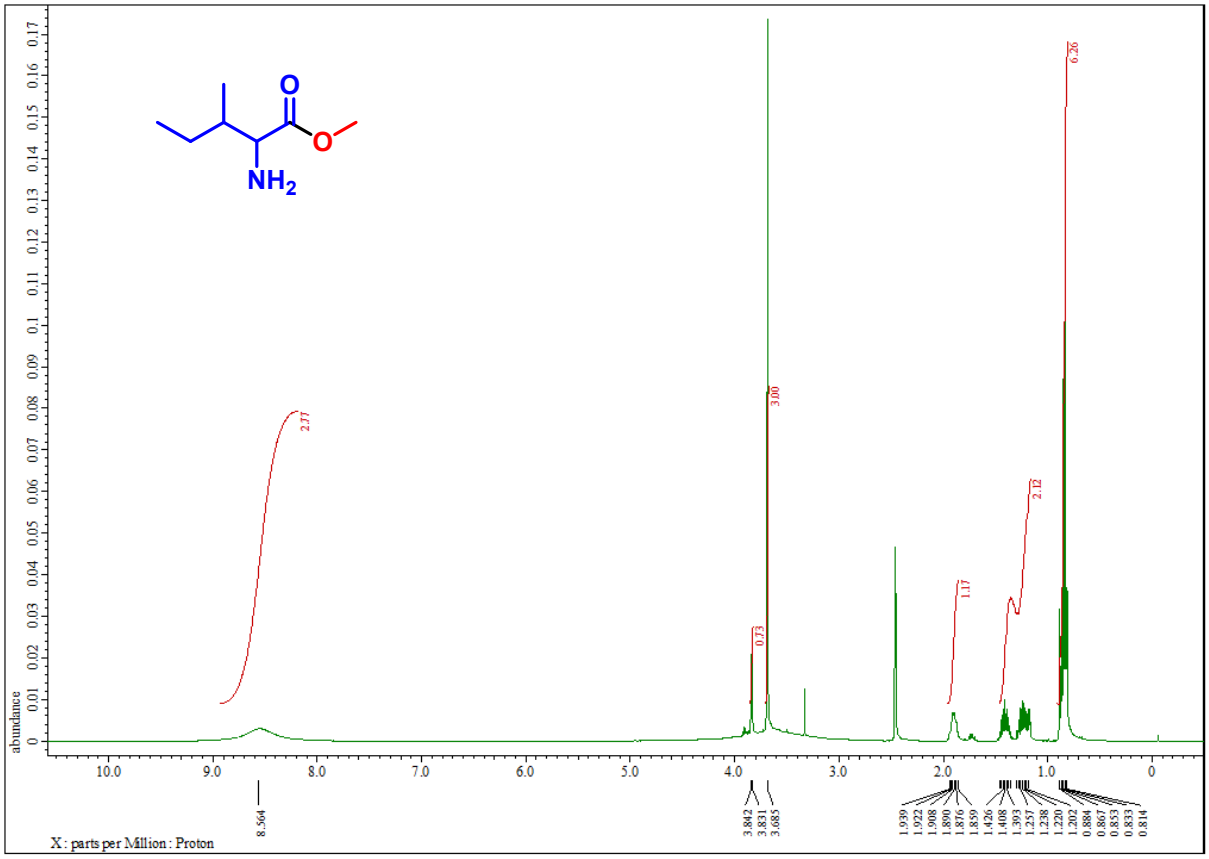


Figure S77. [1]H NMR spectrum of Methyl 2-amino-3-methylpentanoate **D7.**

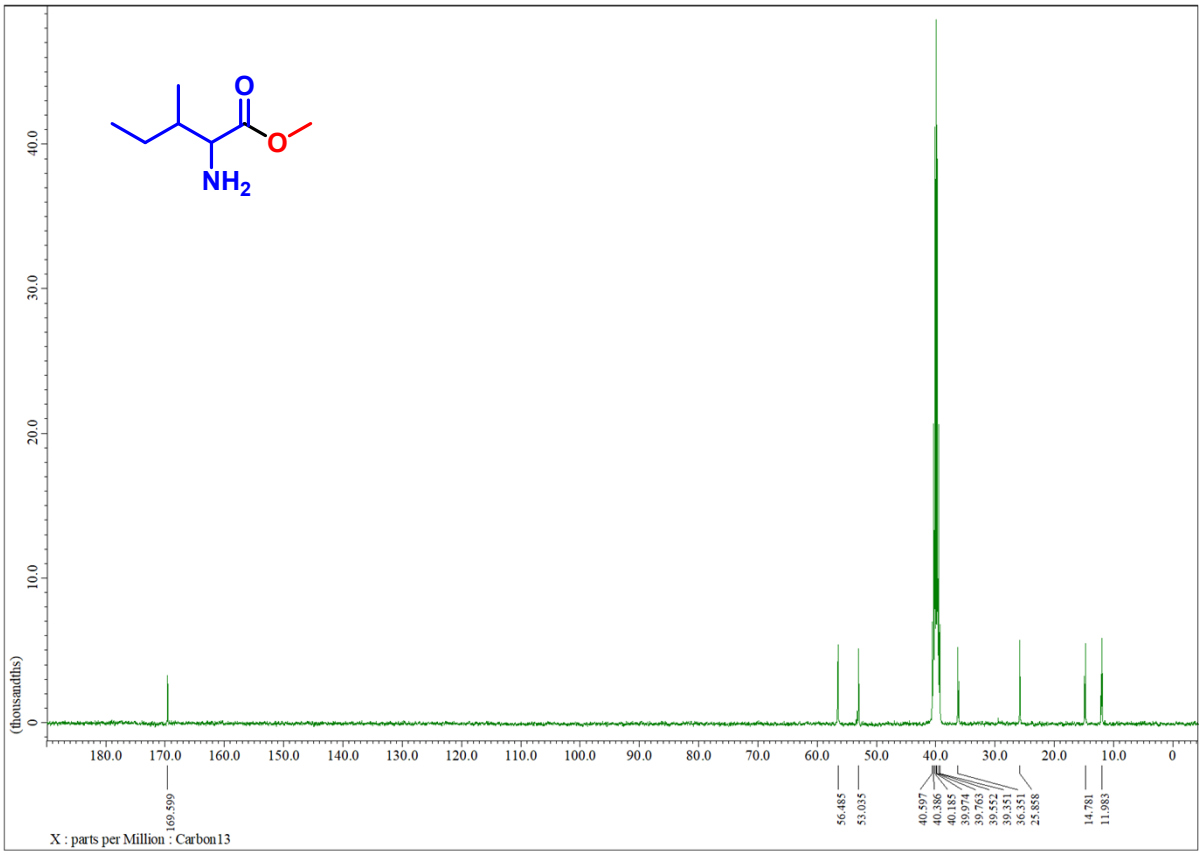


Figure S78. [13]C NMR spectrum of Methyl 2-amino-3-methylpentanoate **D7.**

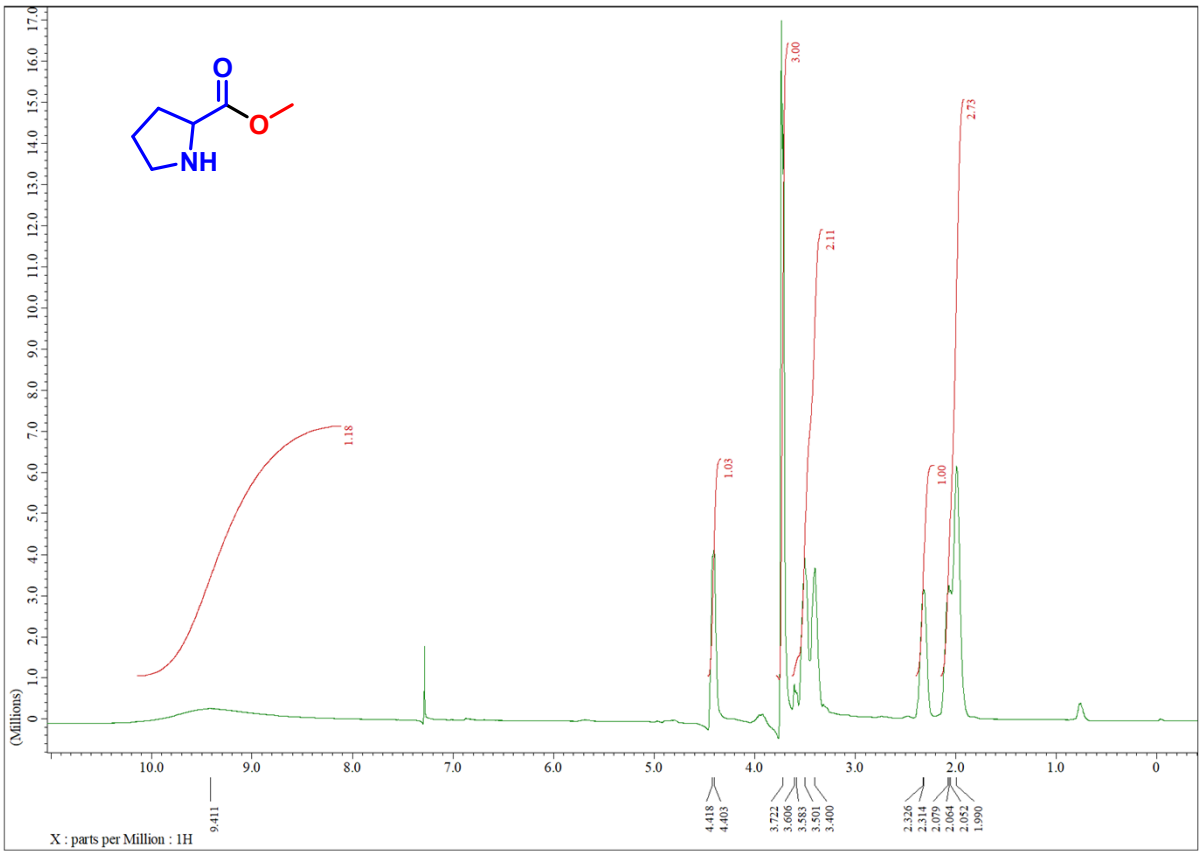


Figure S79. ^{1}H NMR spectrum of Methyl prolinate **D8.**

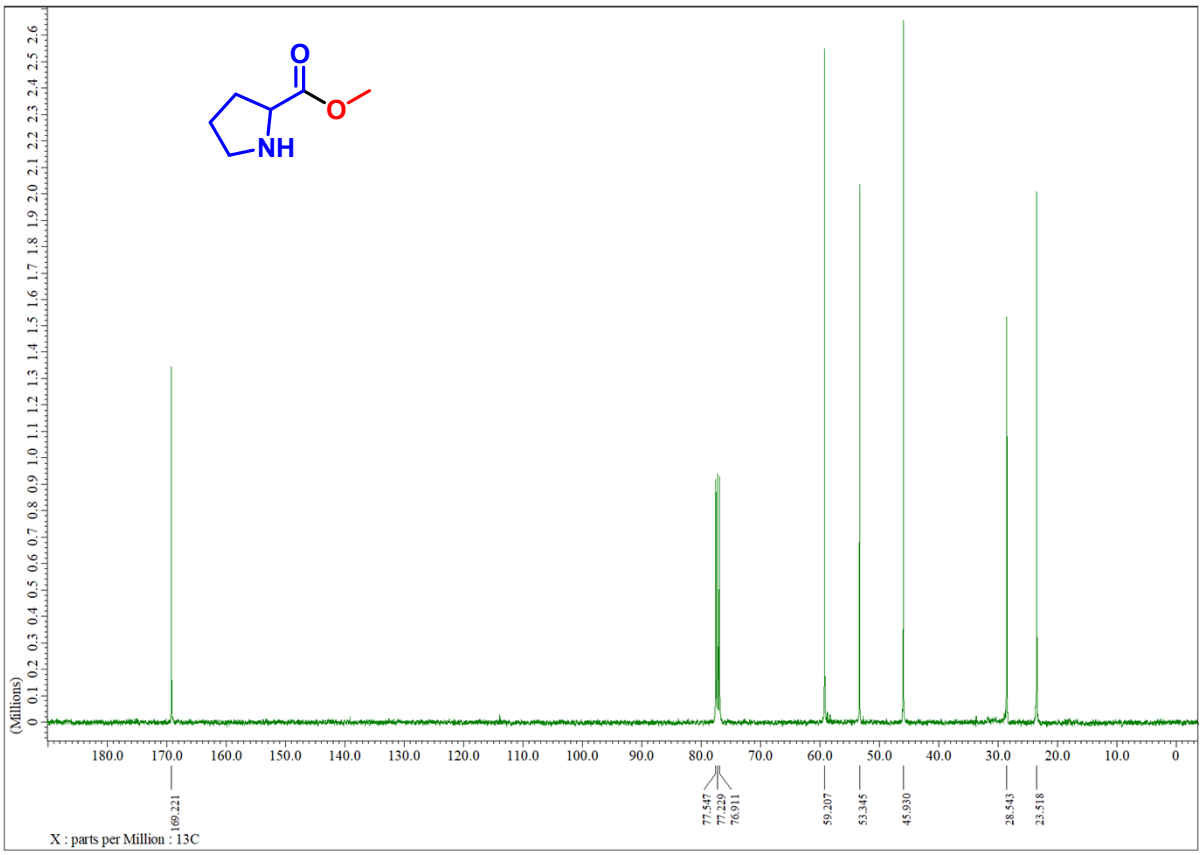


Figure S80. ^{13}C NMR spectrum of Methyl prolinate **D8.**

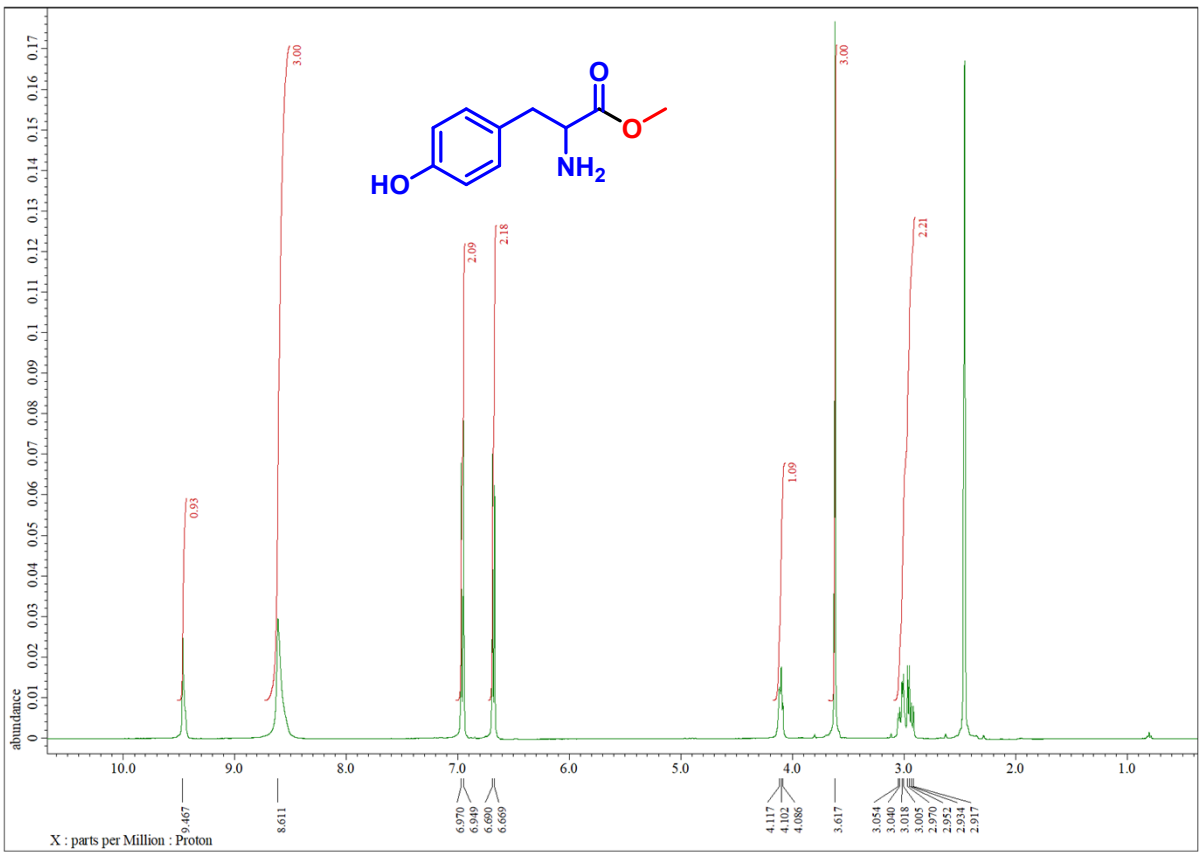


Figure S81. ^{1}H NMR spectrum of Methyl tyrosinate **D9.**

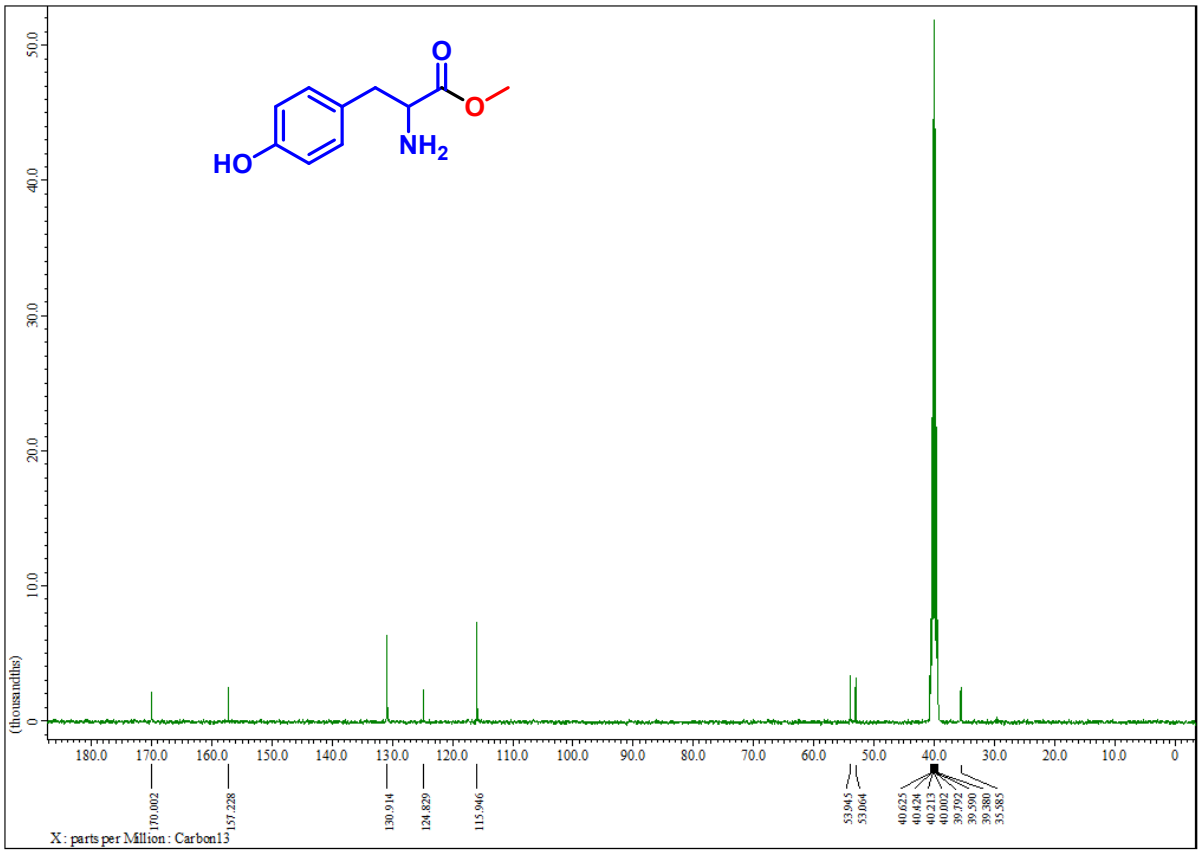


Figure S82. ^{13}C NMR spectrum of Methyl tyrosinate **D9.**

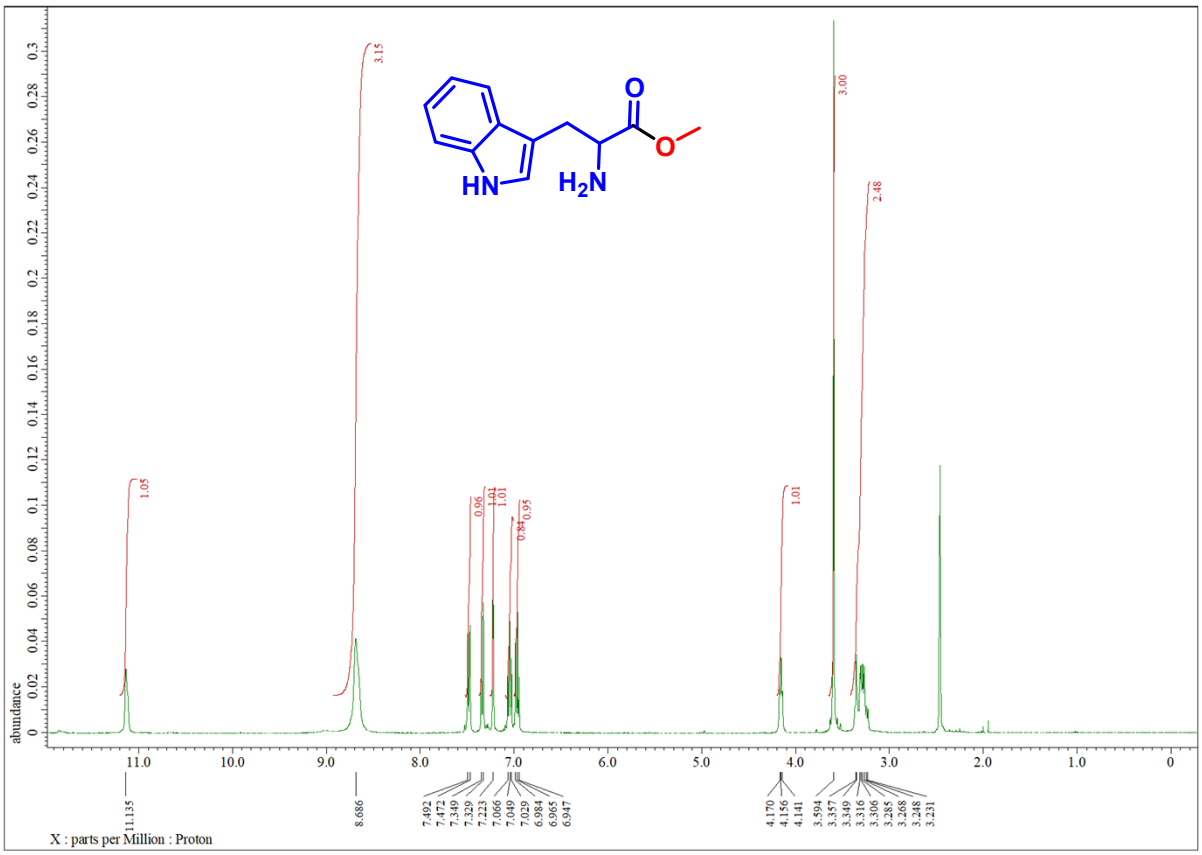


Figure S83. ^{1}H NMR spectrum of Methyl tryptophanate **D10.**

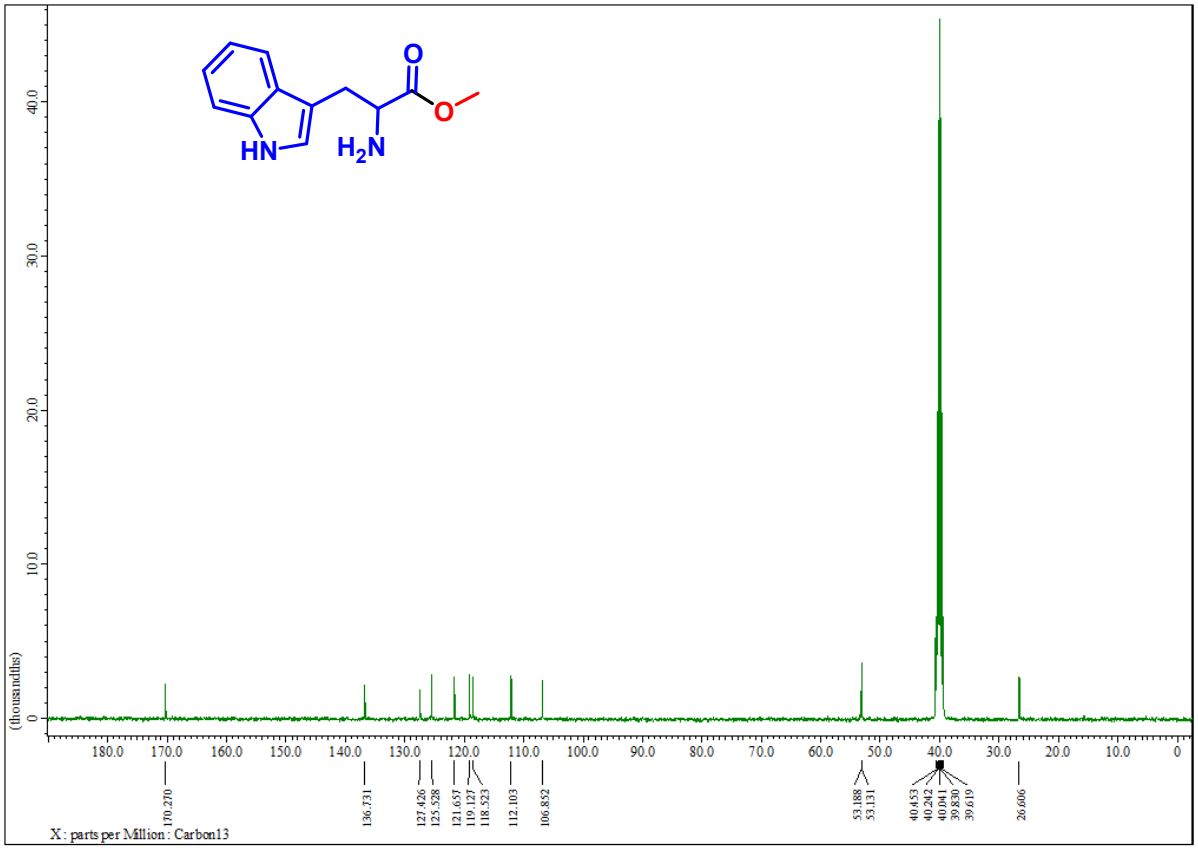


Figure S84. ^{13}C NMR spectrum of Methyl tryptophanate **D10.**

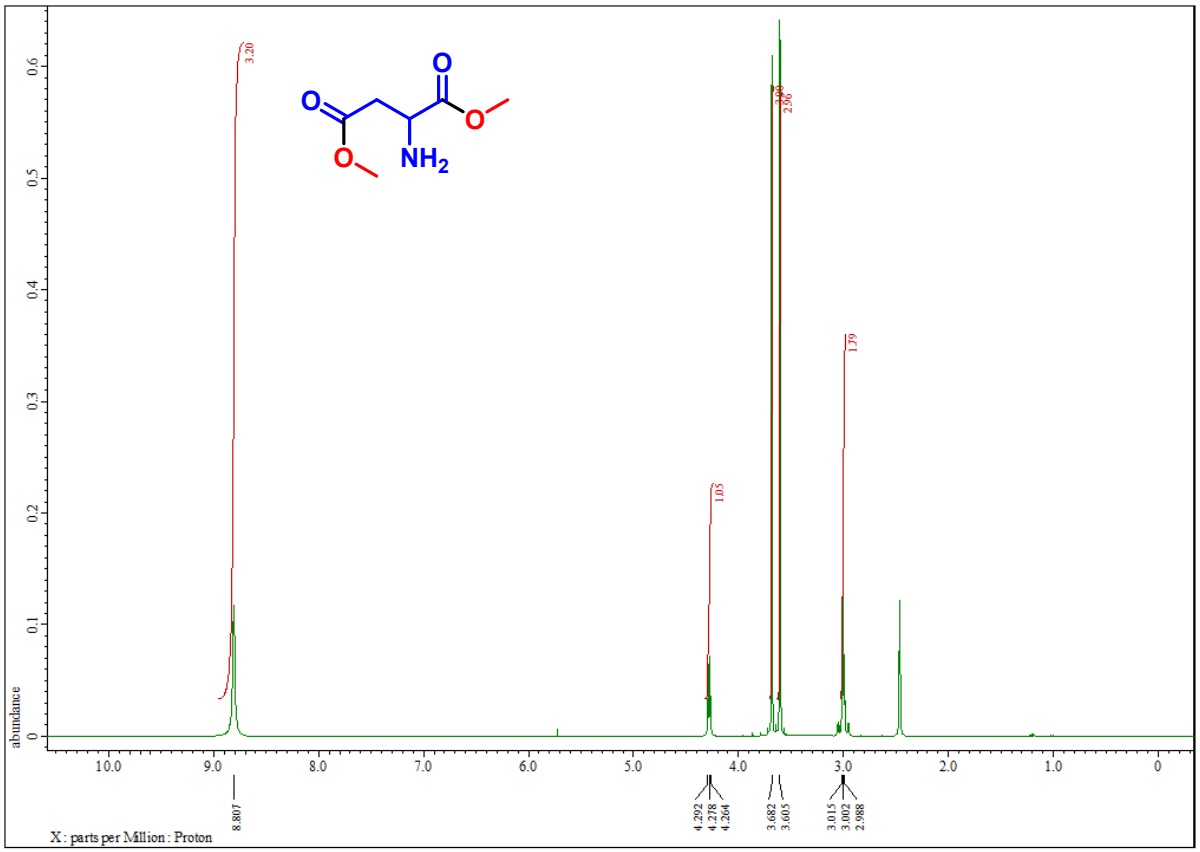


Figure S85. ^{1}H NMR spectrum of Dimethyl aspartate **D11.**

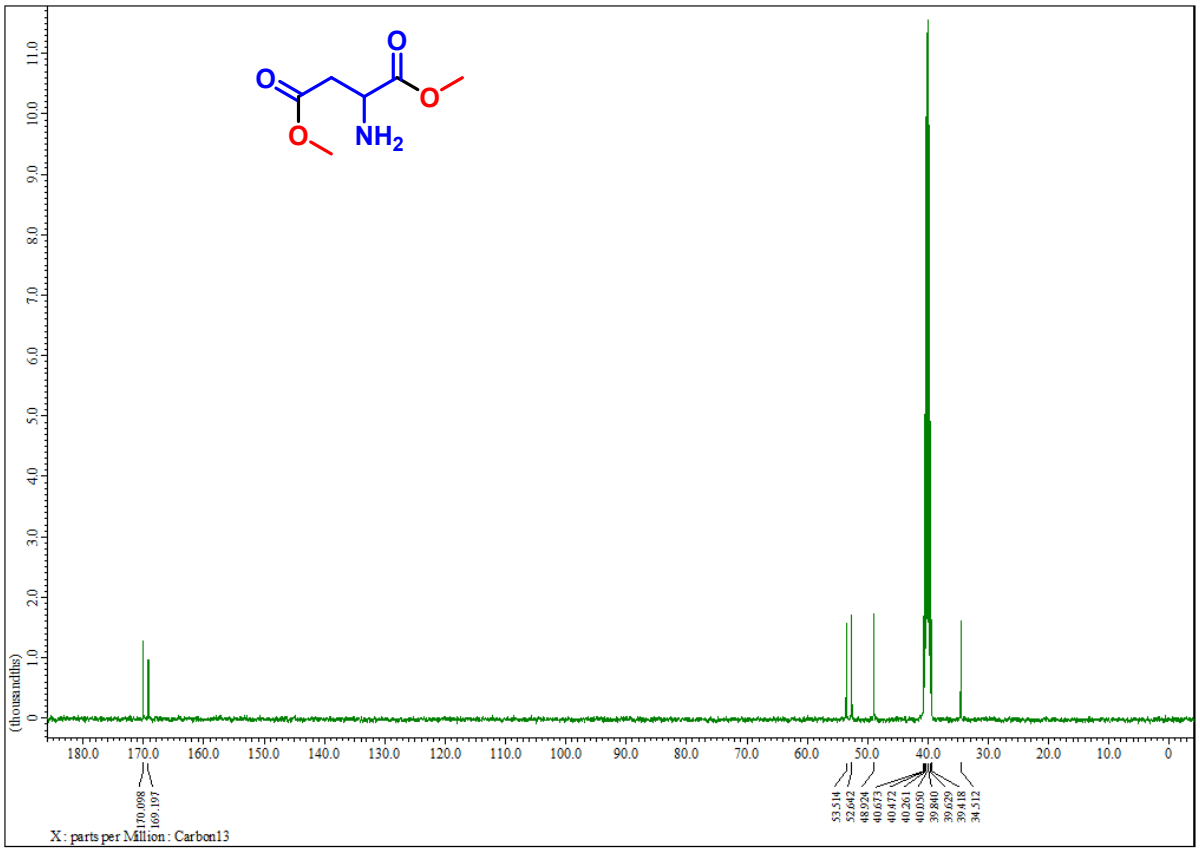


Figure S86. ^{13}C NMR spectrum of Dimethyl aspartate **D11.**

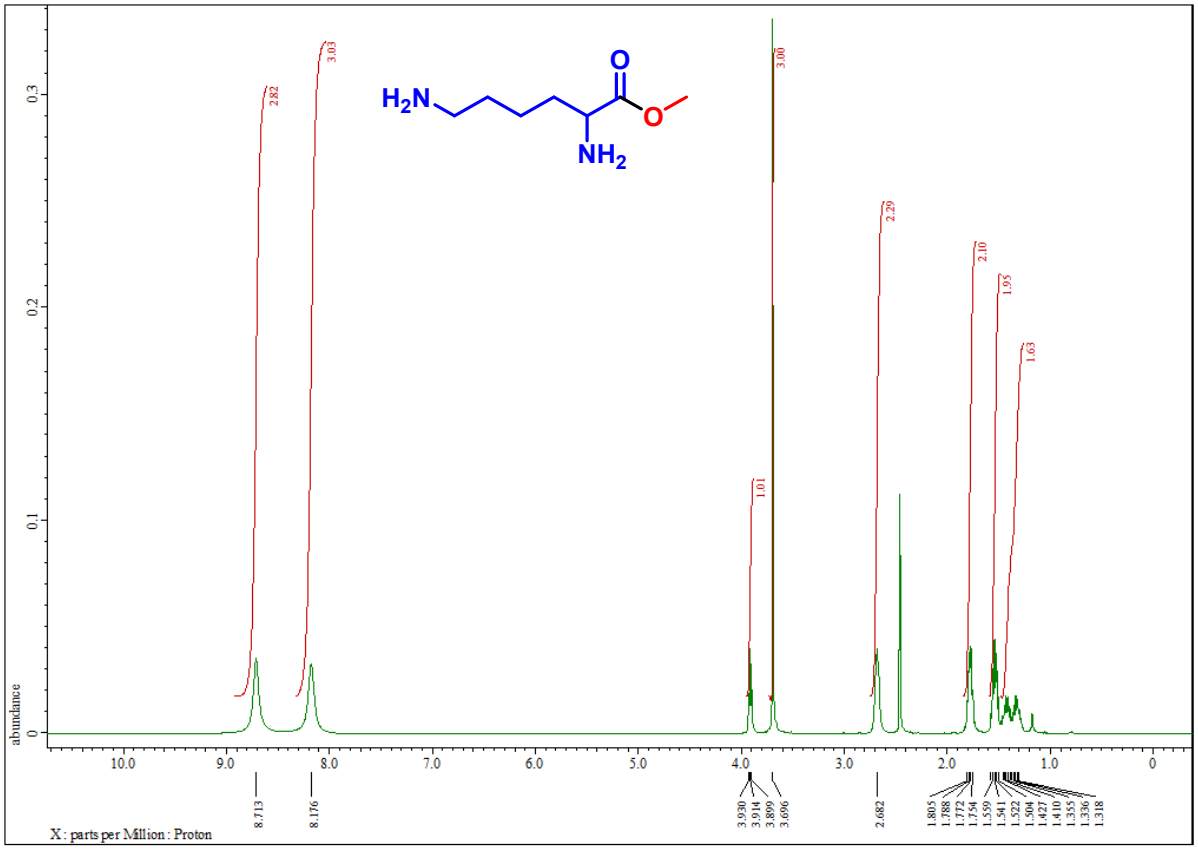


Figure S87. ^{1}H NMR spectrum of Methyl lysinate **D12.**

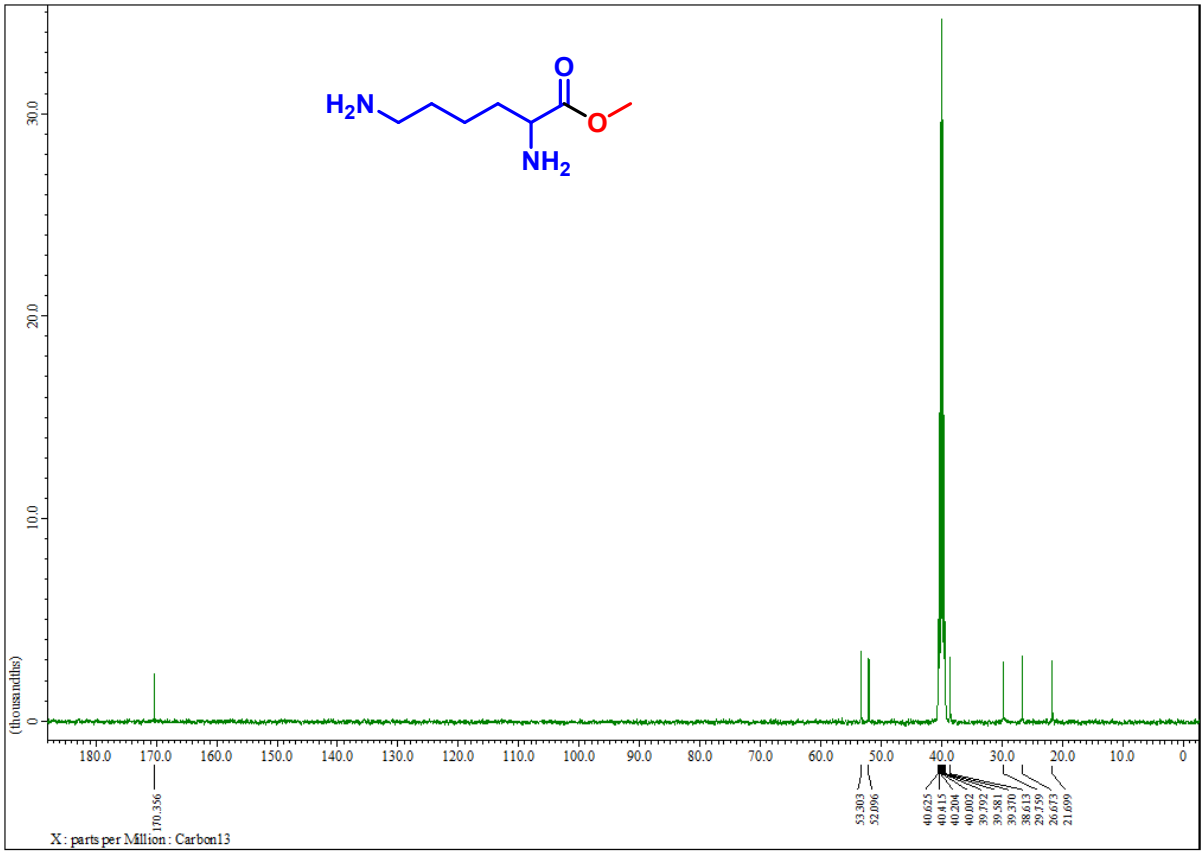


Figure S88. ^{13}C NMR spectrum of Methyl lysinate **D12.**

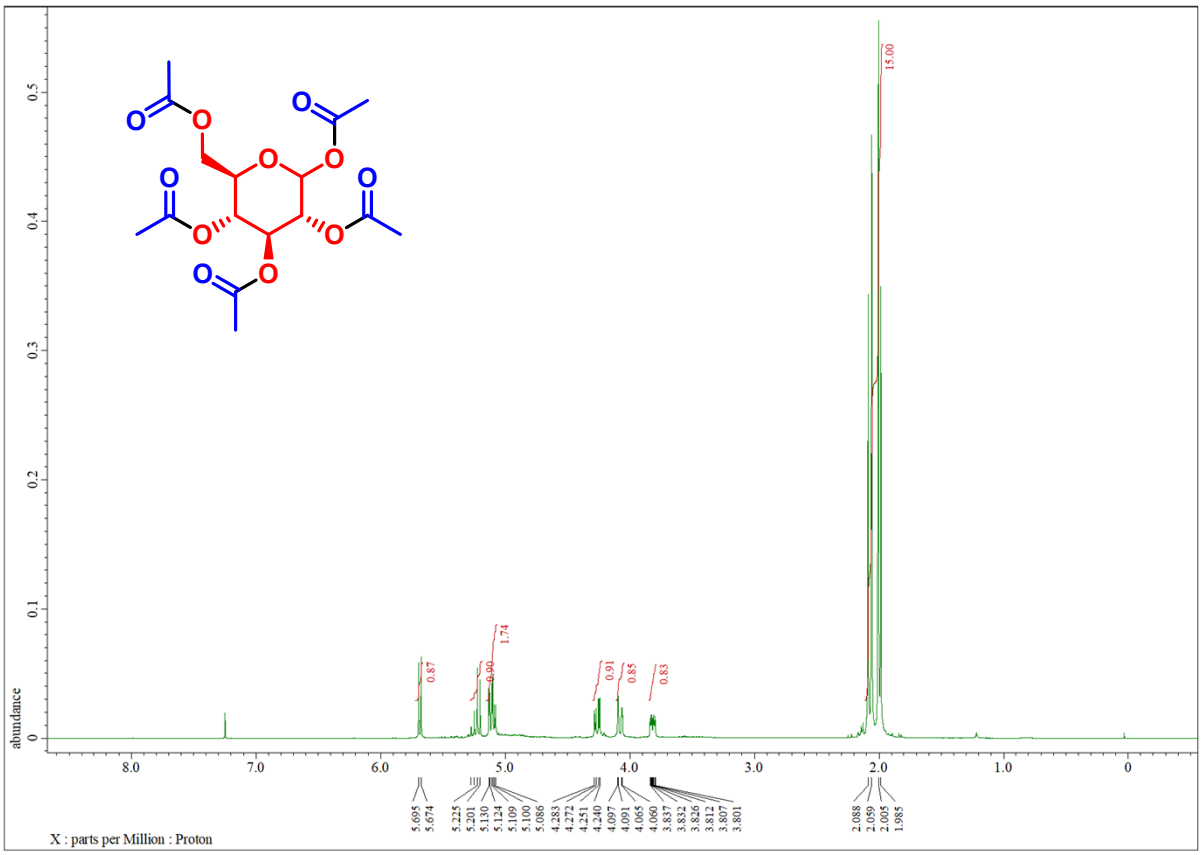


Figure S89. ^{1}H NMR spectrum of Glucose pentaacetate **E1.**

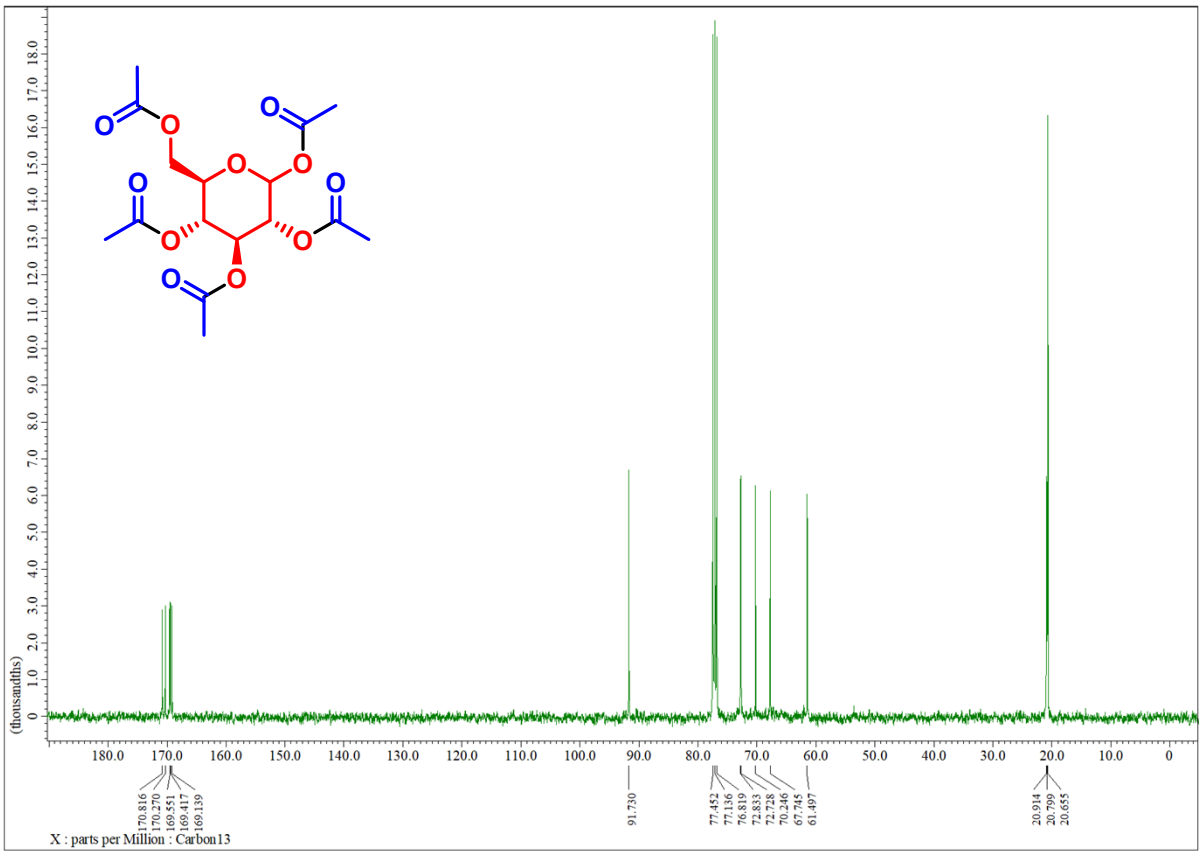


Figure S90. ^{13}C NMR spectrum of Glucose pentaacetate **E1.**

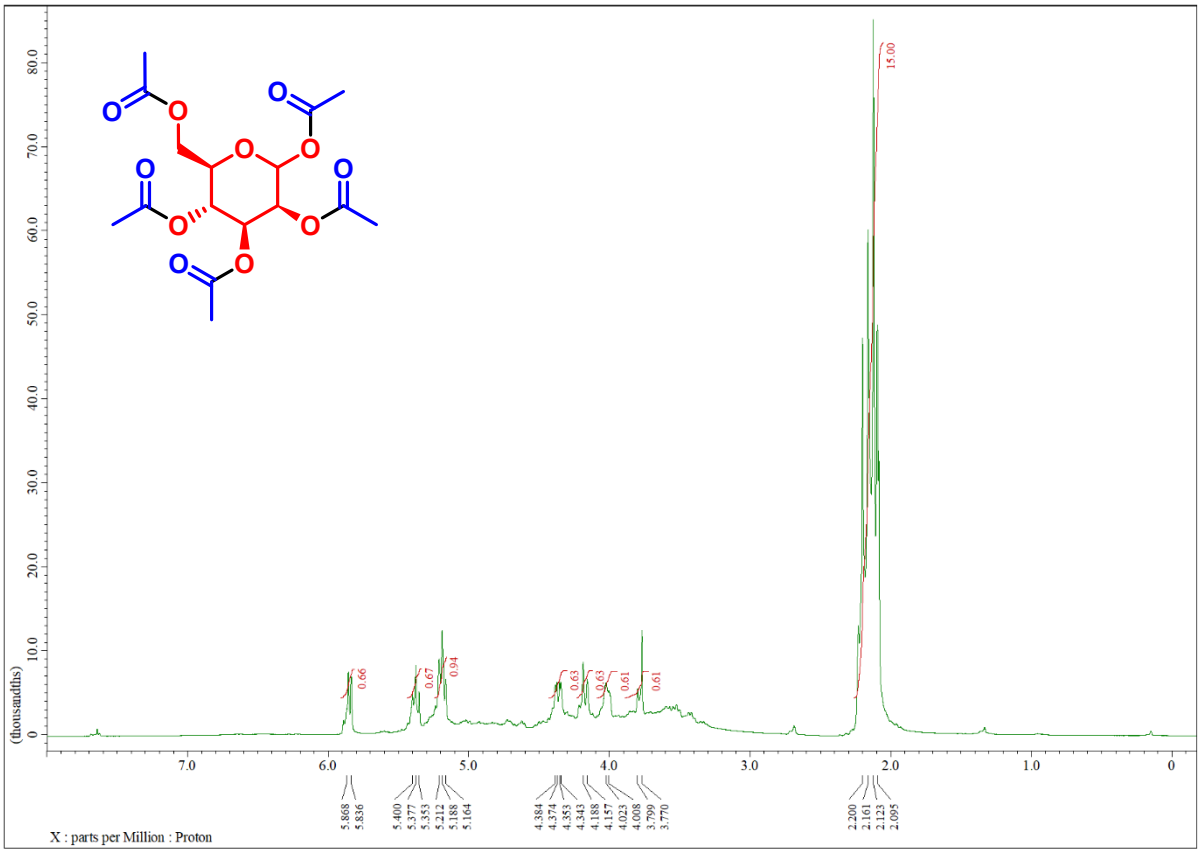


Figure S91. ^{1}H NMR spectrum of Mannose pentaacetate **E2.**

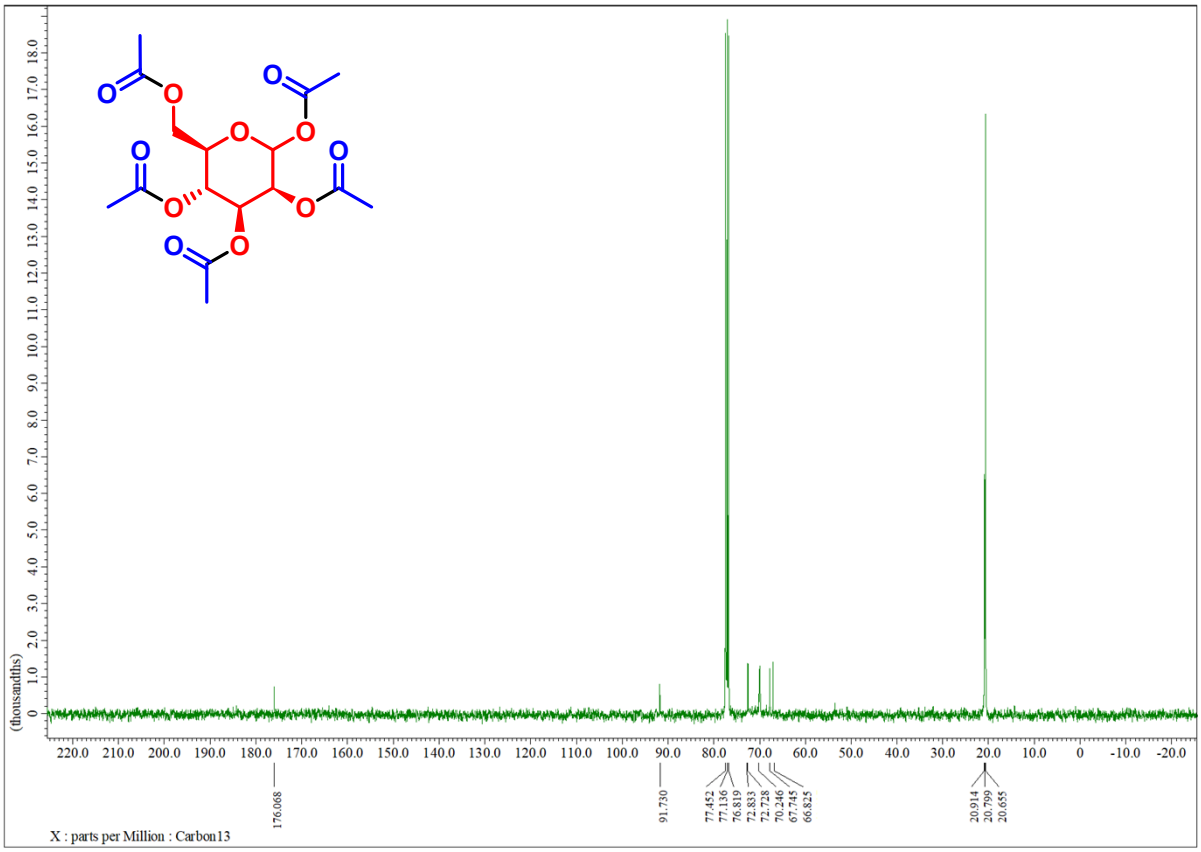


Figure S92. ^{13}C NMR spectrum of Mannose pentaacetate **E2.**

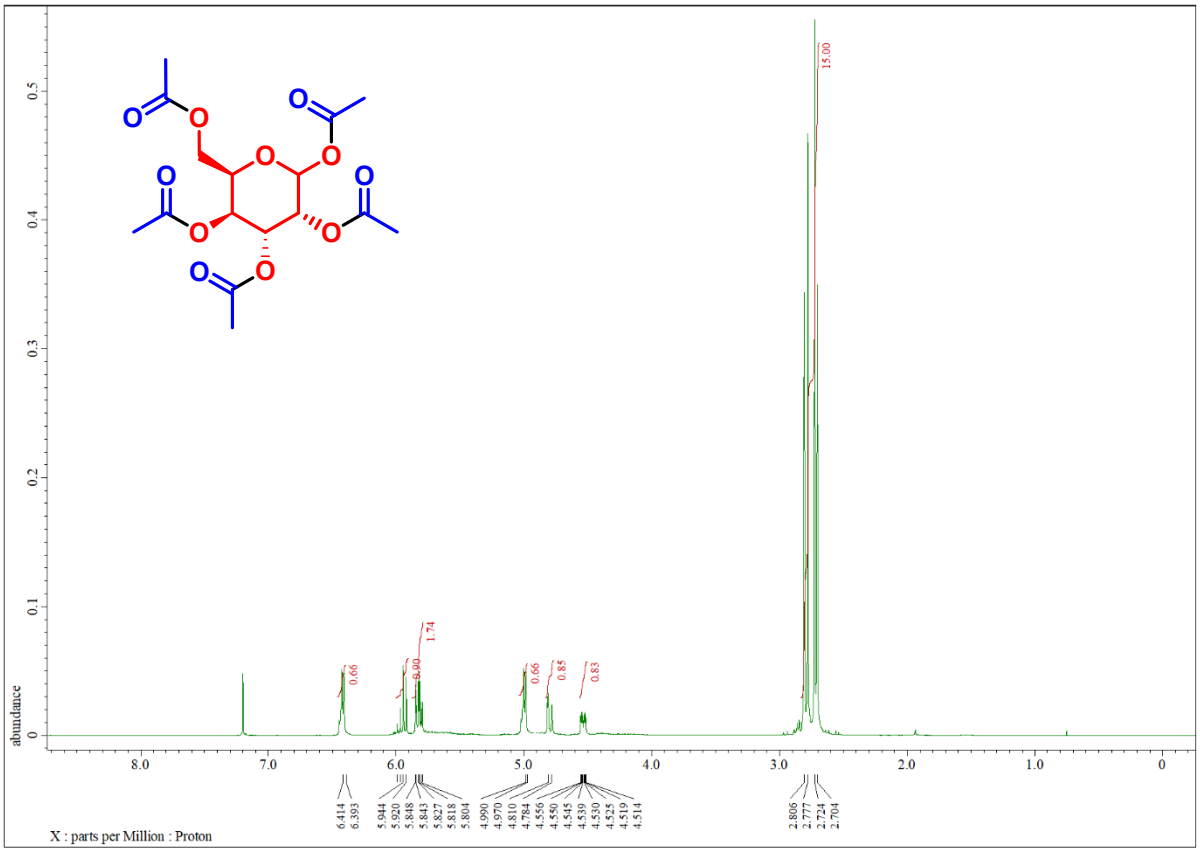


Figure S93. ^{1}H NMR spectrum of Gulose pentaacetate **E3.**

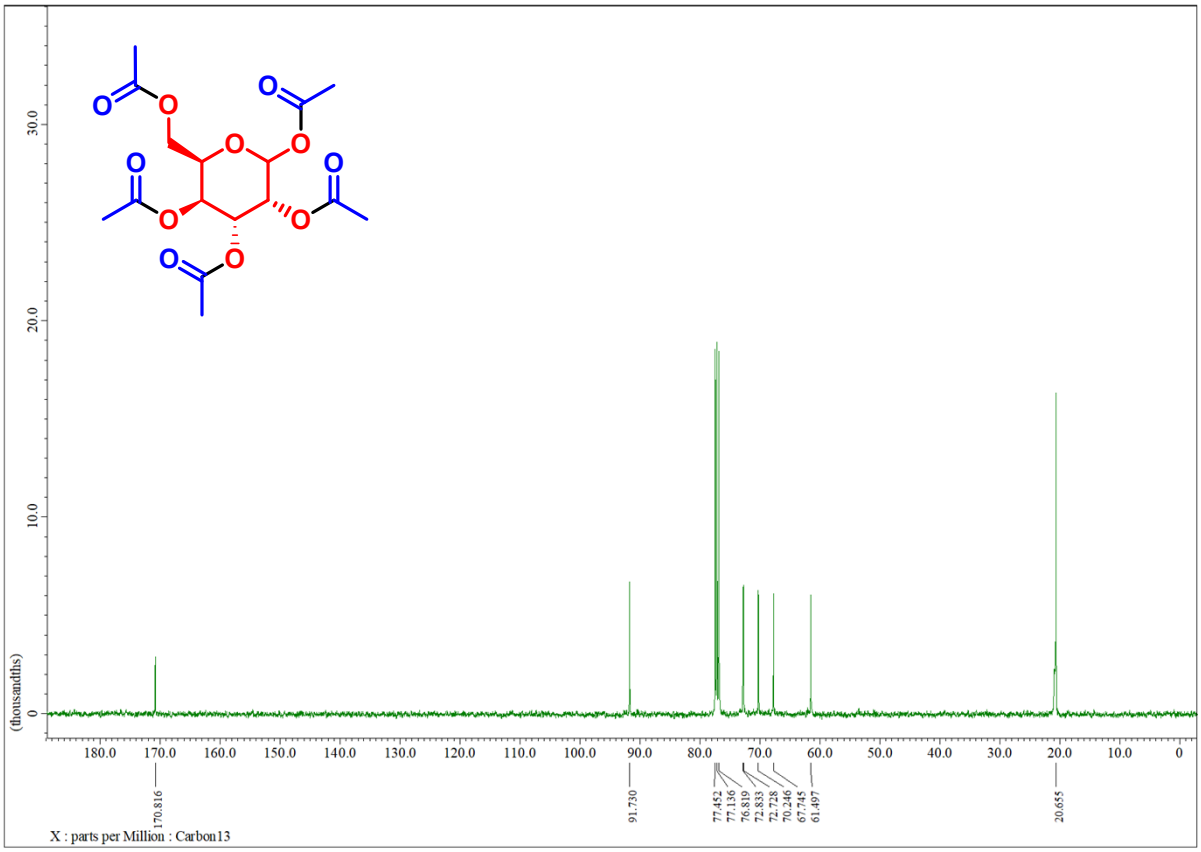


Figure S94. ^{13}C NMR spectrum of Gulose pentaacetate **E3.**

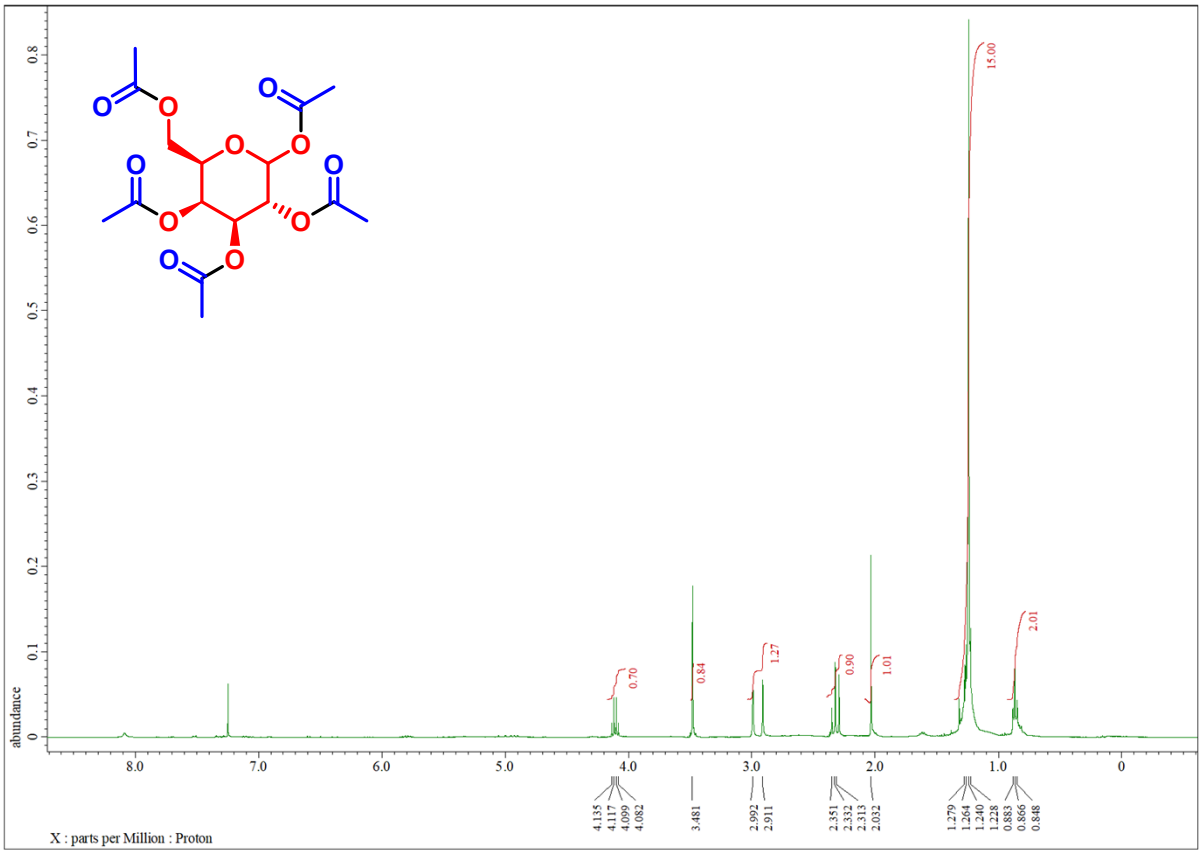


Figure S95. ^{1}H NMR spectrum of Galactose pentaacetate **E4.**

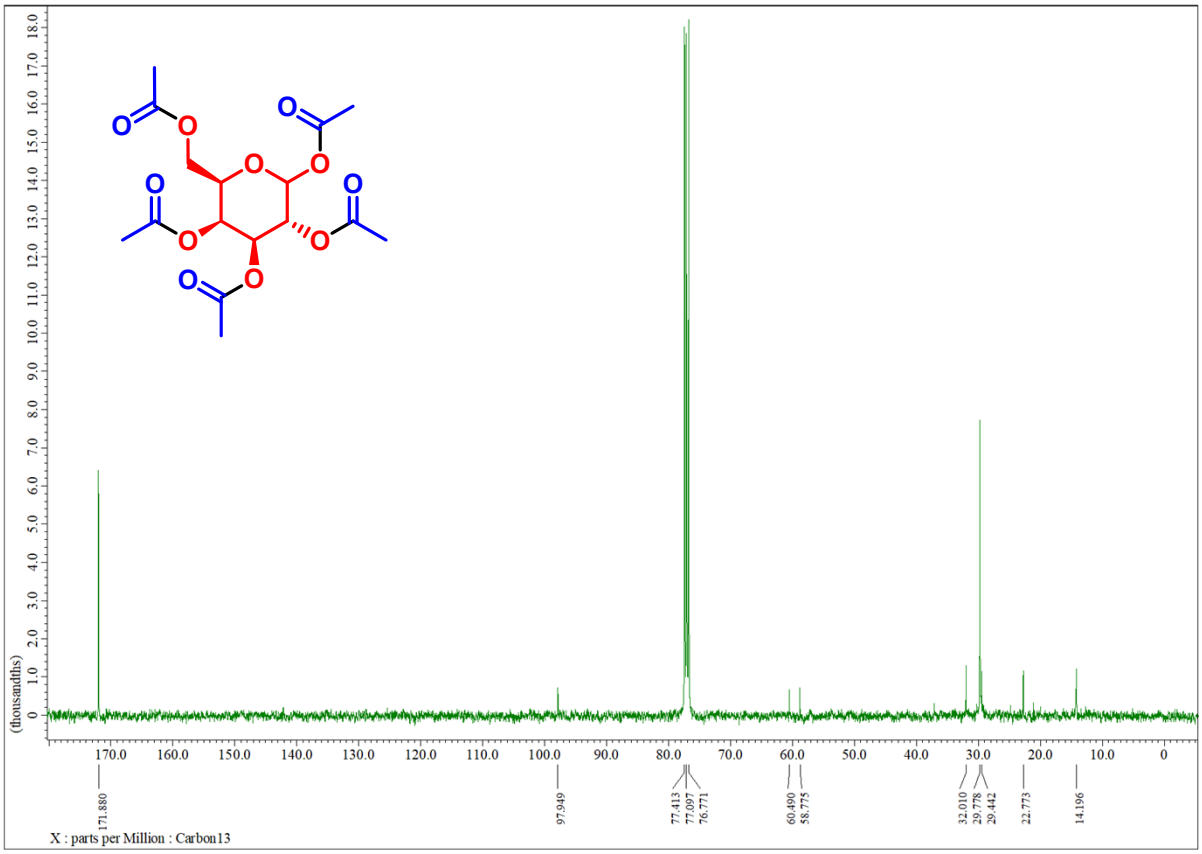


Figure S96. ^{13}C NMR spectrum of Galactose pentaacetate **E4.**

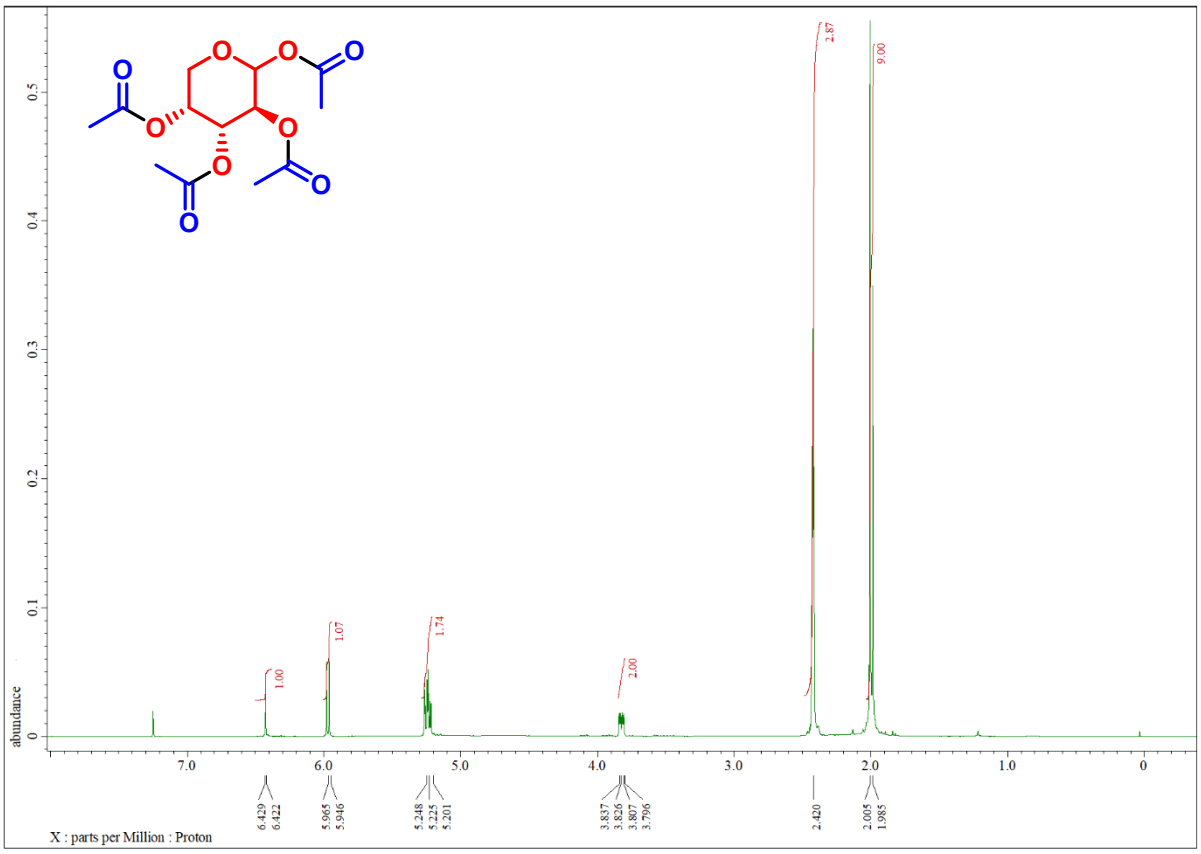


Figure S97. ^{1}H NMR spectrum of Ribose tetraacetate **E5.**

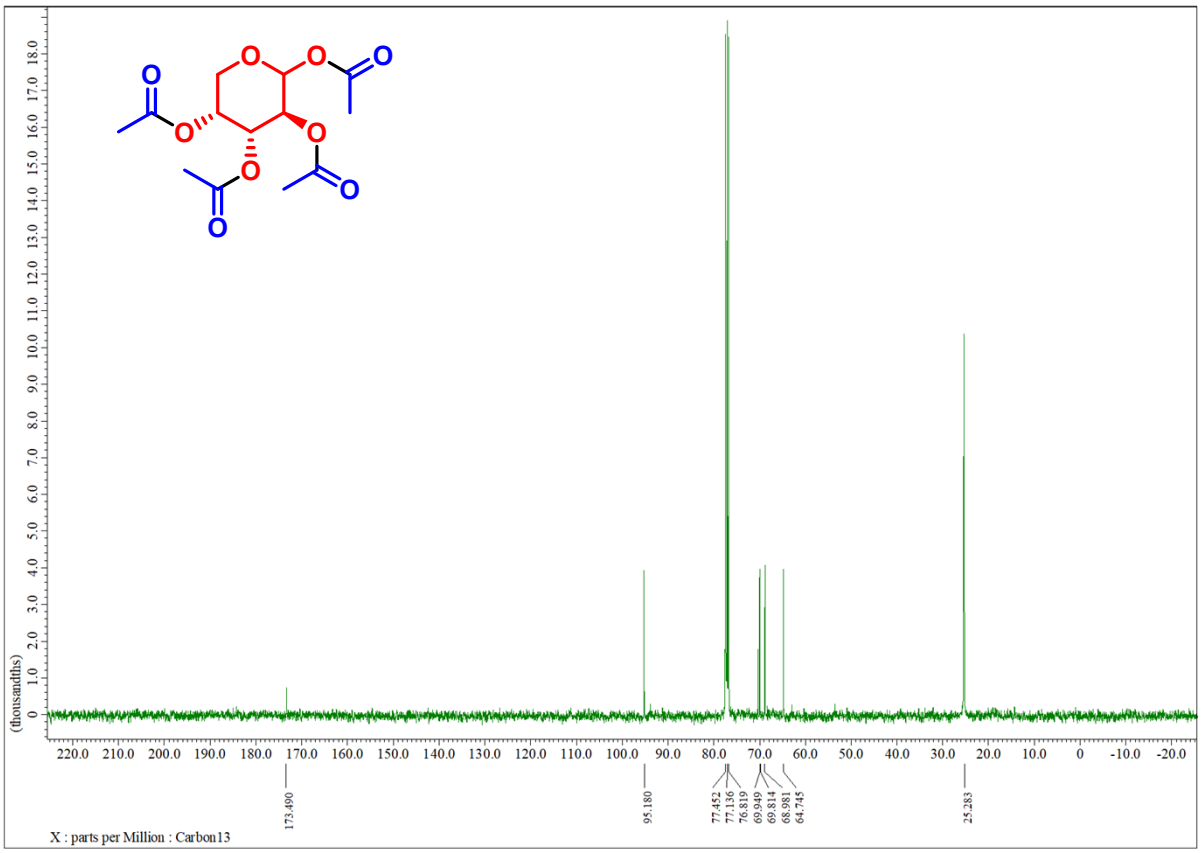


Figure S98. ^{13}C NMR spectrum of Ribose tetraacetate **E5.**

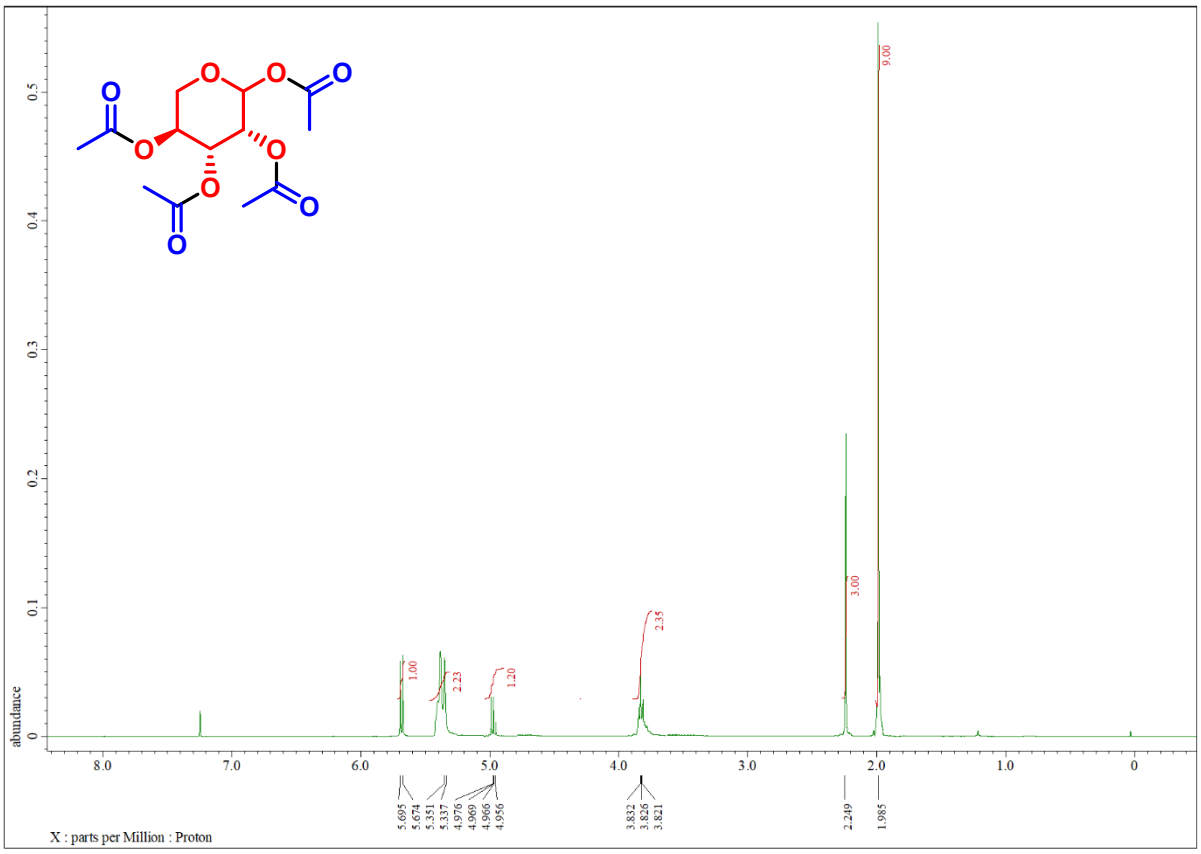


Figure S99. ^{1}H NMR spectrum of Lyxose tetraacetate **E6.**

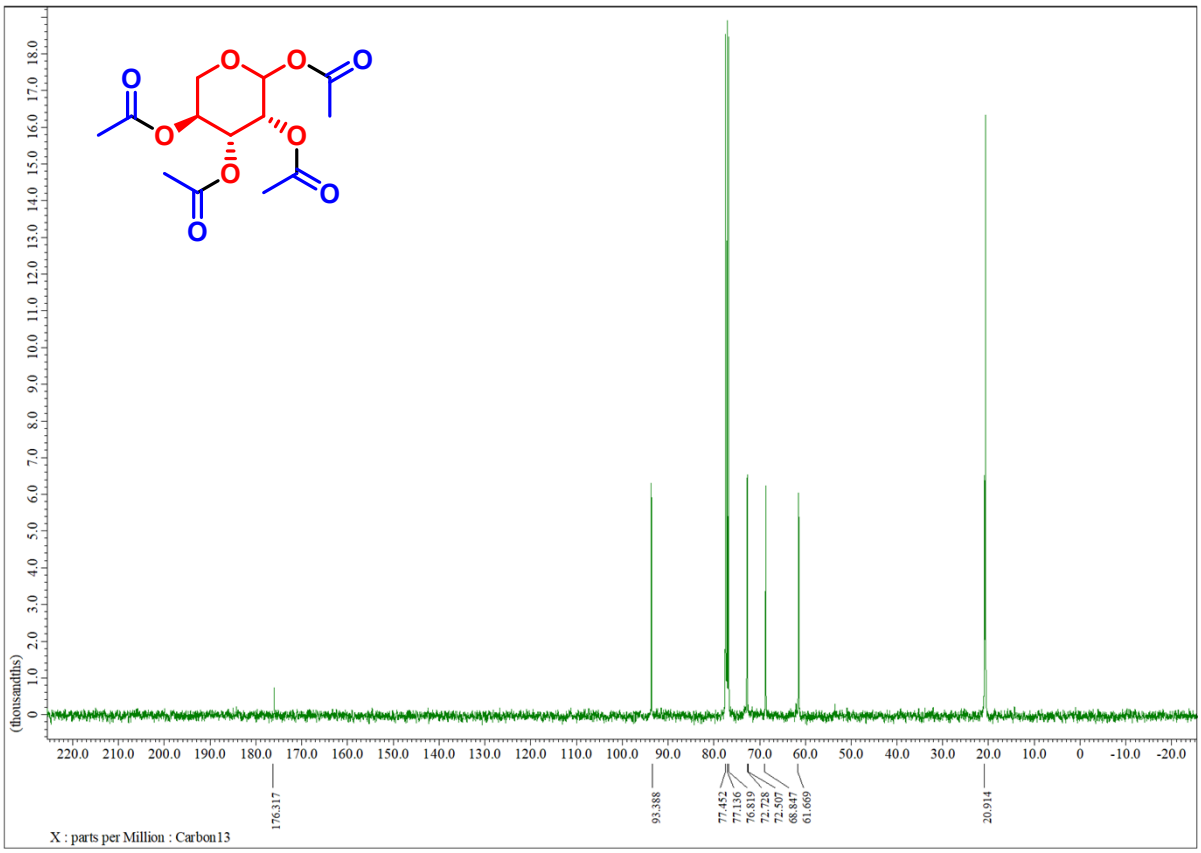


Figure S100. ^{13}C NMR spectrum of Lyxose tetraacetate **E6.**

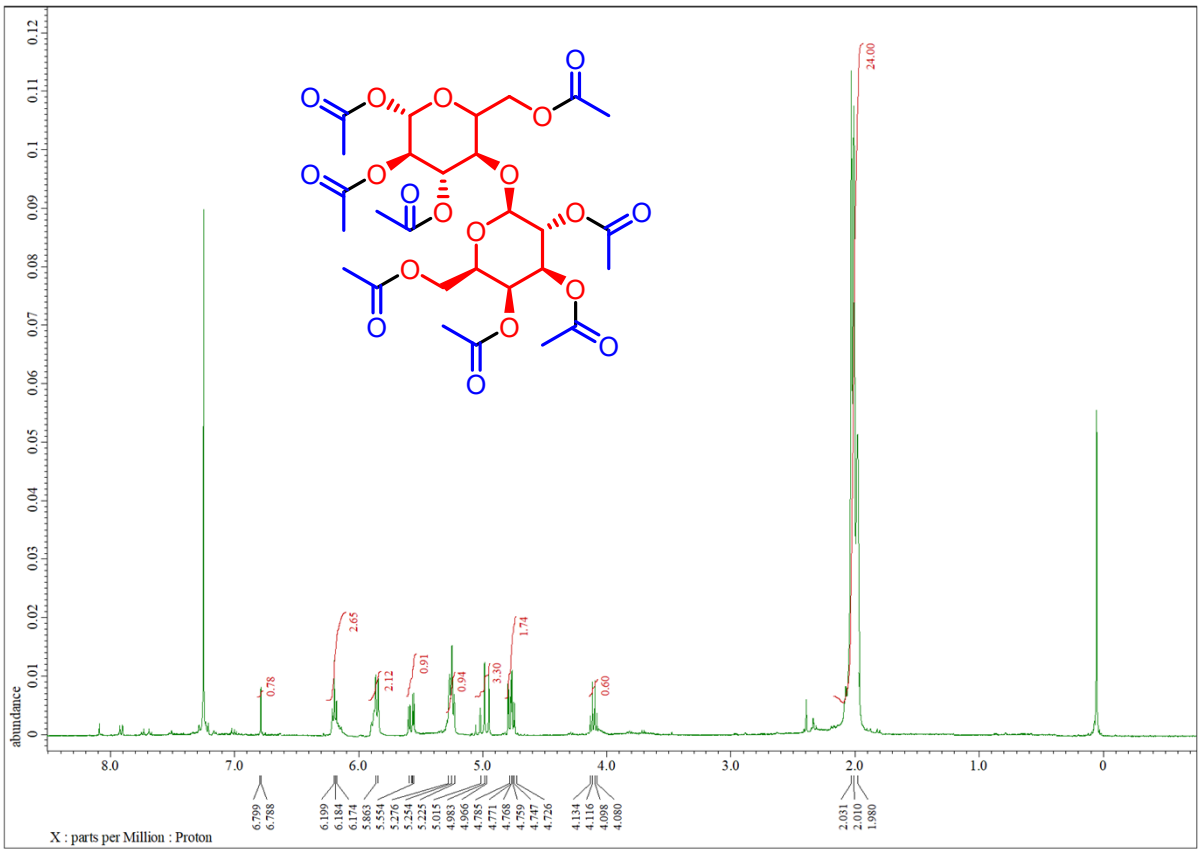


Figure S101. ^{1}H NMR spectrum of Lactose octaacetate **E7.**

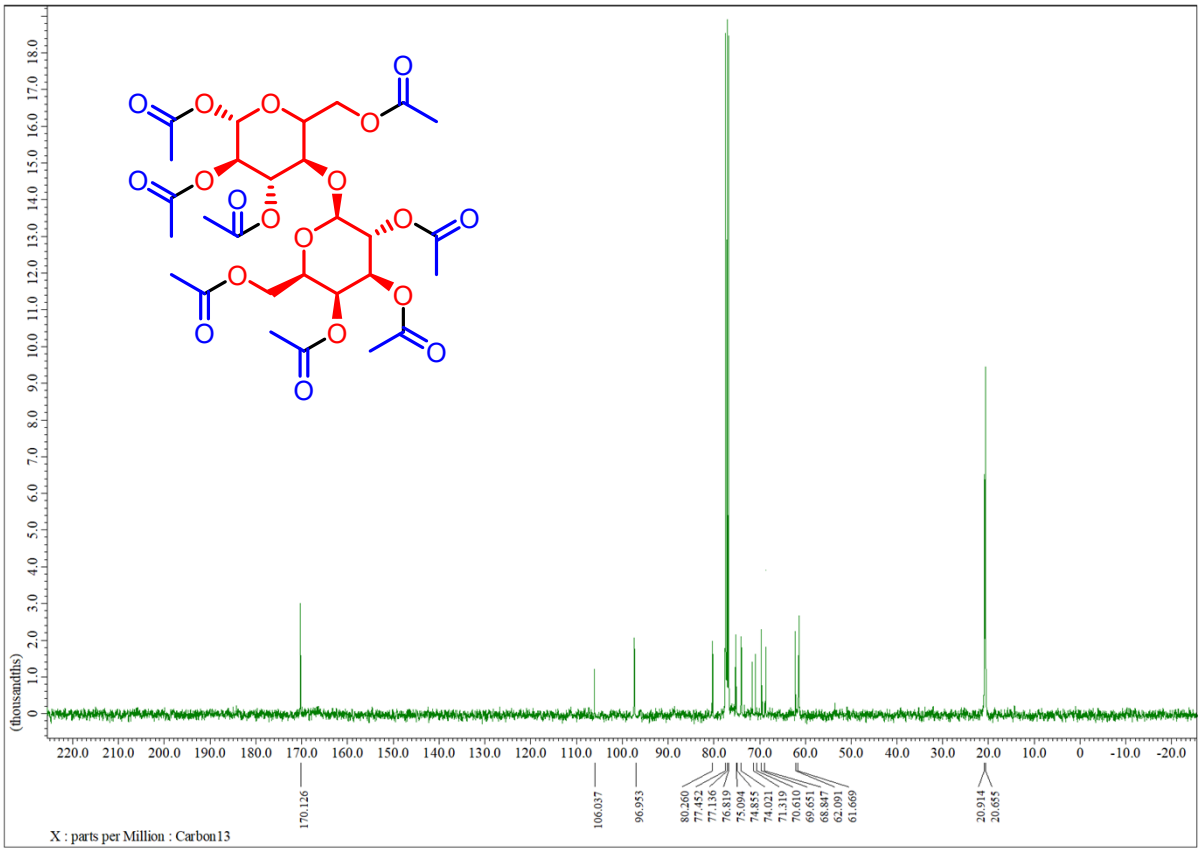


Figure S102. ^{13}C NMR spectrum of Lactose octaacetate **E7.**

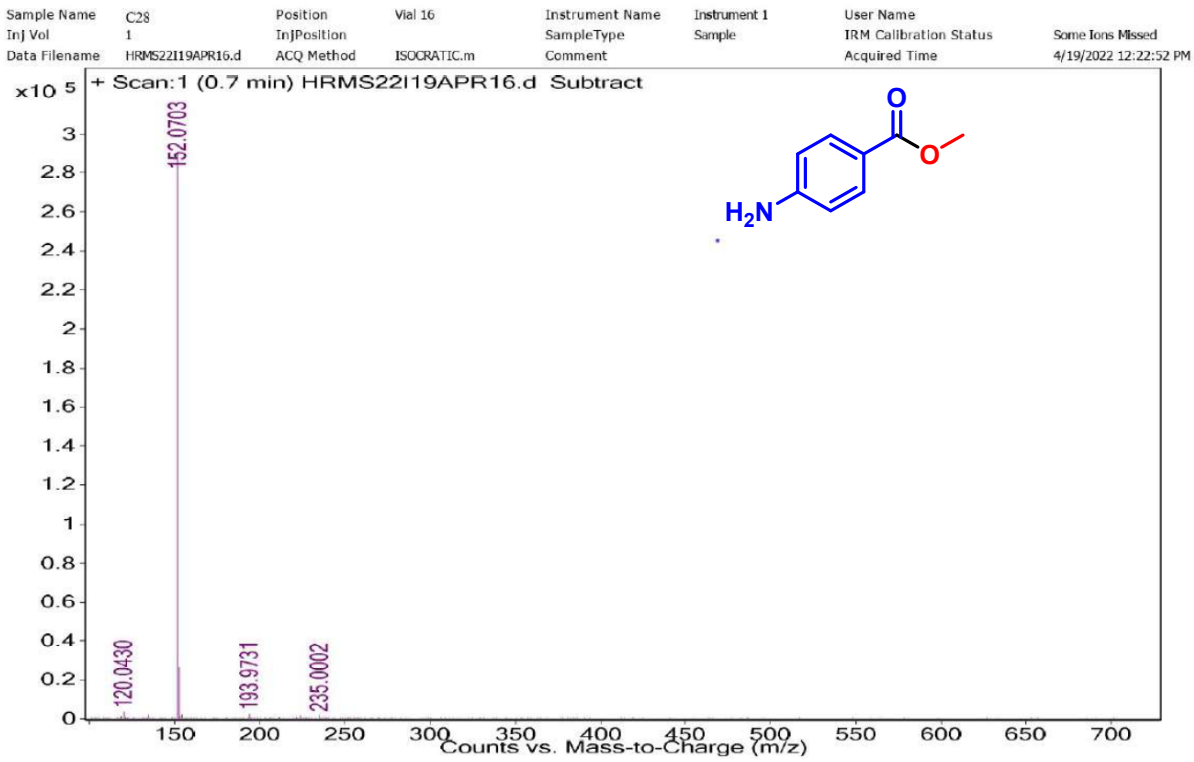


Figure S103. Mass spectrum of Methyl 4-aminobenzoate **C2.**

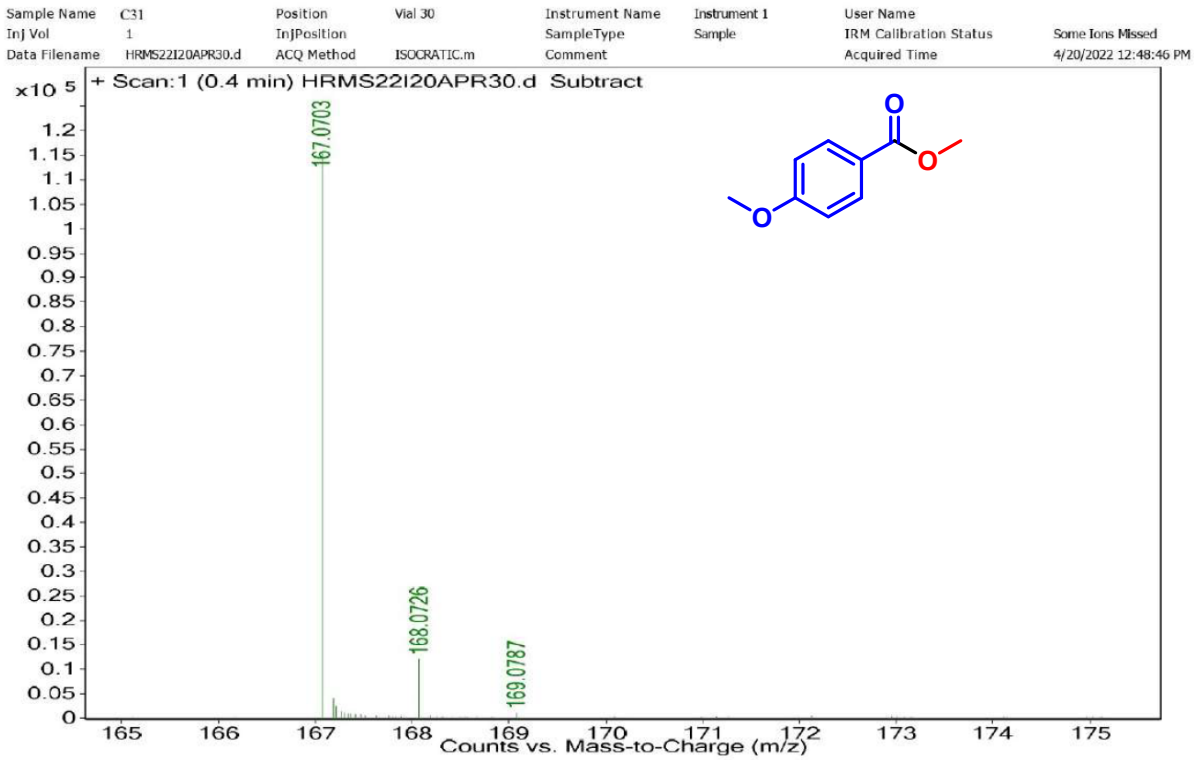
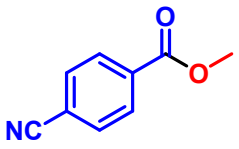
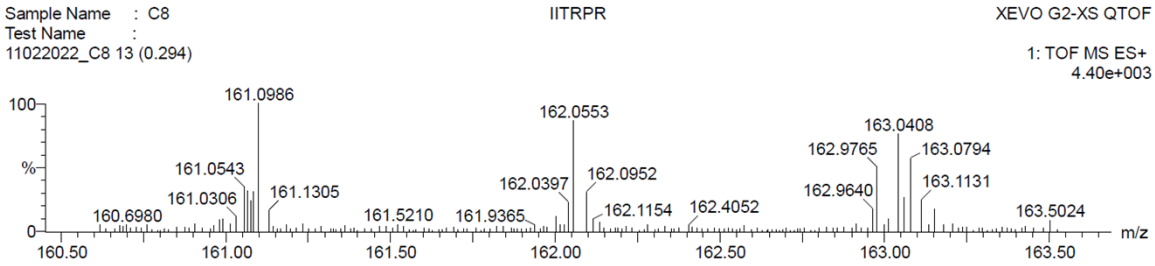


Figure S104. Mass spectrum of Methyl 4-methoxybenzoate **C4.**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5



Monoisotopic Mass, Even Electron Ions
48 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 2-20 H: 2-30 N: 0-2 O: 0-4 Br: 0-4



Minimum:				-1.5				
Maximum:		2.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
162.0553	162.0555	-0.2	-1.2	6.5	838.6	n/a	n/a	C9 H8 N O2

Figure S105. Mass spectrum of Methyl 4-cyanobenzoate **C5.**

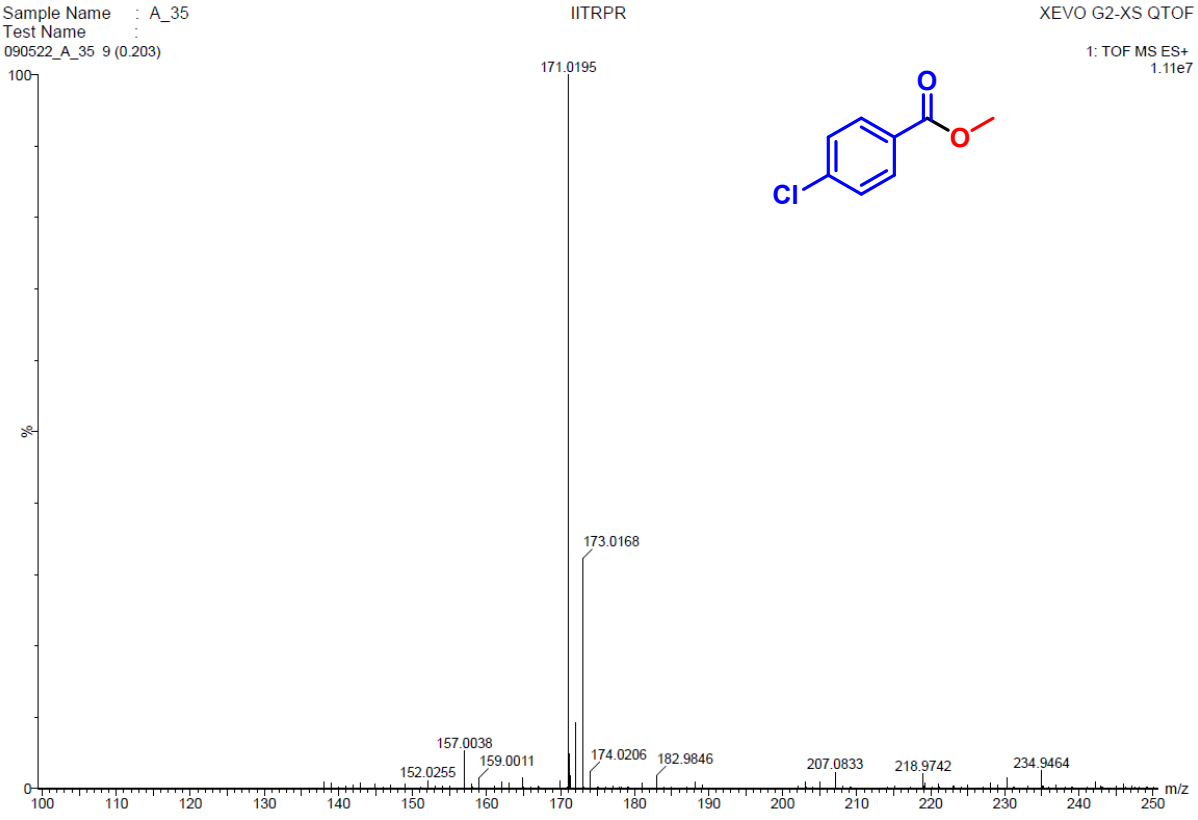


Figure S106. Mass spectrum of Methyl 4-chlorobenzoate **C6.**

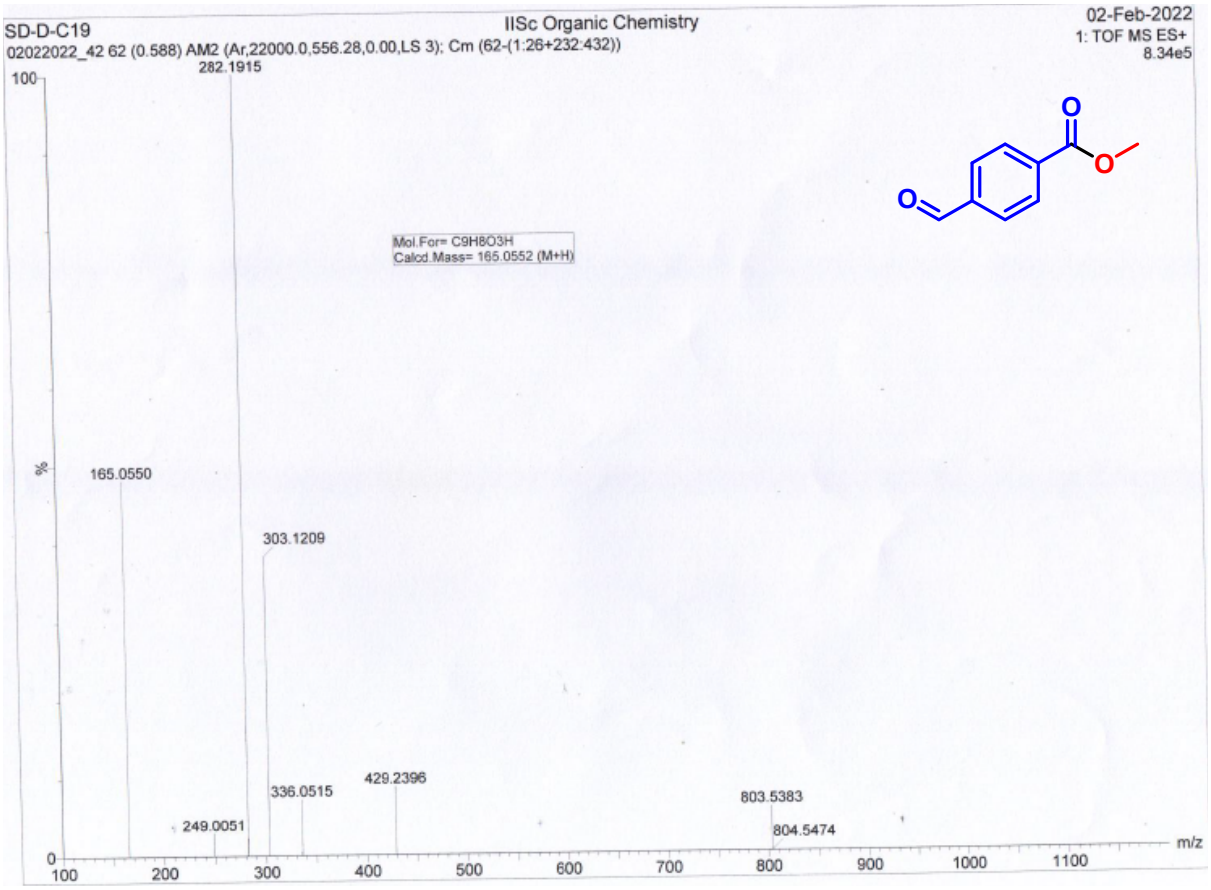


Figure S107. Mass spectrum of Methyl 4-formylbenzoate **C7.**

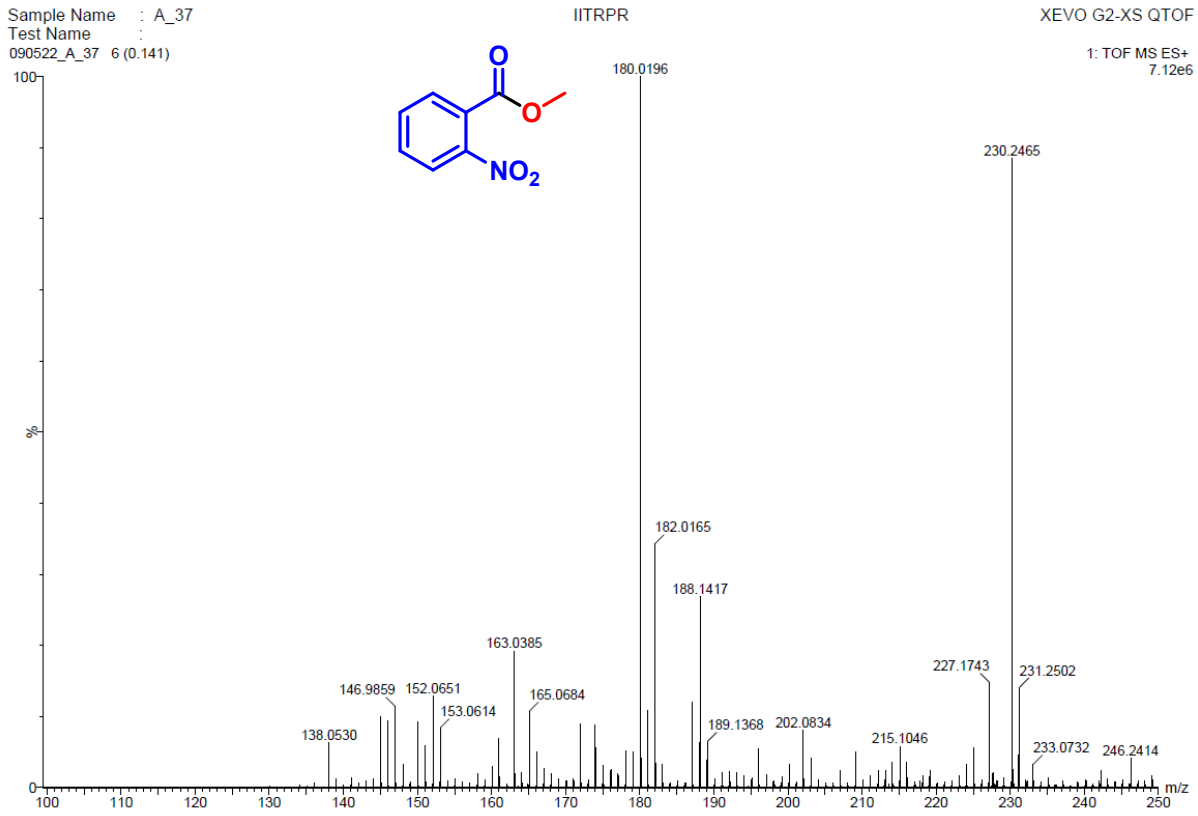


Figure S108. Mass spectrum of Methyl 2-nitrobenzoate **C8.**

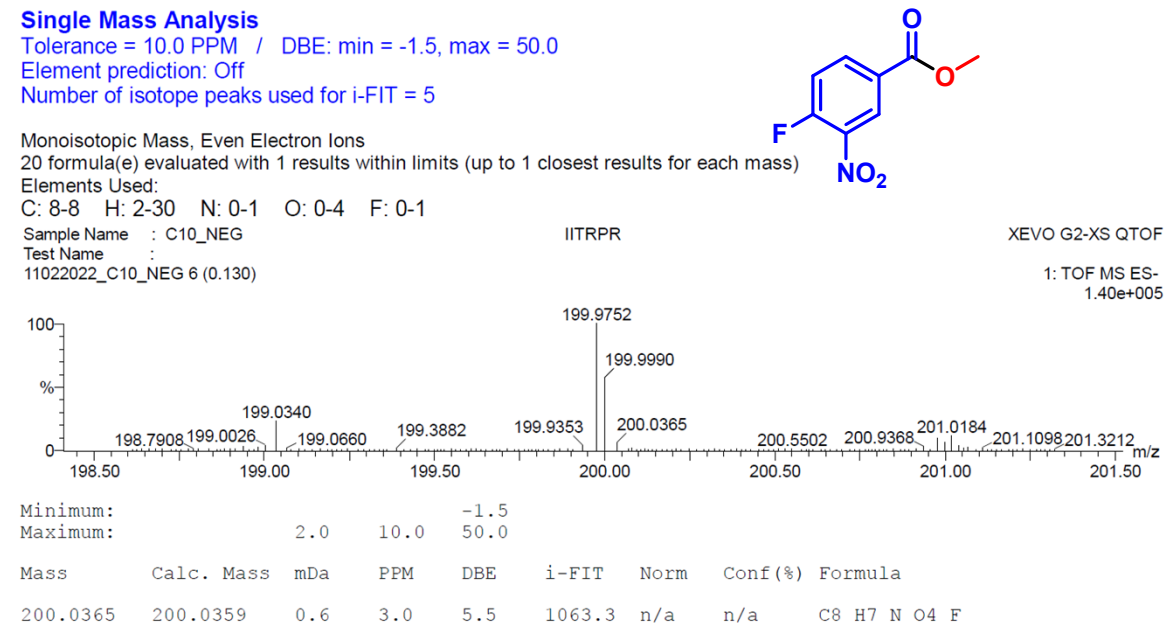


Figure S109. Mass spectrum of Methyl 4-fluoro-3-nitrobenzoate **C9.**

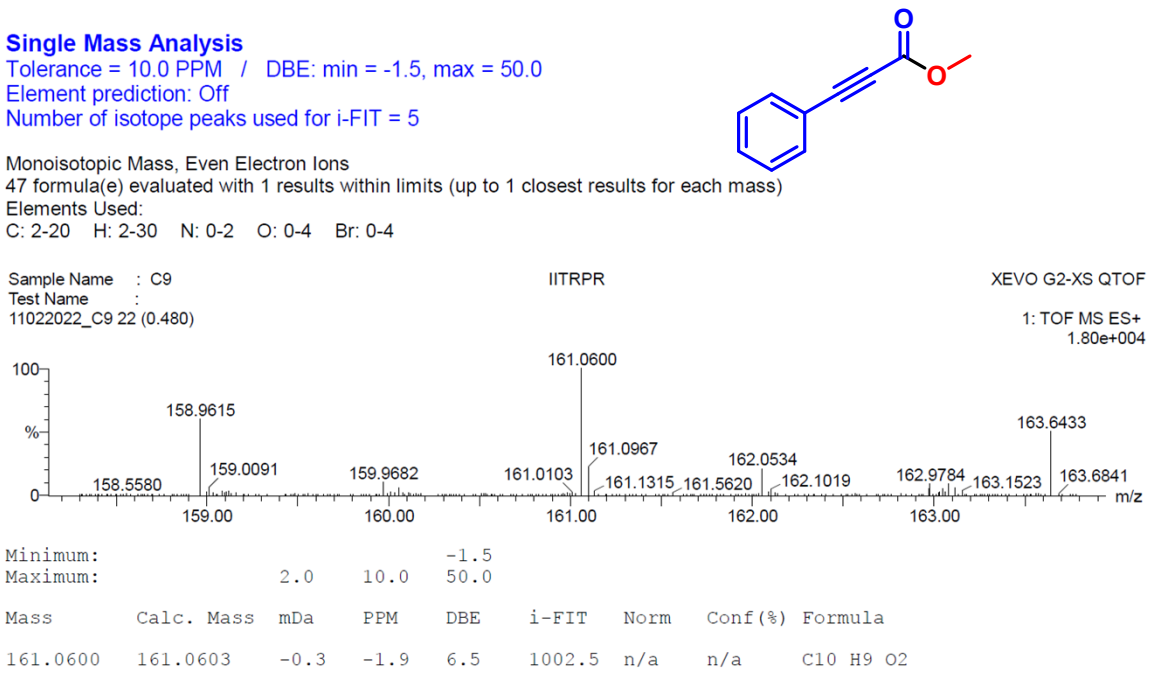


Figure S110. Mass spectrum of Methyl 3-phenylpropiolate **C10**

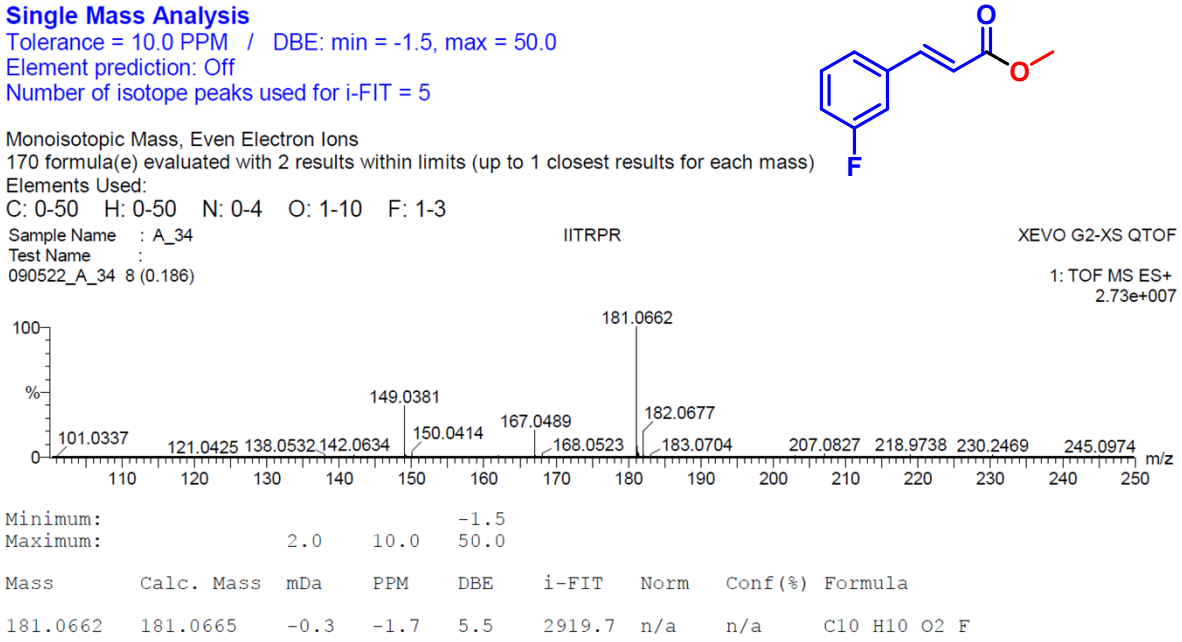
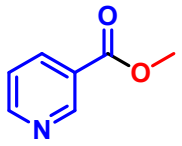


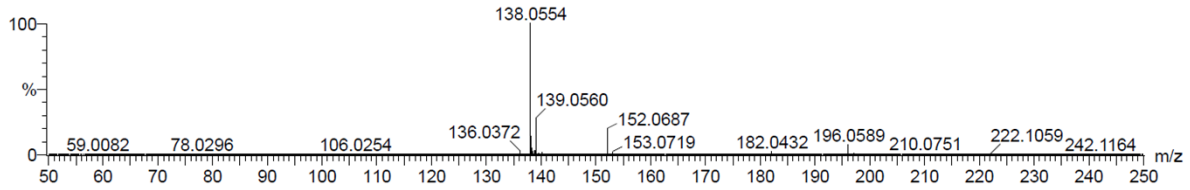
Figure S111. Mass spectrum of Methyl (E)-3-(3-fluorophenyl)acrylate **C11.**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5



Monoisotopic Mass, Even Electron Ions
51 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-4 O: 1-10

Sample Name : A_33 IITRPR XEVO G2-XS QTOF
Test Name :
090522_A_33 8 (0.186) 1: TOF MS ES+
3.54e+007



Minimum:				-1.5				
Maximum:		2.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
138.0554	138.0555	-0.1	-0.7	4.5	3677.0	n/a	n/a	C7 H8 N O2

Figure S112. Mass spectrum of Methyl nicotinate **C13.**

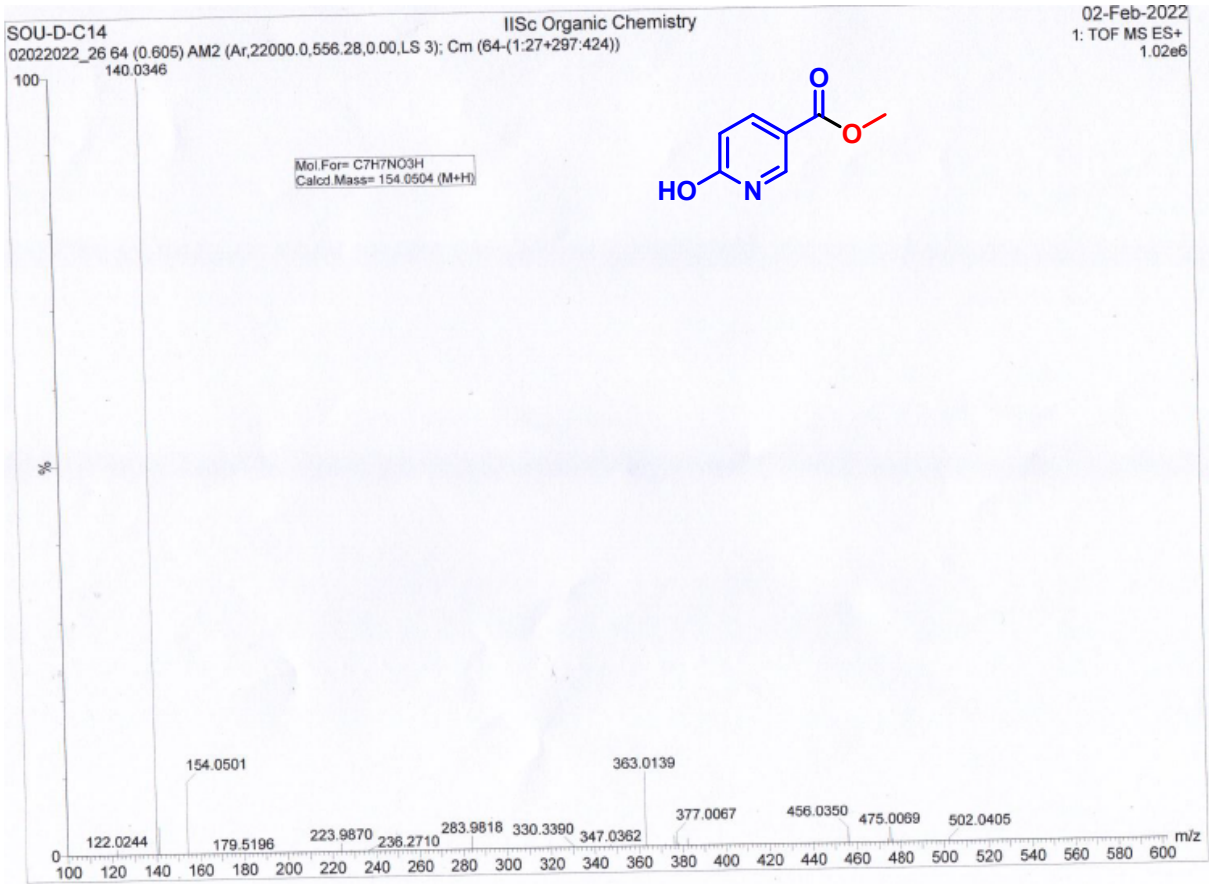


Figure S113. Mass spectrum of Methyl 6-hydroxynicotinate **C14.**

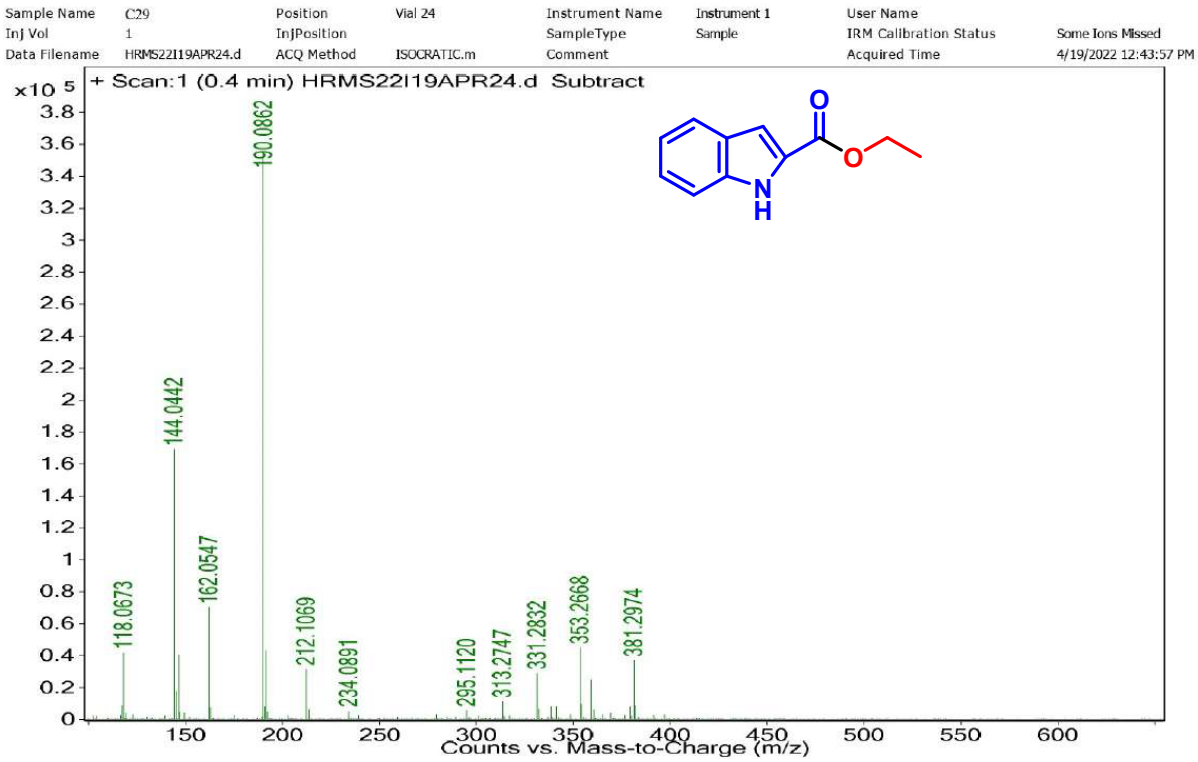


Figure S114. Mass spectrum of Ethyl 1H-indole-2-carboxylate **C15.**

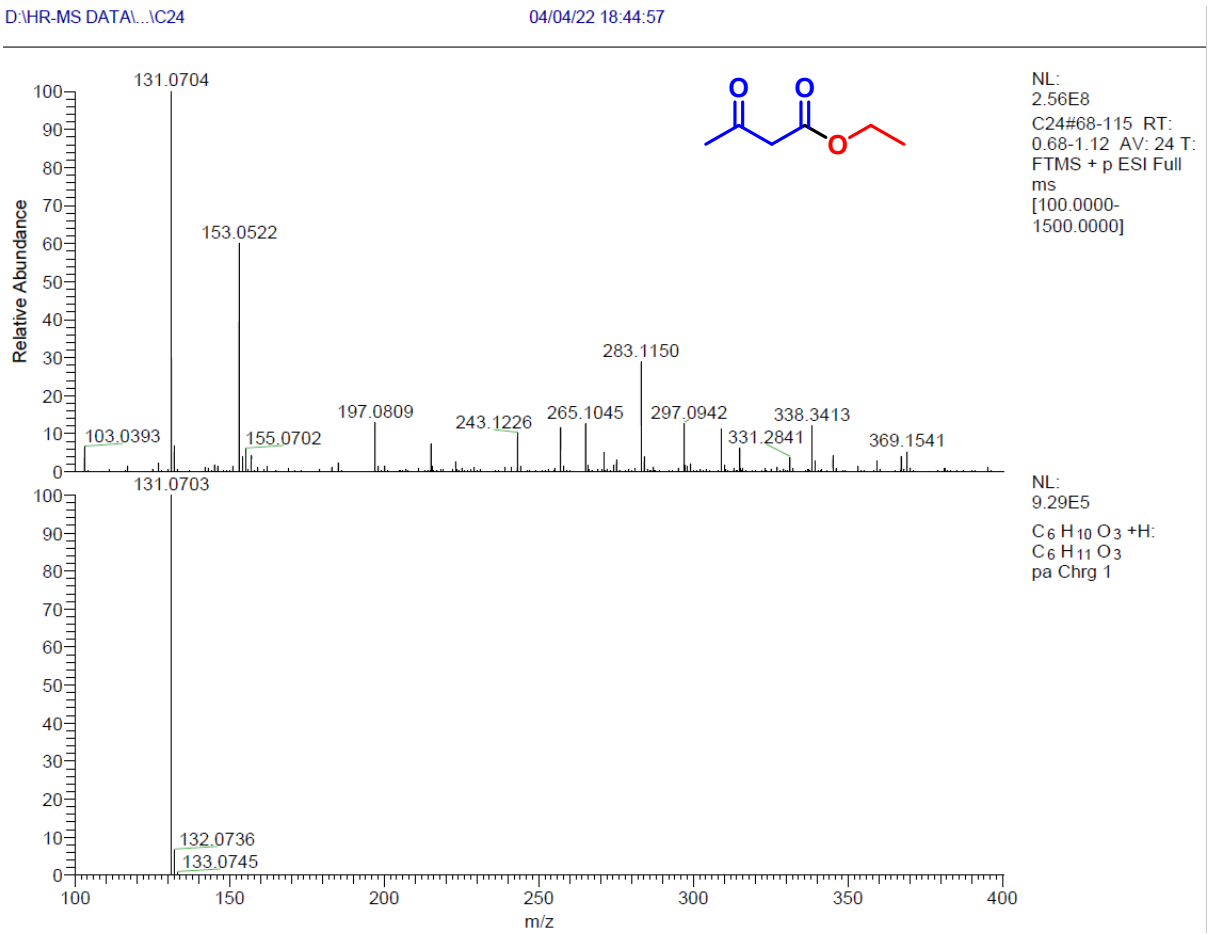


Figure S115. Mass spectrum of Ethyl 3-oxobutanoate **C16.**

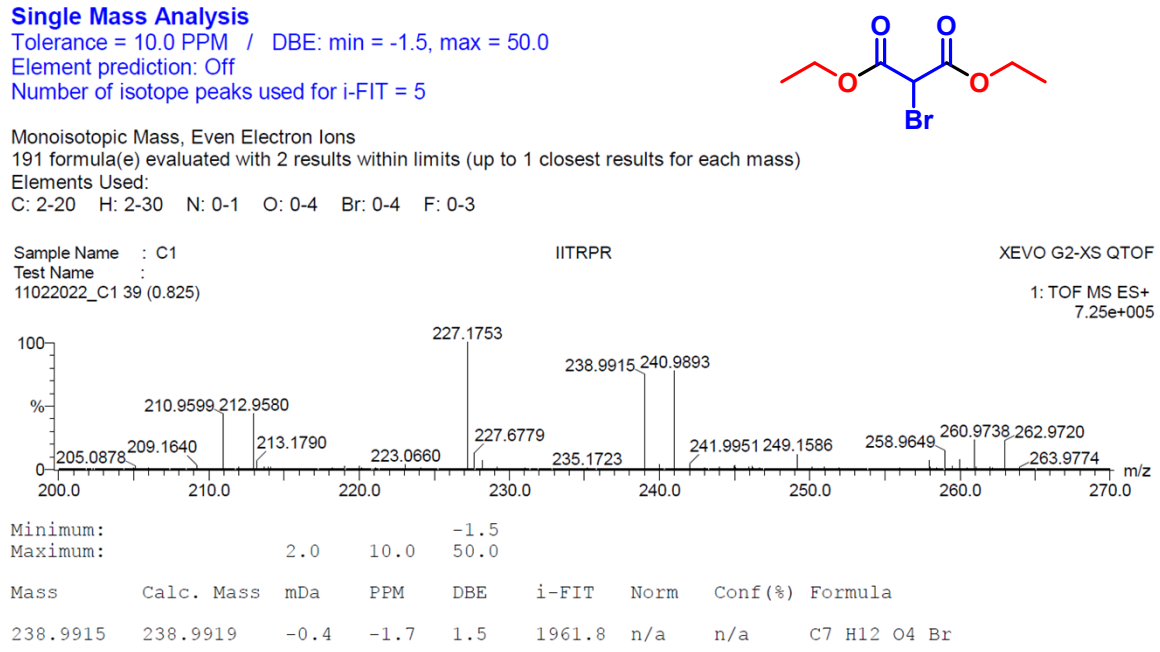
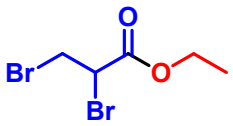


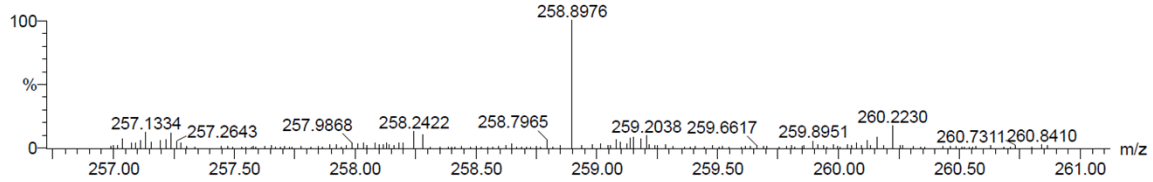
Figure S116. Mass spectrum of Diethyl 2-bromomalonate **C17.**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5



Monoisotopic Mass, Even Electron Ions
303 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 2-20 H: 2-30 N: 0-2 O: 0-4 F: 0-3 Br: 0-4

Sample Name : C4 IITRPR XEVO G2-XS QTOF
Test Name :
11022022_C4 14 (0.311) 1: TOF MS ES+
1.02e+004



Minimum:				-1.5				
Maximum:		2.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
258.8976	258.8969	0.7	2.7	0.5	715.2	n/a	n/a	C5 H9 O2 Br2

Figure S117. Mass spectrum of Ethyl 2,3-dibromopropanoate **C18.**

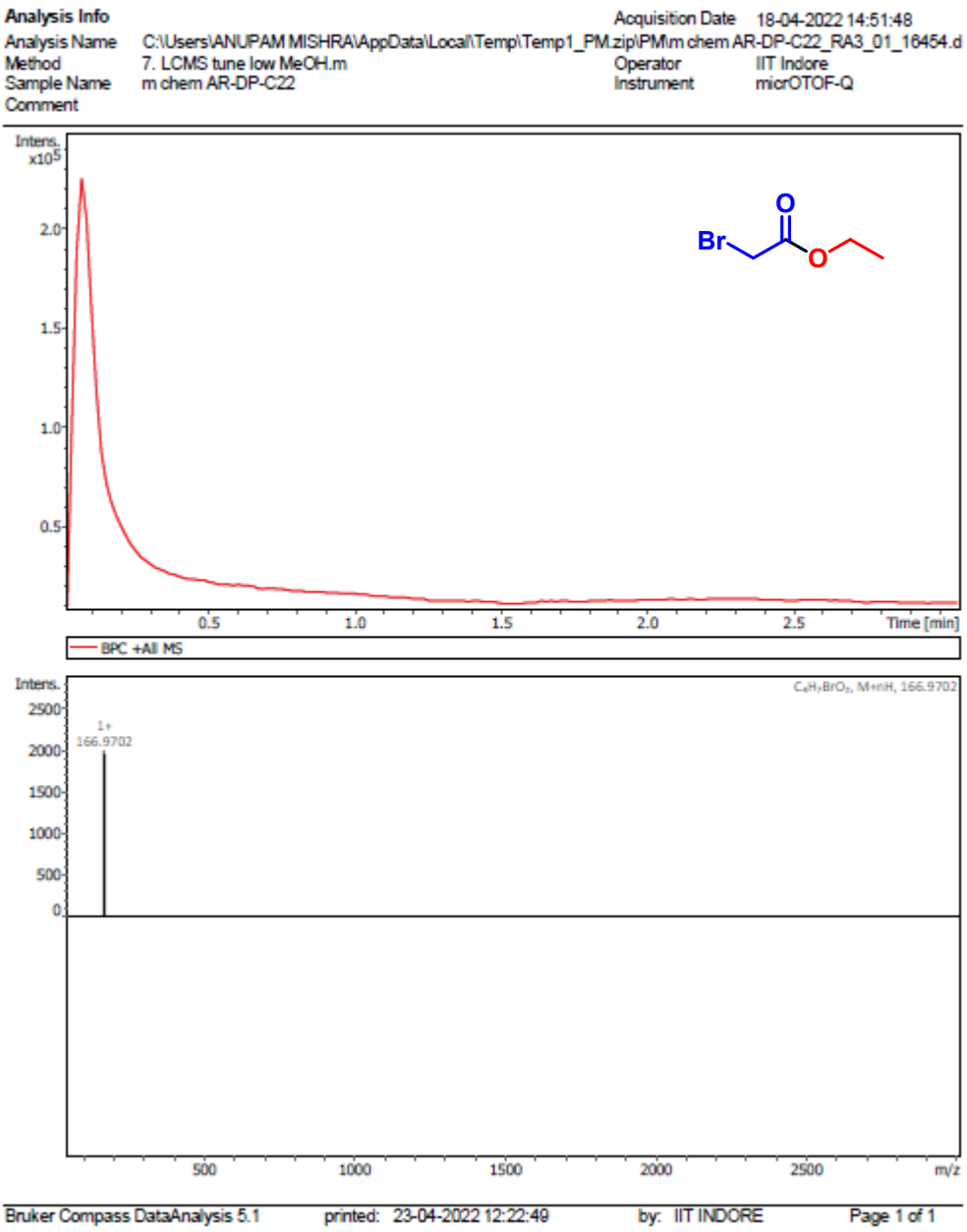


Figure S118. Mass spectrum of Ethyl 2-bromoacetate **C21.**

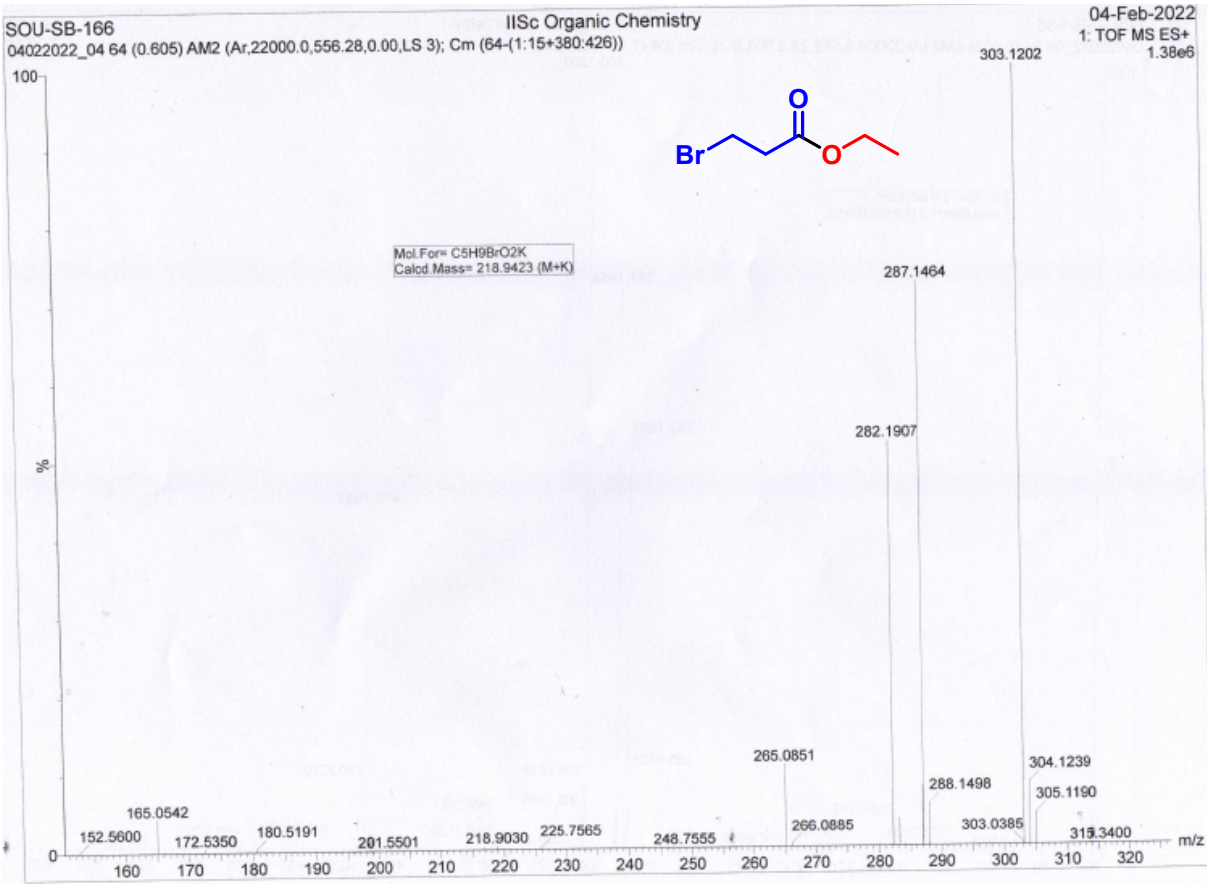


Figure S119. Mass spectrum of Ethyl 3-bromopropanoate **C22.**

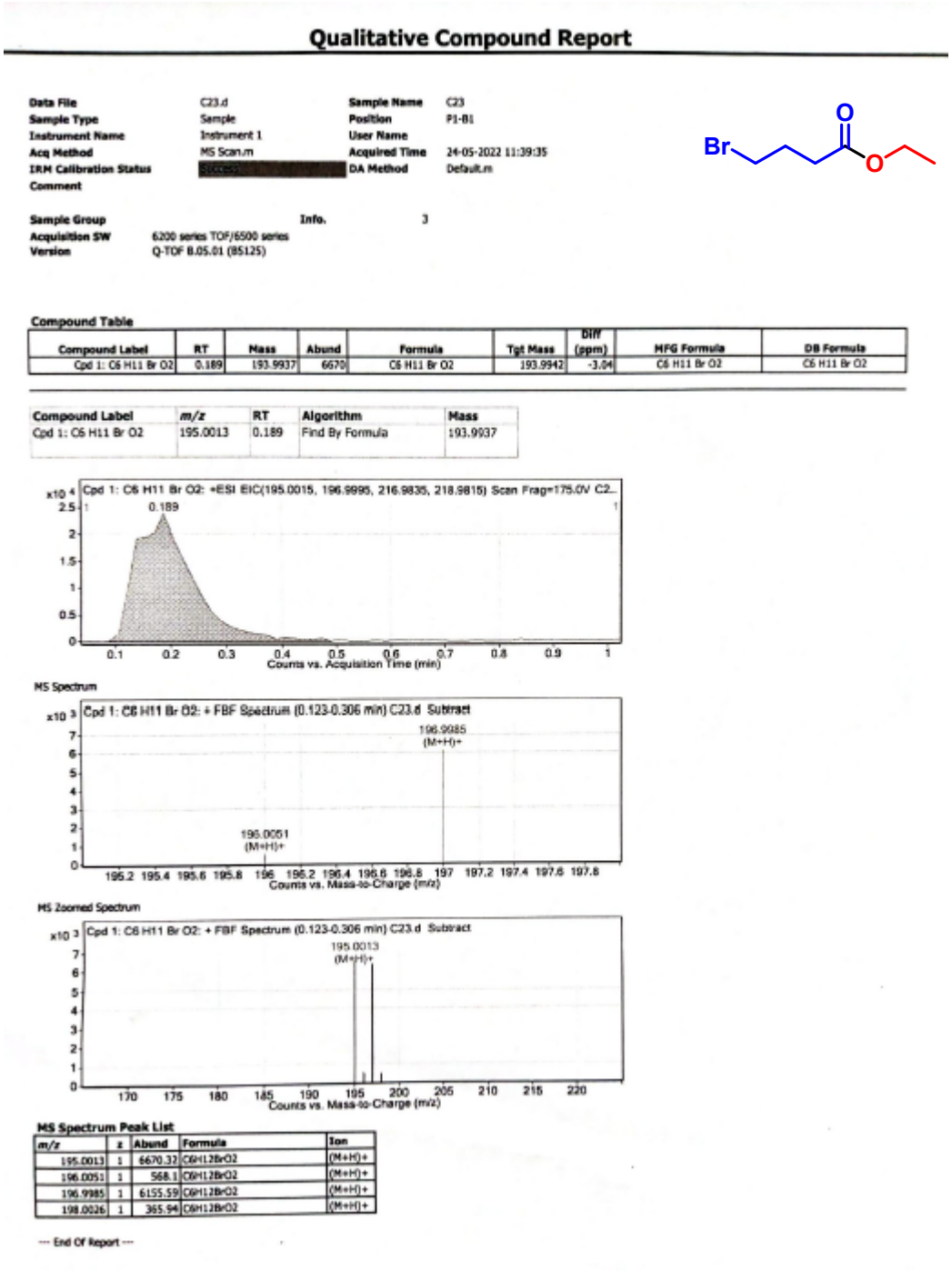
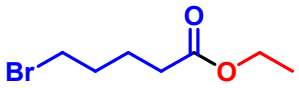


Figure S120. Mass spectrum of Ethyl 4-bromobutanoate **C23.**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5



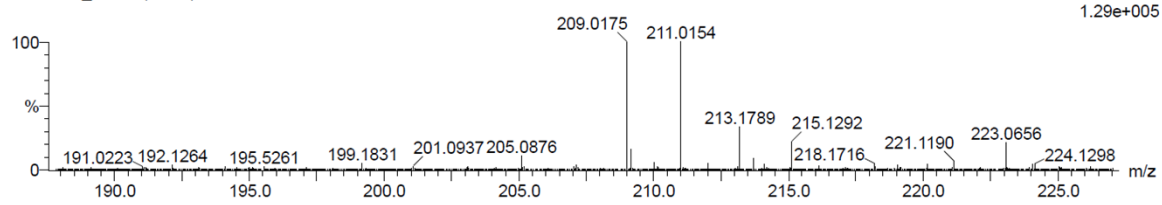
Monoisotopic Mass, Even Electron Ions
68 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 2-20 H: 2-30 N: 0-2 O: 0-4 Br: 0-4

Sample Name : C6
Test Name :
11022022_C6 23 (0.497)

IITRPR

XEVO G2-XS QTOF

1: TOF MS ES+
1.29e+005



Minimum:				-1.5				
Maximum:		2.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
209.0175	209.0177	-0.2	-1.0	0.5	1657.9	n/a	n/a	C7 H14 O2 Br

Figure S121. Mass spectrum of Ethyl 5-bromopentanoate **C24.**

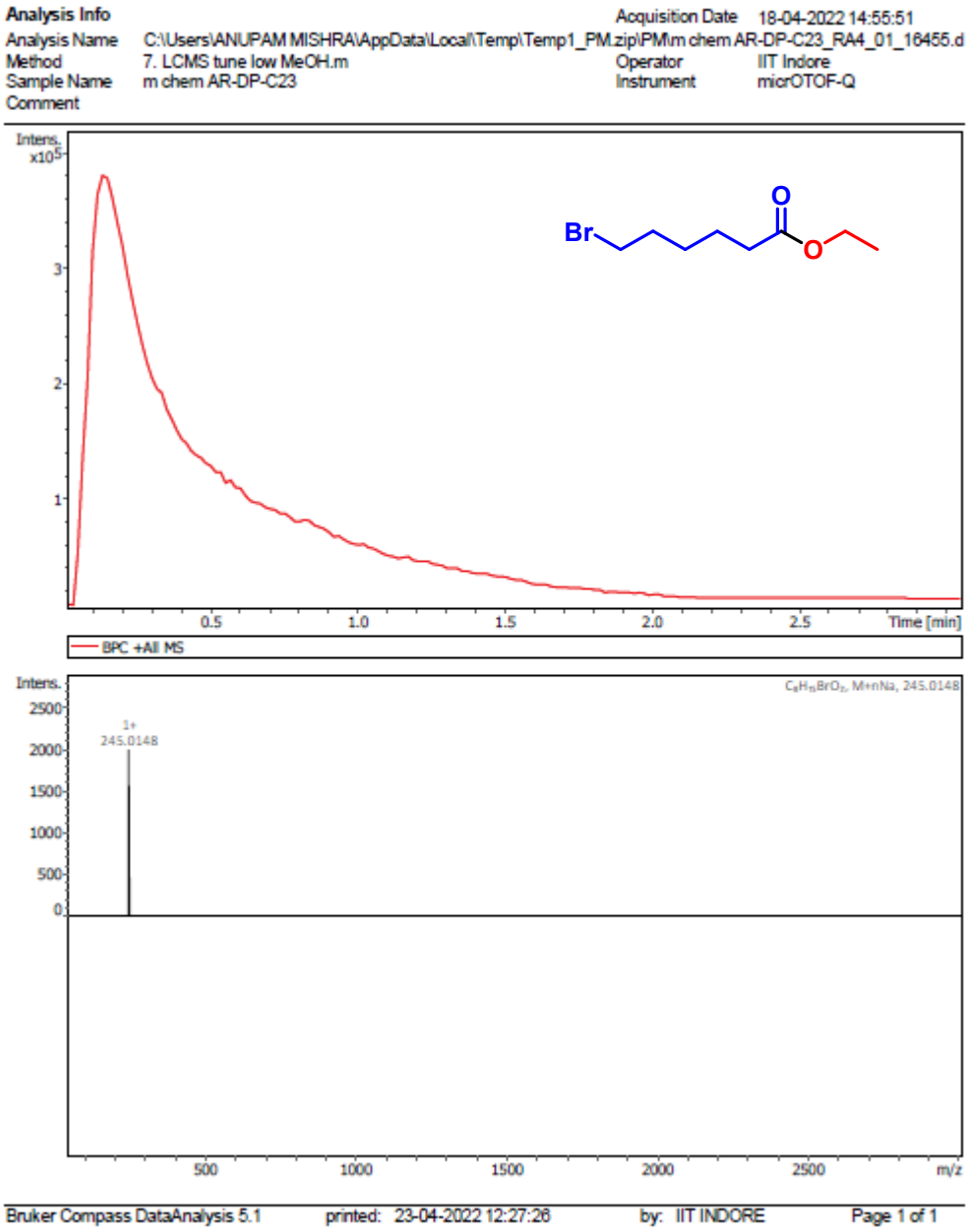
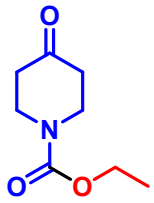


Figure S122. Mass spectrum of Ethyl 6-bromohexanoate **C25.**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5



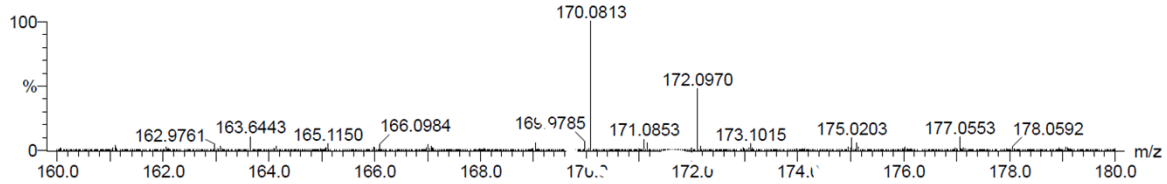
Monoisotopic Mass, Even Electron Ions
111 formula(e) evaluated with 2 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 2-20 H: 2-30 N: 0-1 O: 0-4 F: 0-3 Br: 0-4

Sample Name : C2
Test Name :
11022022_C2 65 (1.368)

IITRPR

XEVO G2-XS QTOF

1: TOF MS ES+
9.00e+004



Minimum:				-1.5				
Maximum:		2.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
172.0970	172.0974	-0.4	-2.3	2.5	1816.7	n/a	n/a	C8 H14 N O3

Figure S123. Mass spectrum of Ethyl 4-oxopiperidine-1-carboxylate **C26.**

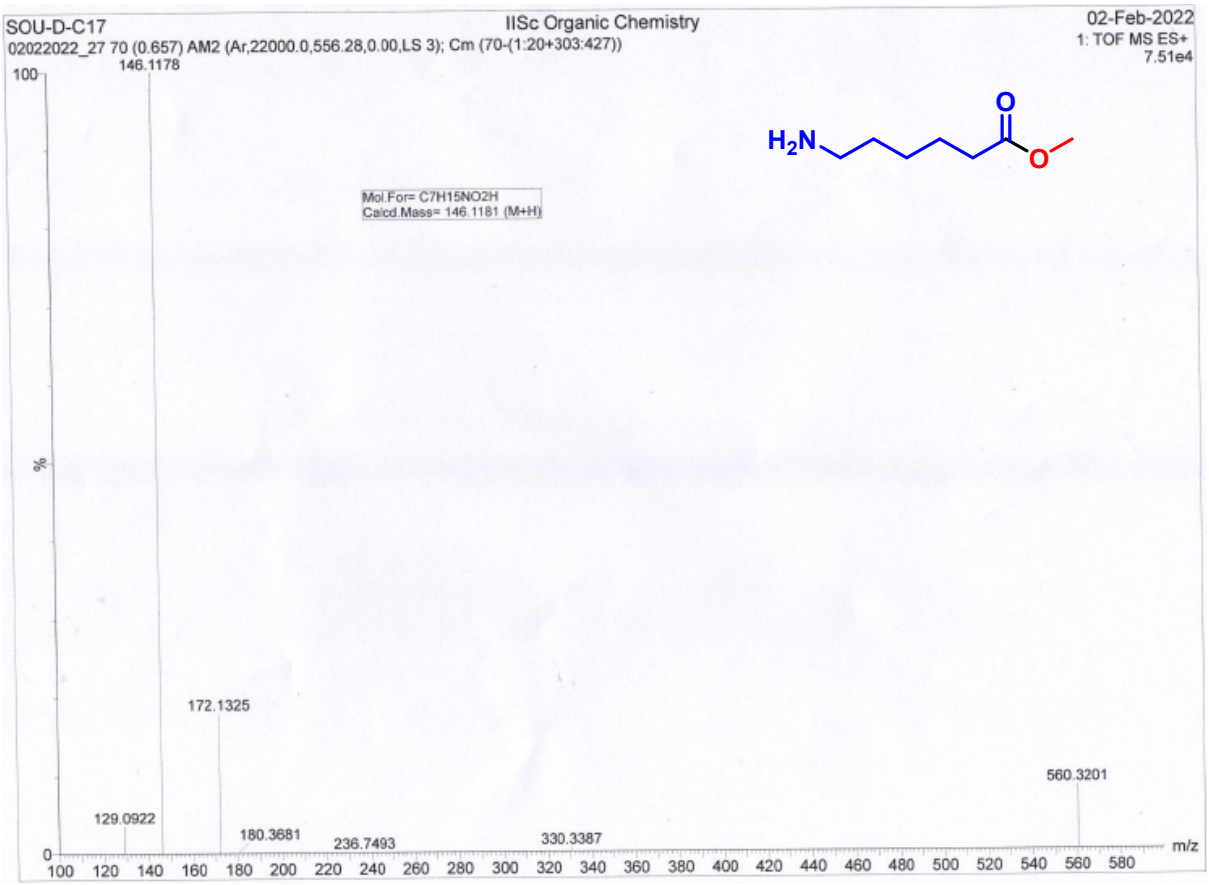


Figure S124. Mass spectrum of Methyl 6-aminohexanoate **C28.**

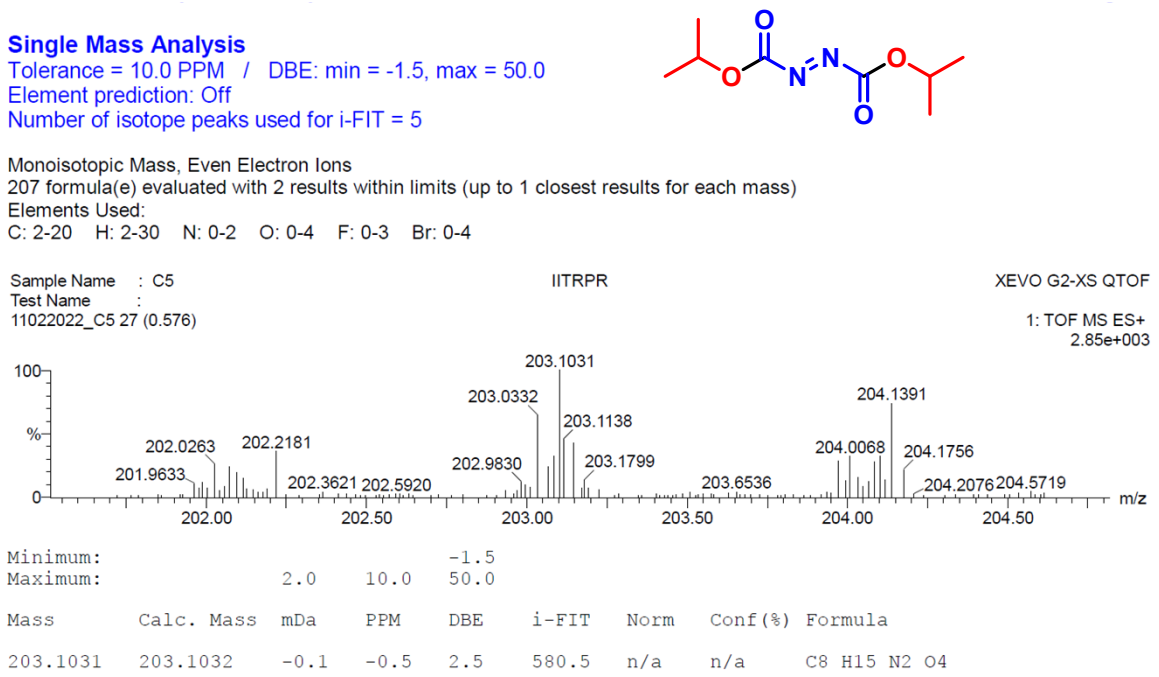


Figure S125. Mass spectrum of Diisopropyl (E)-diazene-1,2-dicarboxylate **C29.**

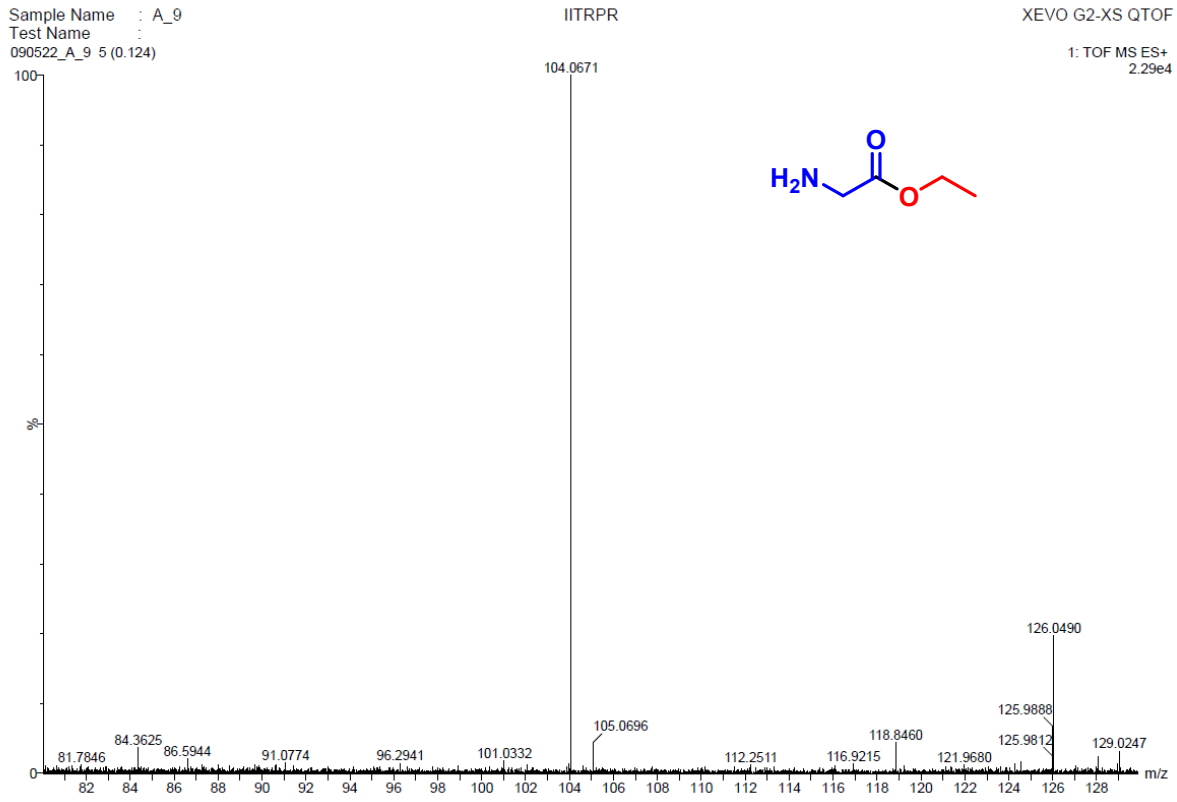


Figure S126. Mass spectrum of Ethyl glycinate **D1.**

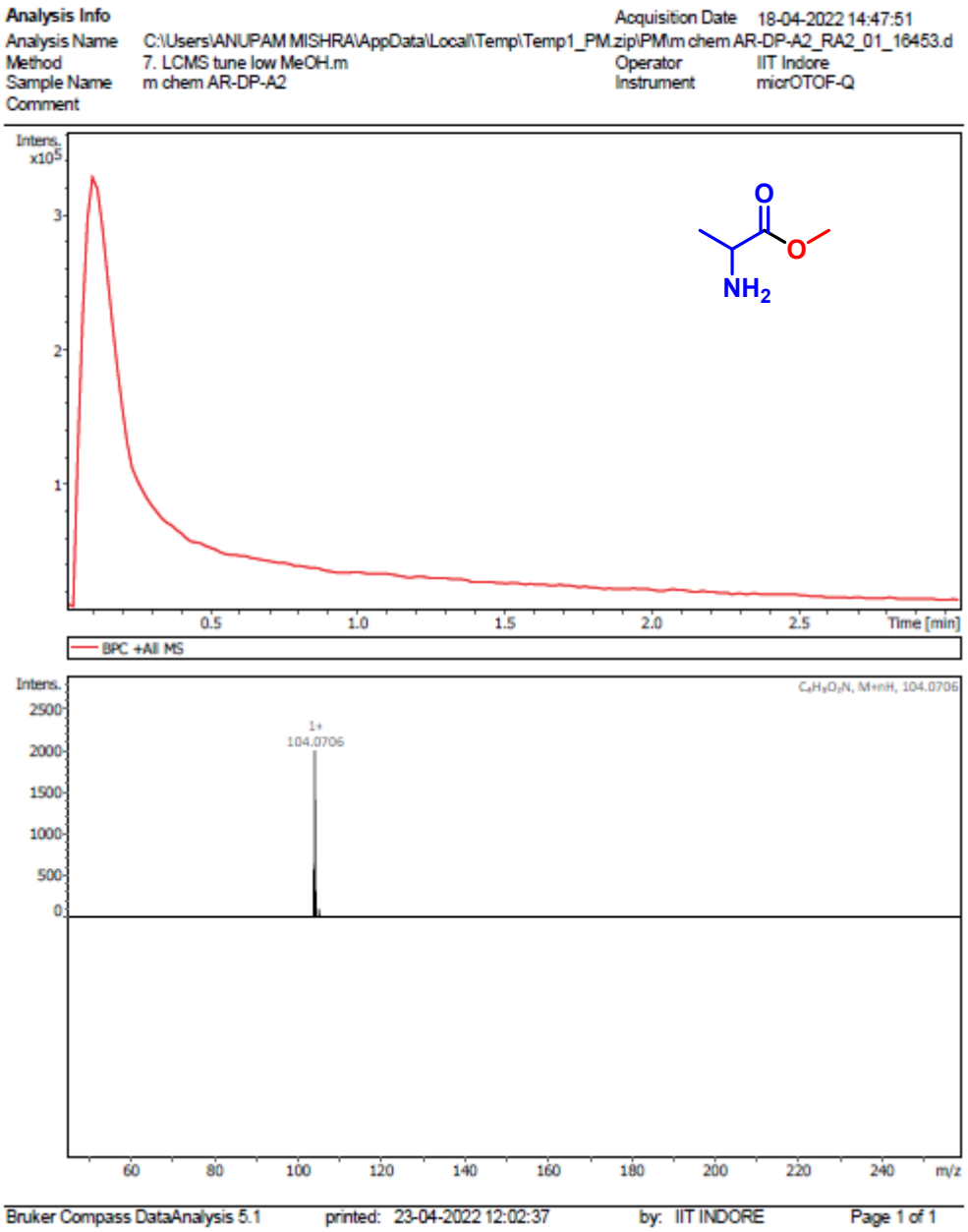


Figure S127. Mass spectrum of Methyl alaninate **D2.**

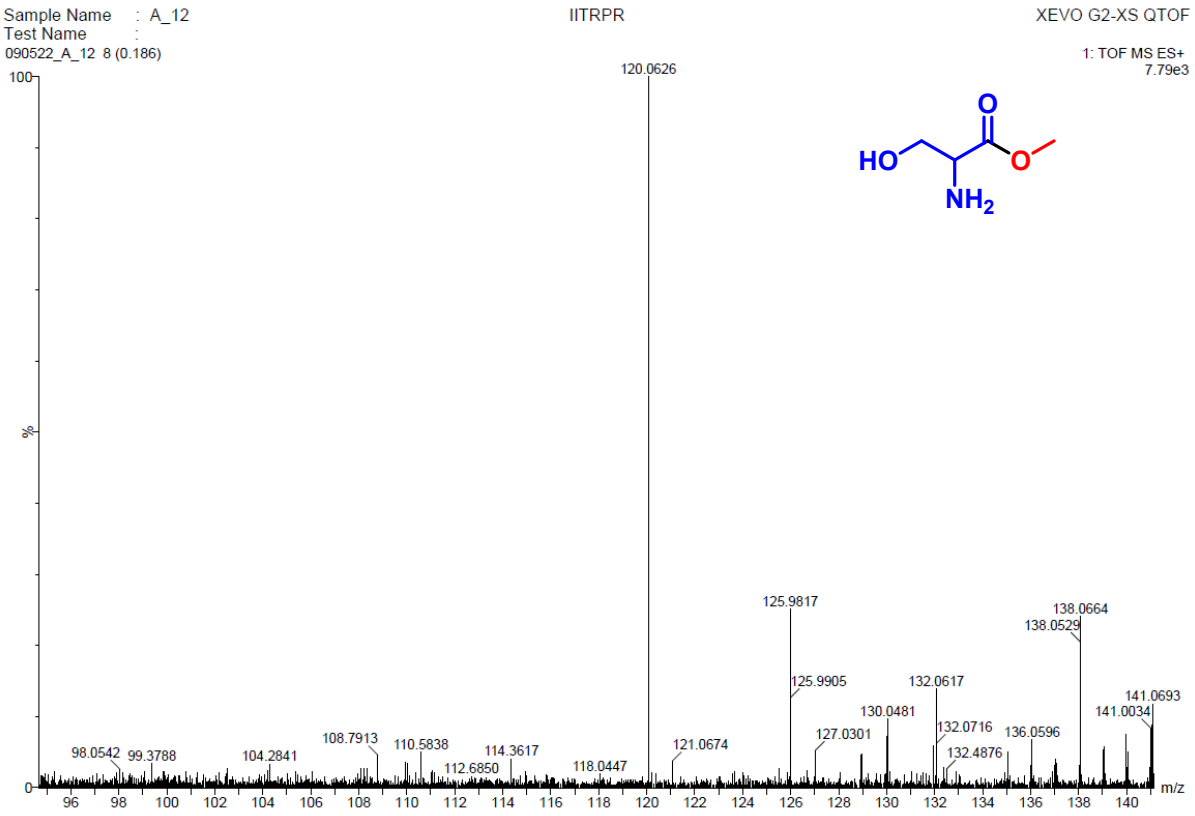


Figure S128. Mass spectrum of Methyl serinate **D3.**

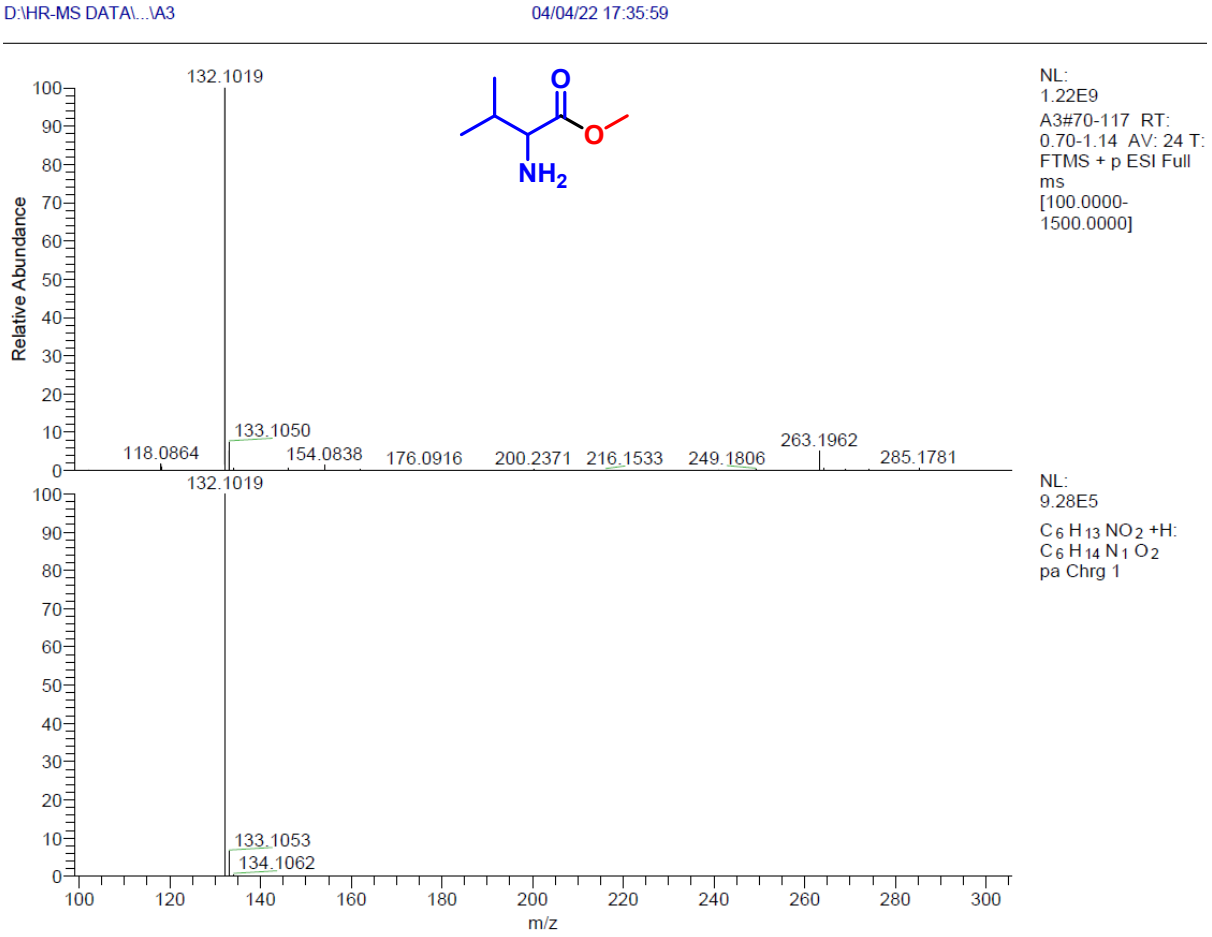


Figure S129. Mass spectrum of Methyl valinate **D5.**

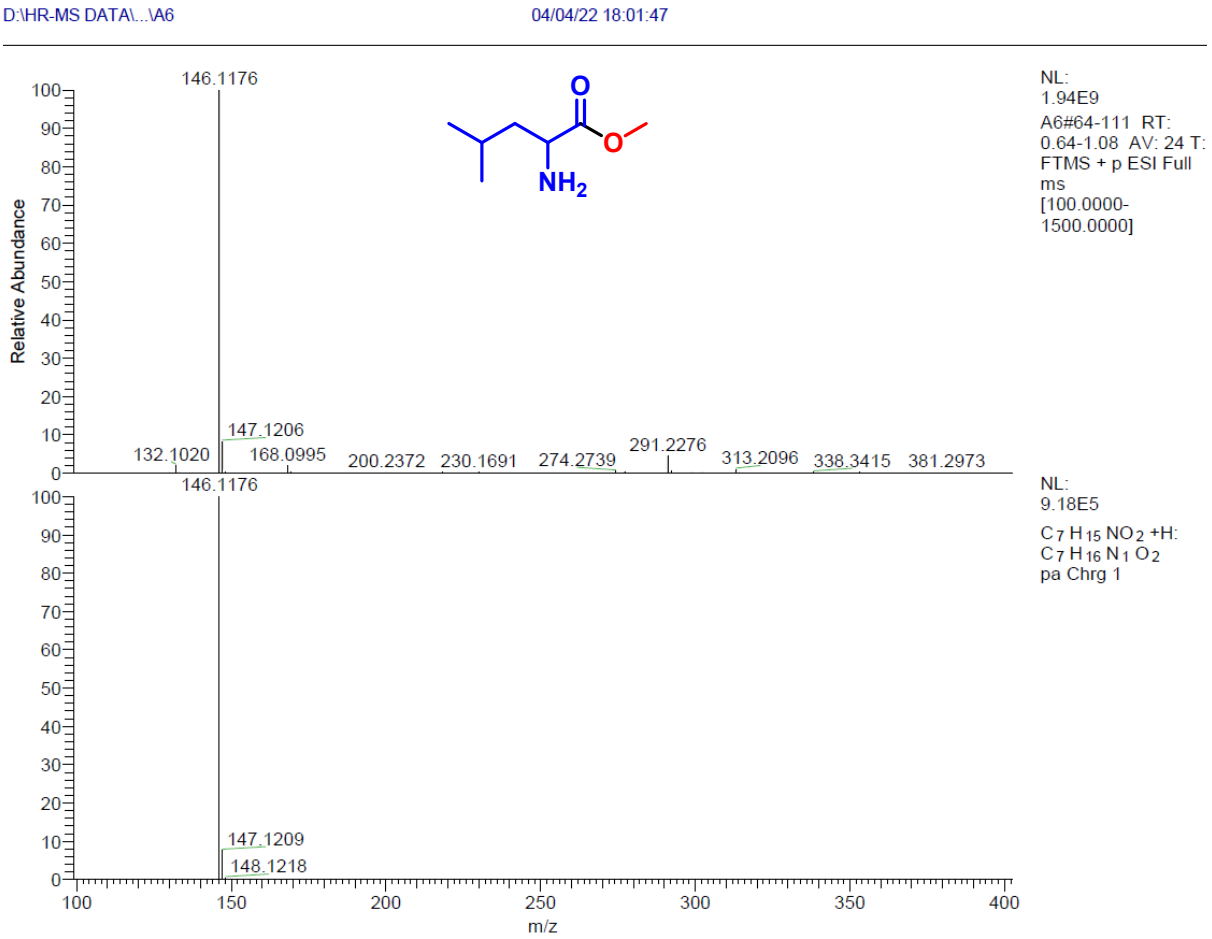


Figure S130. Mass spectrum of Methyl leucinate **D6.**

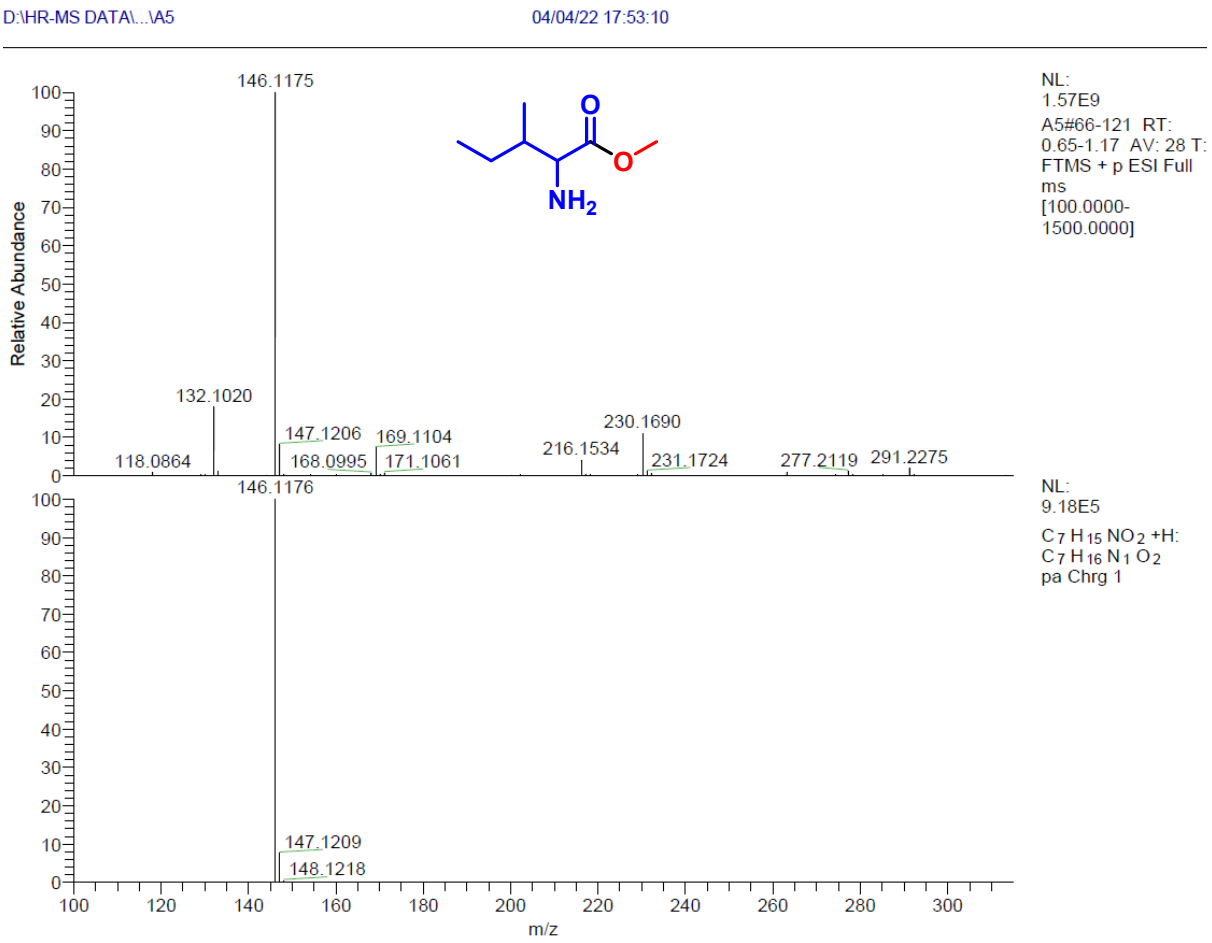


Figure S131. Mass spectrum of Methyl 2-amino-3-methylpentanoate **D7.**

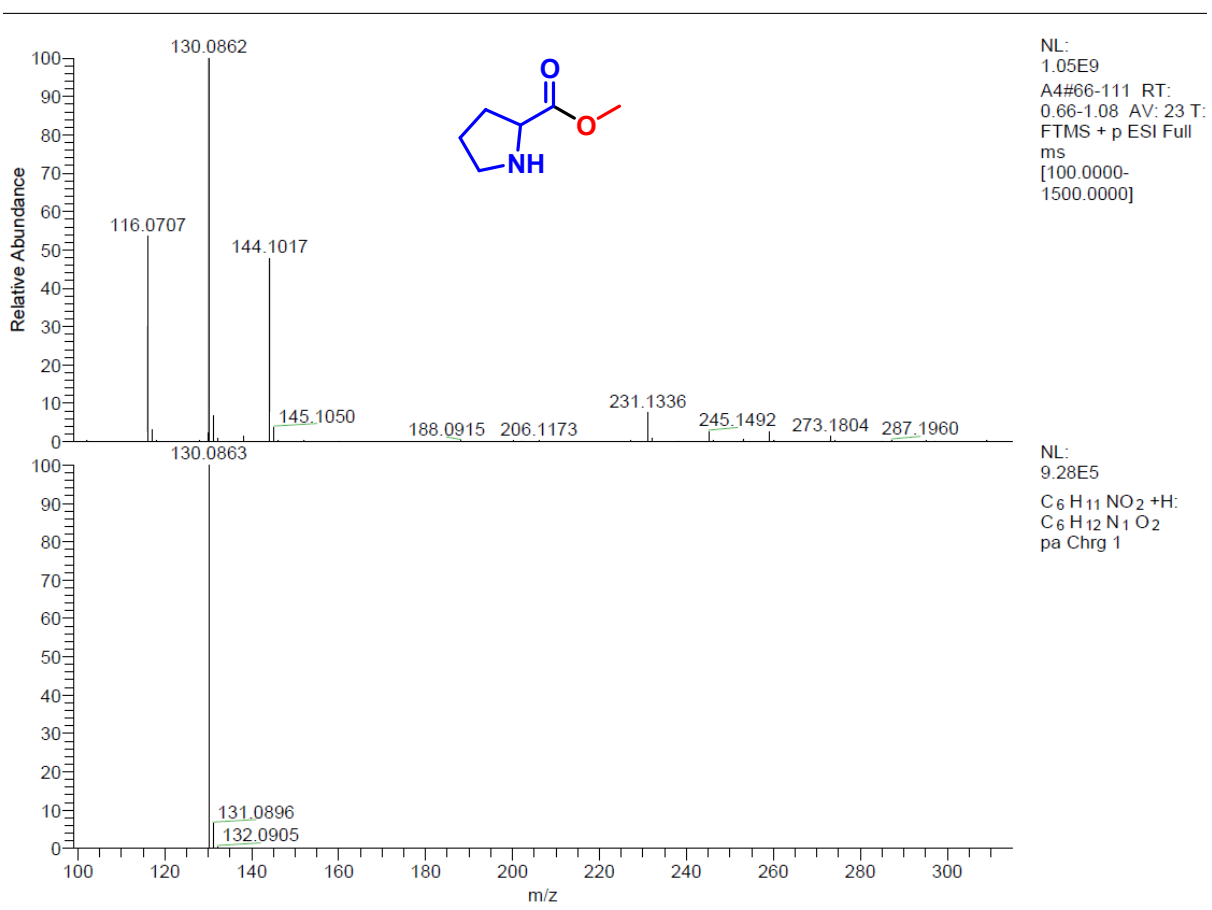


Figure S132. Mass spectrum of Methyl prolinate **D8.**

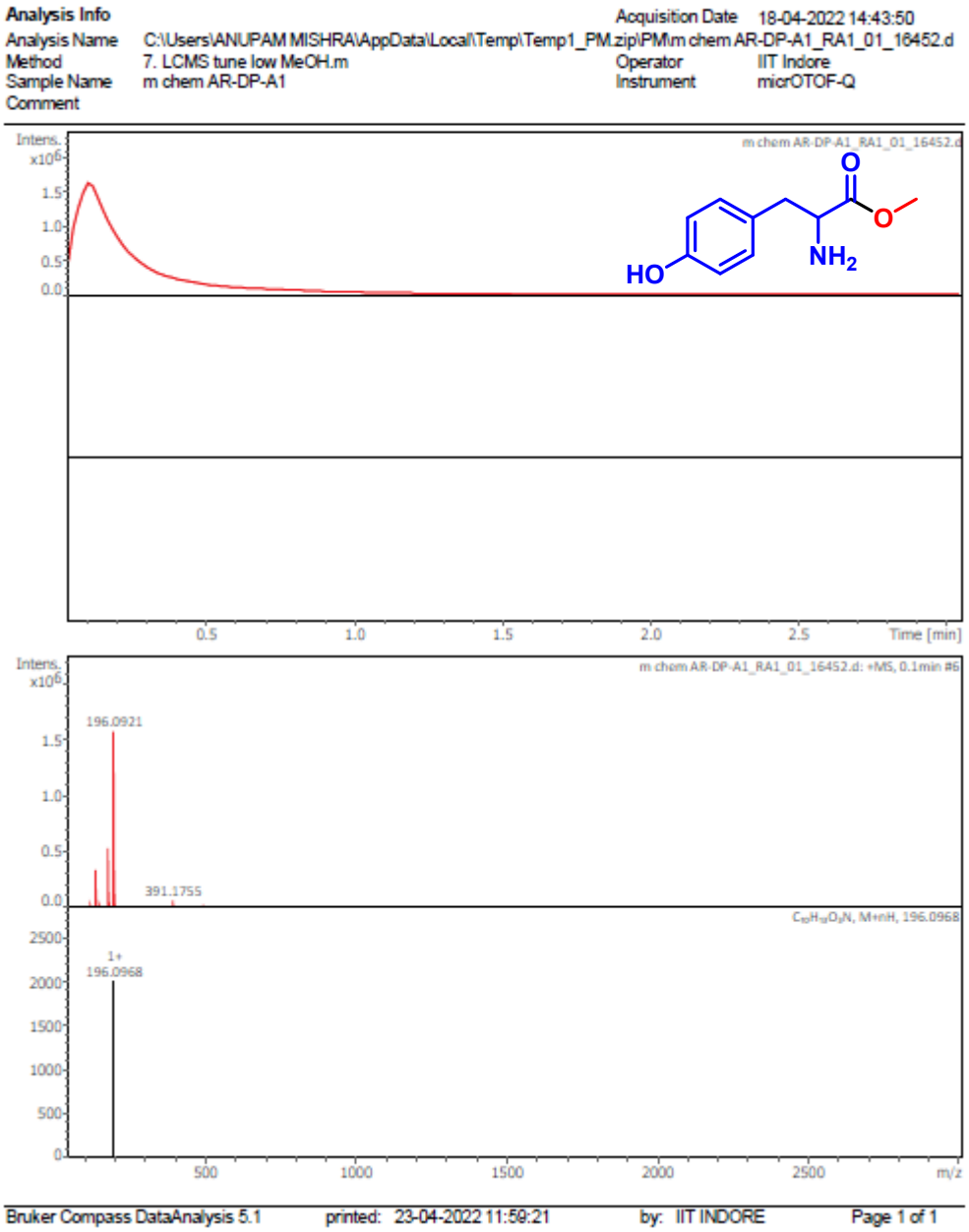


Figure S133. Mass spectrum of Methyl tyrosinate **D9.**

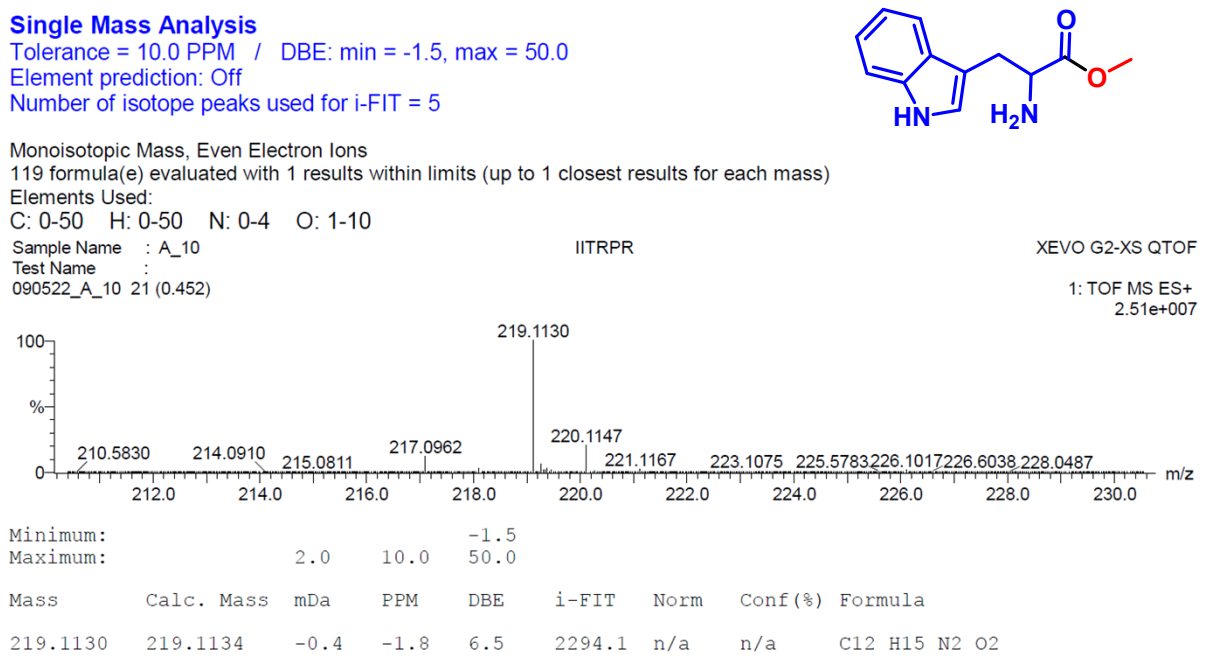


Figure S134. Mass spectrum of Methyl tryptophanate **D10.**

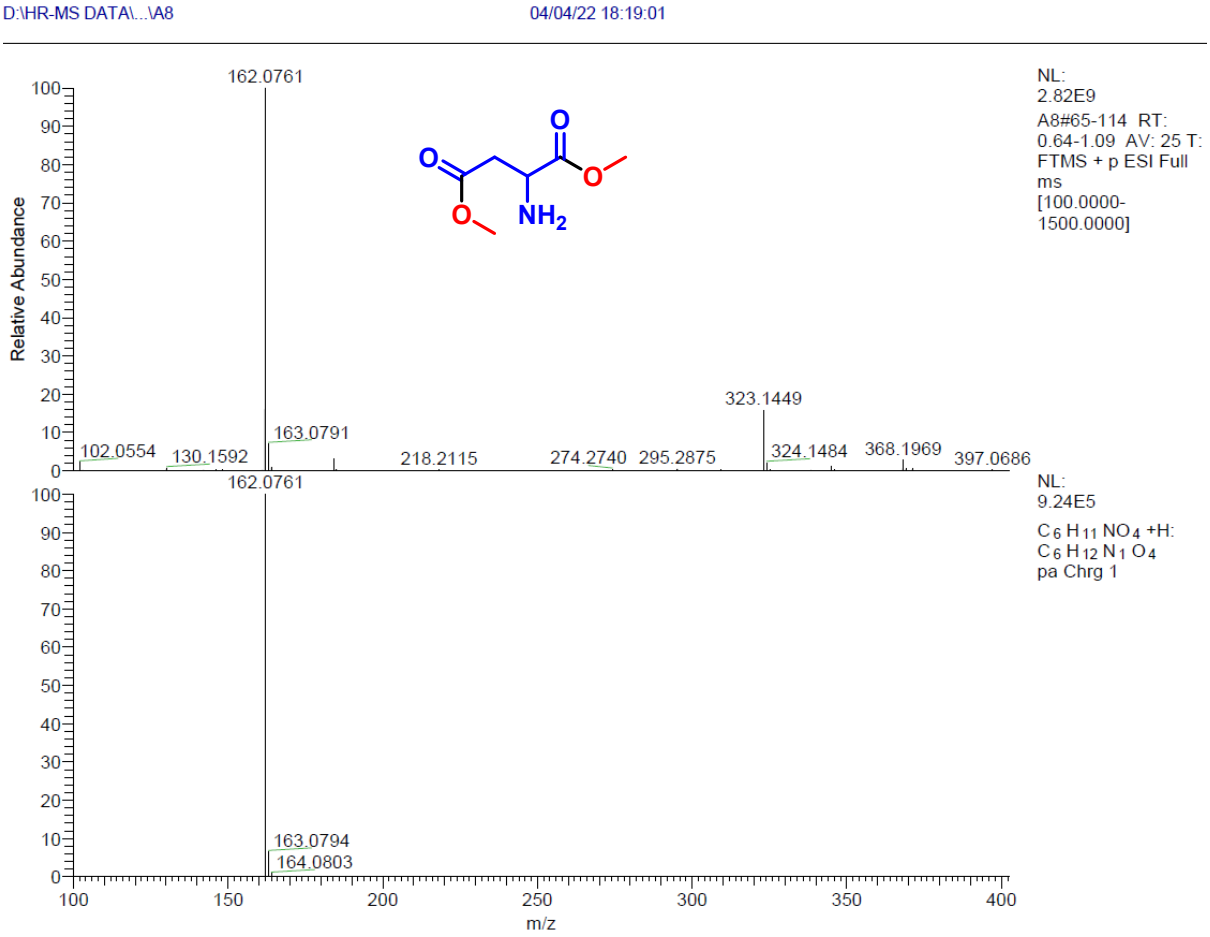


Figure S135. Mass spectrum of Dimethyl aspartate **D11.**

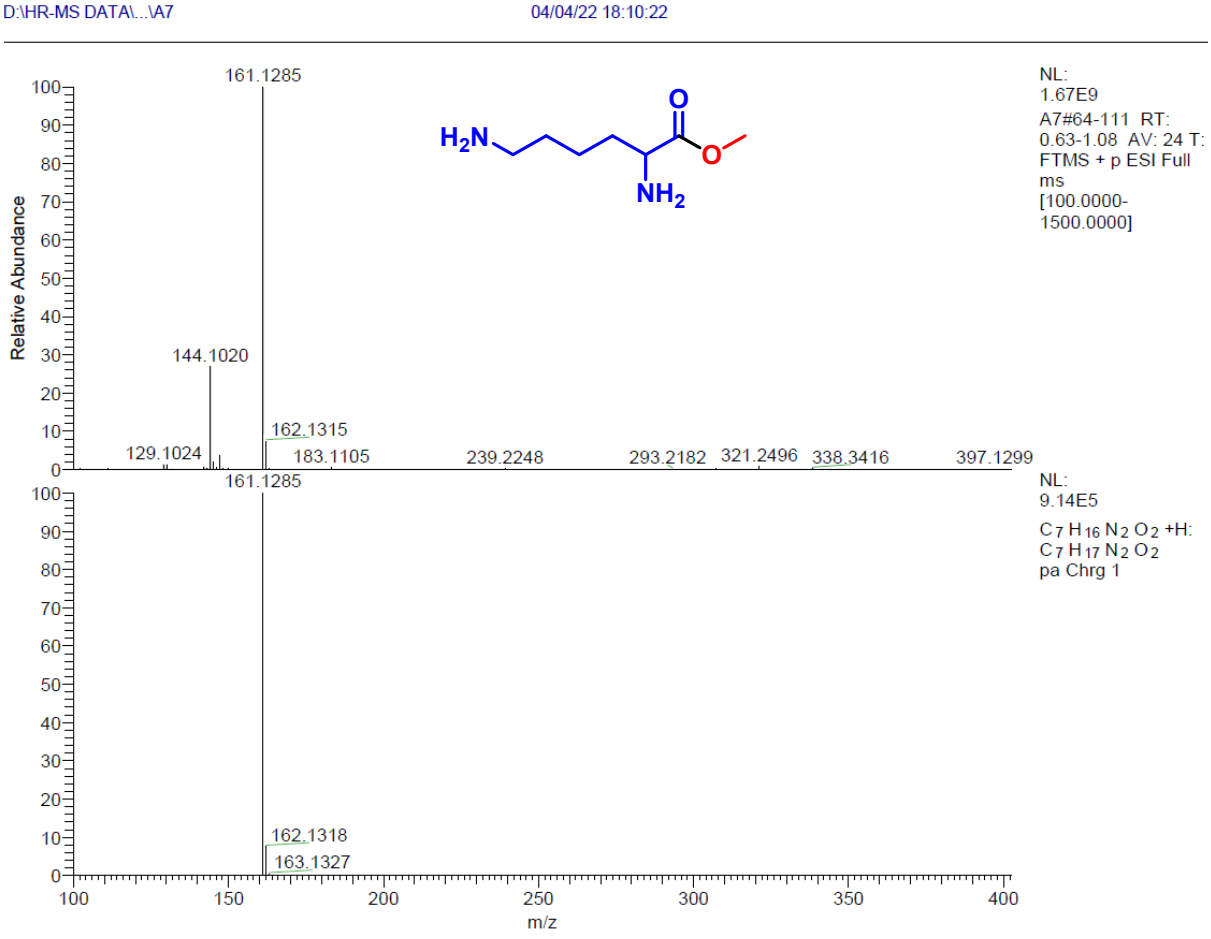


Figure S136. Mass spectrum of Methyl lysinate **D12.**

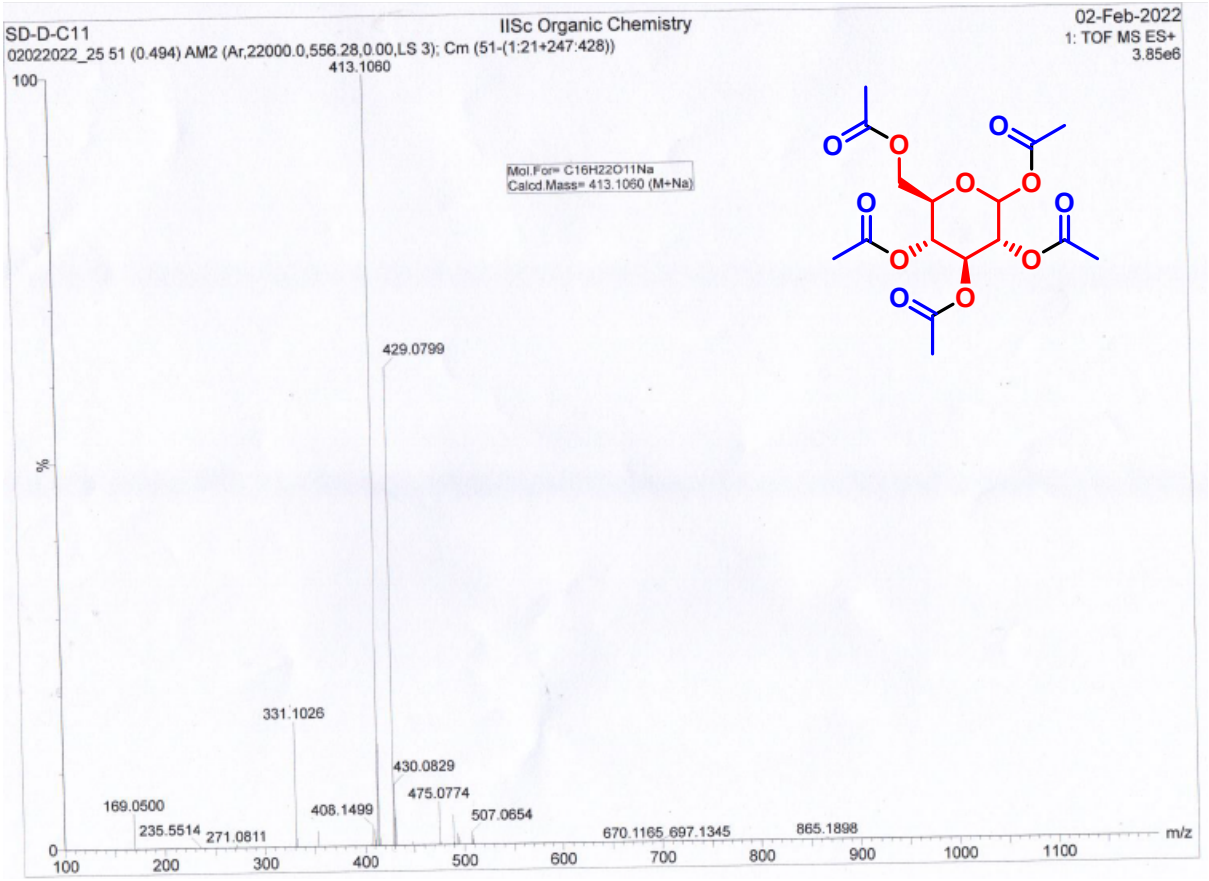


Figure S137. Mass spectrum of Glucose pentaacetate **E1.**

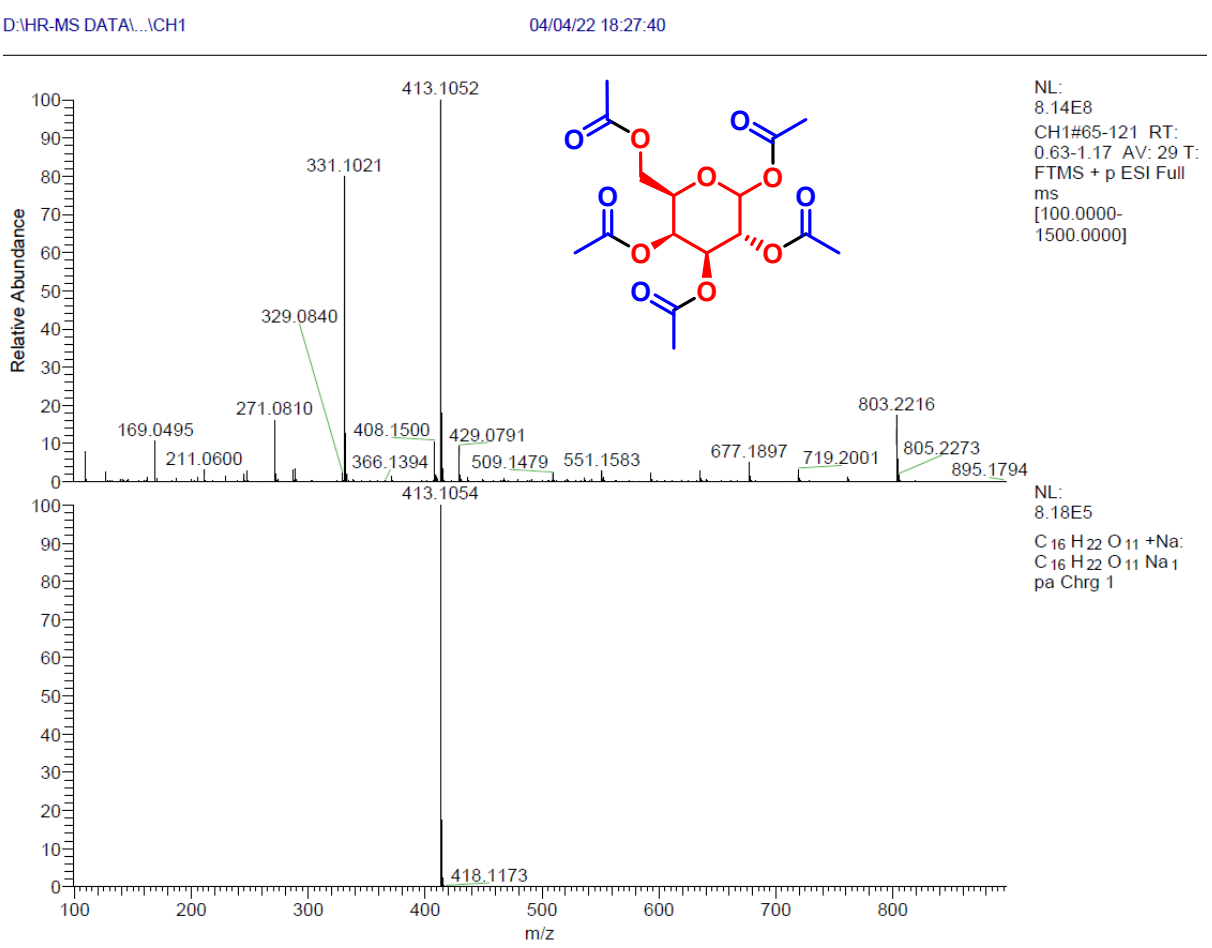
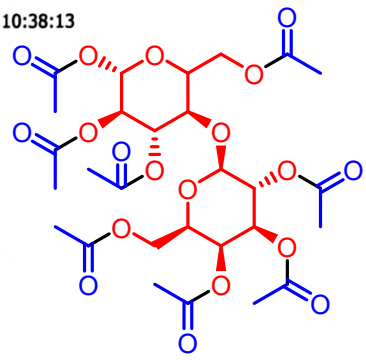


Figure S138. Mass spectrum of Galactose pentaacetate **E4.**

Qualitative Compound Report

Data File	LAC.d	**Sample Name**	LAC
Sample Type	Sample	**Position**	P1-A2
Instrument Name	Instrument 1	**User Name**	
Acq Method	MS Scan.m	**Acquired Time**	28-04-2022 10:38:13
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			



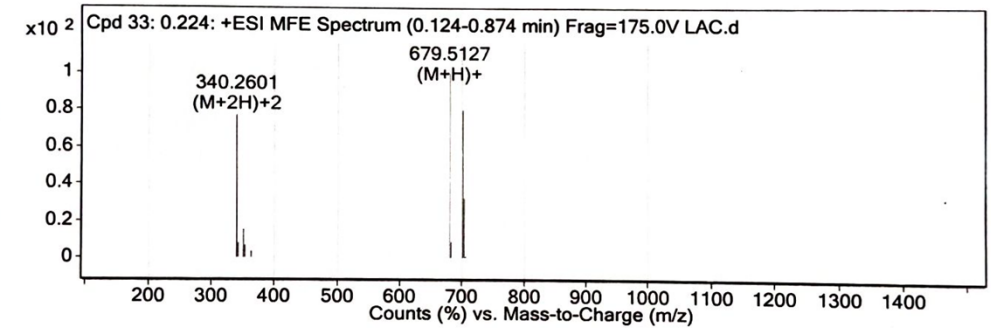
Sample Group		**Info.**	3
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125)		

Compound Table

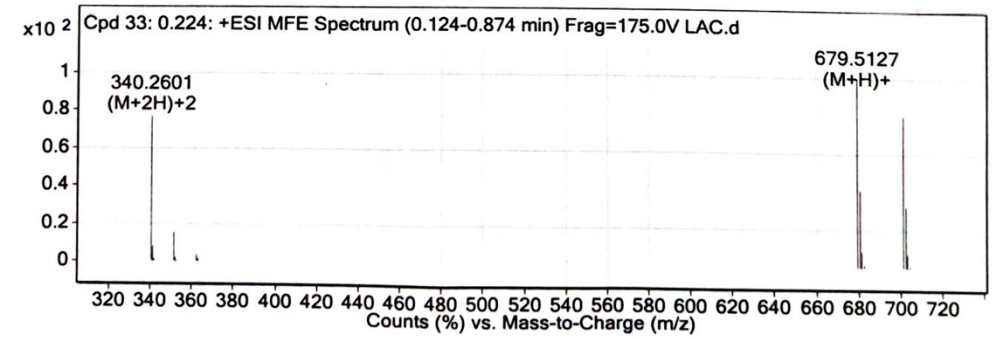
Compound Label	RT	Mass	MFG Formula
Cpd 33: 0.224	0.224	678.5053	<none>

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 33: 0.224	679.5127	0.224	Find by Molecular Feature	678.5053

MFE MS Spectrum



MFE MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Ion
340.2601	2	597327.88	(M+2H)+2
340.7615	2	249486.43	(M+2H)+2
341.2632	2	61259.82	(M+2H)+2
351.2492	2	118892.21	(M+H+Na)+2
679.5127	1	778768.94	(M+H)+

Figure S139. Mass spectrum of Lactose octaacetate **E7.**

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